

INFLUENCE OF ION-ADDITIVES ON INHIBITORY ACTION OF EXTRACT OF *TRIGONELLA FOENUM GRACEUMS* SEEDS FOR AA6063 IN ACID MEDIUM

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ABSTRACT

The effect of some ion-additives on the inhibitive effect of extract of *Trigonella foenum graceums* seeds (TfgS) on acid corrosion of aluminium alloy (AA6063) was studied. The investigation was carried out for different immersion periods in 0.5 N HCl at room temperature employing weight loss method. An optimum concentration (1.056 g/L) of the inhibitor was used for the 0.05 g/L of various ion-additives (halide and Zn^{2+} ions). Various corrosion parameters were evaluated using weight loss data. The inhibition efficiency was observed to increase synergistically on adding the additives. The TfgS extract is a potential inhibitor for acid-induced corrosion of AA6063.

Keywords: Aluminium alloy (AA6063); Weight loss; Acid corrosion; *Trigonella foenum graceums* seeds (TfgS); Additives; Synergism.

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INTRODUCTION

The corrosion of metallic materials in acidic solution causes considerable costs¹⁻². In order to combat the corrosion of metals, several techniques have been applied. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media²⁻⁹. It has been well established that the organic compounds with hetero-atoms such as oxygen, nitrogen, sulphur, and phosphorus tend to be most effective inhibitors as they get adsorbed on the specimen surface¹⁰⁻¹¹. While selecting inhibitors factors like, cost, toxicity, availability and environmental safety need to be focused. Hence, now a day's researchers are inclined to opt natural products as corrosion inhibitor¹²⁻²⁷. The plant extracts being biodegradable poses no threat to the environment. Moreover they are the rich source of active chemical constituents having significant inhibitive property, hence can be a good replacement for synthetic organic compounds. The presence of anions and cations in the solution had been found to stabilize the adsorption of some organic cations and anions leading to improved inhibition efficiency. This increased efficiency to retard the corrosion process has been ascribed as synergistic effect^{12, 28-29}. It has been proposed that formation of intermediate bridges between the metal surface and the positive end of the organic inhibitor are responsible for the improved adsorption of the organic cations. Hence increase in surface coverage arising from ion-pair interactions between the organic cations and the anions improve corrosion inhibition synergism. Synergistic studies have become an increasing important phenomenon and serves as the basic criterion for selection of most modern corrosion inhibitors.

An attempt has been made to evaluate synergism in the inhibitory action of ethanolic extracts of *Trigonella foenum graceums* seeds (EETfgS) and some ion-additives, viz. halide ions (anions) and zinc ions (cations) for aluminium alloy (AA6063) in 0.5N hydrochloric acid medium for various immersion periods at room temperature.

EXPERIMENTAL

The corrosion inhibition property of different test solutions was investigated by weight loss method at various immersion periods. All the solutions were made in doubly distilled water and the experimentations were carried out at room temperature.

Weight loss measurements

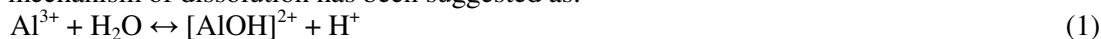
Aluminium alloy (AA6063) sheets with 0.016 cm thickness were mechanically press-cut into 3cm × 2.4cm coupons. AnalR grade HCl was employed to prepare standard 0.5 N HCl as the corrodent. The preparations of test coupons, electrolyte test solution and ethanolic extraction of *Trigonella foenum-graceums* seeds (EETfgS) were carried out as reported earlier^{19, 26}.

Preparation of test solutions

The experimentation was carried out in 10 different beakers, labeled S0 to S9; each with a constant volume of aggressive solution (0.5 N HCl). The first beaker, S0, contained only aggressive medium and no plant extract / additives; while an optimum concentration of plant extracts, EETfgS (1.056 g/L) was added to the beakers labeled S1, S3, S5, S7 and S9. In the beakers labeled as S2 and S3; S4 and S5; S6 and S7; S8 and S9 – in a set of two beakers each – a fixed quantity (0.5 g/100 ml) of ion-additive (KI, KCl, KBr and Zn²⁺ respectively) was added. Thus, the beakers labeled S3, S5, S7 and S9 contained KI+ EETfgS, KCl+ EETfgS, KBr+ EETfgS, and Zn²⁺ + EETfgS respectively. The experiments were carried out for various immersion periods ranging from 3 h to 72 h at room temperature to evaluate synergism between EETfgS and ion-additives for inhibition towards acid corrosion of AA6063.

RESULTS AND DISCUSSION

Corrosion of Al in aqueous solution depends on the concentration of anions in solution³⁰⁻³¹ for which general mechanism of dissolution has been suggested as:



The controlling step in the metal dissolution is the complex cation reaction between the hydrated cation and the anion present is the controlling step in the metal dissolution in equation 2; while in the presence of chloride ions the reaction will be:



Hence, the metal dissolution rate depends on the chloride concentration.

Natural products are rich source of active chemical constituents like tannins, amino acids, alkaloids, and pigments, known to exhibit inhibiting action. The adsorption of these active constituents on the metal surface reduces the surface area available for corrosion. The inhibitive tendency of anions (like halides) depends on their ionic size and charge; the electrostatic field set up by the negative charge of the anion on adsorption sites; nature and concentration of the halide ion³². It has also been reported³³ that the inhibitive effect increases in the order Cl⁻ (radius: 90pm) < Br⁻ (radius: 114pm) < I⁻ (radius: 135pm), which indicates that the radii of halide ions have an important role in the synergism.

Weight loss and corrosion rates

Using weight loss technique, inhibitive synergism of EETfgS and ion-additives on AA6063 at various immersion periods was studied at room temperature. Corrosion and adsorptive parameters like corrosion rate (ρ_{corr} mmy⁻¹), percentage inhibition efficiency (IE%), fractional surface coverage (θ), have been calculated and tabulated in table 1.

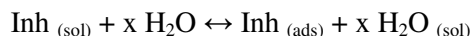
The results reveal that the corrosion rate was reduced sharply on adding EETfgS in the aggressive medium. Similarly, reduction in corrosion rate was observed on adding ion-additives in corrodent solution, indicating the inhibitive property of the ion-additives. The minimum corrosion rate was found in presence of EETfgS, when immersed for 48 h, indicating that the adsorptive tendency of the active constituents of the plant extracts. When coupons were immersed for long hours, due to the increase in dissolution / desorption of the adsorbed constituents, the corrosion rate was increased slightly. Whereas, keeping the coupons for longer period, again a decrease in corrosion rate was seen, which depicts the formation of an adsorbed film over the metal surface. Addition of halide and zinc ions as additives to the solution containing plant extract causes further reduction in the corrosion rate, clearly illustrating synergistic inhibition.

The maximum inhibition efficiency (88.95 %) of EETfgS alone was observed at 48 h immersion period; which significantly rises on adding ion-additives, 95.79 % for $[\text{Br}^- + \text{EETfgS}]$ and 98.95 % for $[\text{Zn}^{2+} + \text{EETfgS}]$. This substantial rise in IE % shows the synergistic inhibition of EETfgS and ion-additives for AA6063.

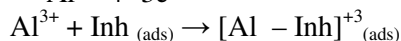
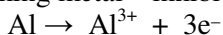
The results have been very well analyzed and represented graphically (figures 1 – 3). The variation of mass loss (mg) as a function of immersion time period without and with inhibitors (plant extract /and ion-additives) has been illustrated in figure 1. It's clear from the graph that in corrodent, a linear increase in weight loss with immersion period and a sharp decline in weight loss in the presence of inhibitor and ion-additives have been observed. The metal dissolution has been slowed down with the addition of inhibitors.

The variation of corrosion rate with immersion time has been depicted graphically by figure 2, which shows a decrease in corrosion rate with immersion time. This behavior could be attributed to the increase in adsorption of inhibitors over the metal surface. Figure 3 illustrates the inhibition efficiency of the inhibitors with immersion time (h). The graph is self explanatory that the addition of ion-additives along with EETfgS leads to a significant rise in the inhibition efficiency. The maximum IE (98.95%) was obtained for test with EETfgS + Zn^{2+} ions immersed for 48 h. This is further validated on the basis of Synergistic parameter (S) (table 2). It has been further observed that the synergistic effect also vary on addition of ions to EETfgS in the order $\text{Zn}^{+2} > \text{Br}^- > \text{Cl}^- > \text{I}^-$.

The protection action of the inhibitors is based on the adsorption ability of their active molecules; the resulting adsorbed film isolates the metal surface from the corrosive medium^{28-29, 32-34}. Consequently, in inhibited solutions, the corrosion rate is indicative of the number of free corrosion sites left after some sites have been effectively blocked by inhibitor adsorption. It is generally accepted that the first step during the adsorption of an inhibitor molecule over the metal surface involves the replacement of one or more water molecules adsorbed over the metal surface³⁴.



The inhibitor may then combine with freshly generated Al^{+3} ions on the aluminium surface, forming metal – inhibitor complexes:



The resulting complex could, depending on its relative solubility, either inhibit or catalyze further metal dissolution; hence the integrity depends on the capacity of the environment to dilute it. The adsorption of these inhibitors over the metal surface reduces the exposed surface area available for corrodent²⁸⁻²⁹.

The Synergism

The synergistic parameter, S, was evaluated using the relationship given by Aramaki and Hackerman and reported elsewhere³⁵:

$$\begin{aligned} S &= \frac{1 - I_{A+B}}{1 - I_{A+B}} \\ &= \{1 - I_A - I_B + I_A I_B\} / (1 - I_{A+B}) \end{aligned}$$

Where, $I_{A+B} = I_A + I_B$; I_A and I_B are the inhibition efficiencies of ion-additives and EETfgS respectively, when employed alone and I_{A+B} = the inhibition efficiency of co-employment of the two inhibitors.

From the value of S thus obtained following inferences can be drawn: if $S > 1$: the two inhibitors act synergistically; if $S < 1$: the two inhibitors act antagonistically; and if $S=1$: there is no interaction between the inhibitor molecules.

The value of S for $[\text{EETfgS} + \text{ion-additives}]$ has been evaluated and found to be more than unity (table 2), thereby two inhibitors act synergistically.

The mechanism of the synergism can be envisaged as the ion-additives get initially adsorbed over the metal surface; the active components of extracts then get adsorbed by the coulombic attraction over the metal surface where the ion-additives have already been adsorbed and thus suppressing the corrosion rate by the stabilization of the adsorbed ions and by the increase in surface coverage. Since the metal

surface is positively charged in HCl medium, the extract's constituents get adsorbed over aluminium³⁴. However, adsorption of ion-additives caused a decrease in the positive charge of Al due to formation of Al-ion surface bond, which produces a negative pole, facilitating the adsorption of the extract's active constituents³³.

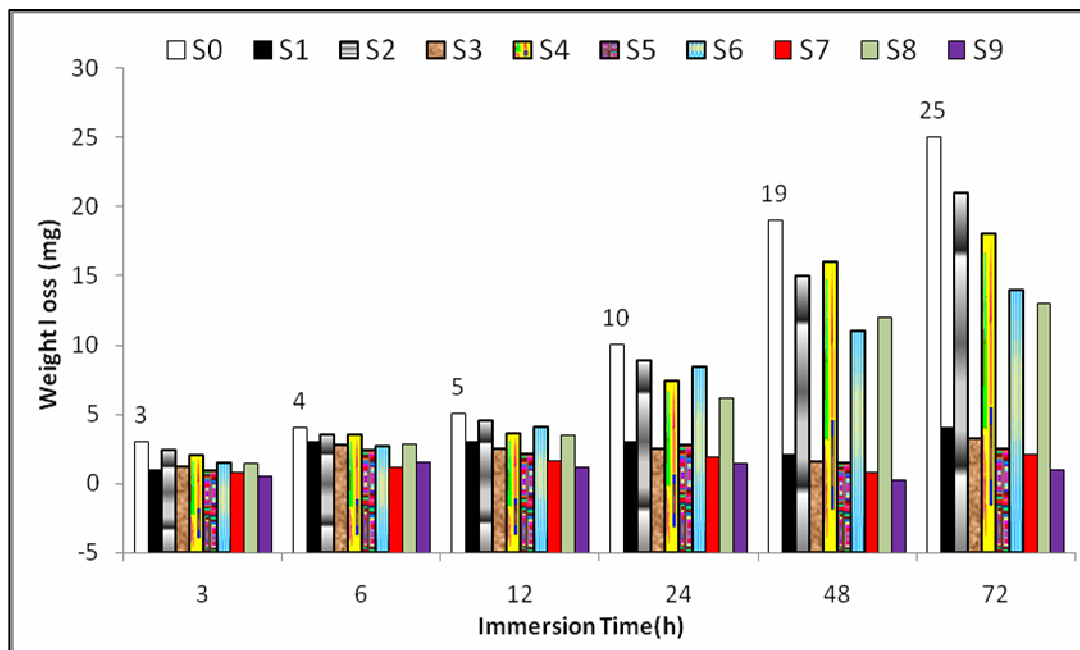


Fig.-1: Weight loss (mg) vs. immersion time (h).

{for corroderent (S0); with EETfgS (1.056g/L) (S1); with ion-additives (0.5 g/100 ml) (Cl^- S2 / Br^- S4 / I^- S6 and Zn^{2+} S8) and with [EETfgS + ion-additives] (S3, S5, S7, and S9)}

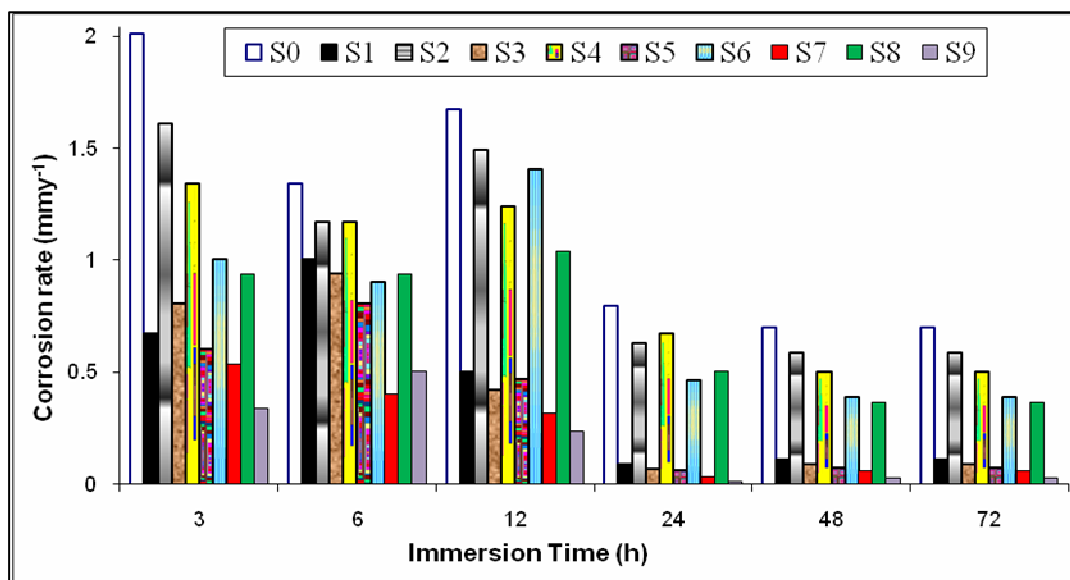


Fig.-2: Corrosion rate (ρ_{corro}) ($\text{mm}\cdot\text{y}^{-1}$) vs. immersion time (h)

{for corroderent (S0); with EETfgS (1.056g/L) (S1); with ion-additives (0.5 g/100 ml) (Cl^- S2 / Br^- S4 / I^- S6 and Zn^{2+} S8) and with [EETfgS + ion-additives] (S3, S5, S7, and S9)}

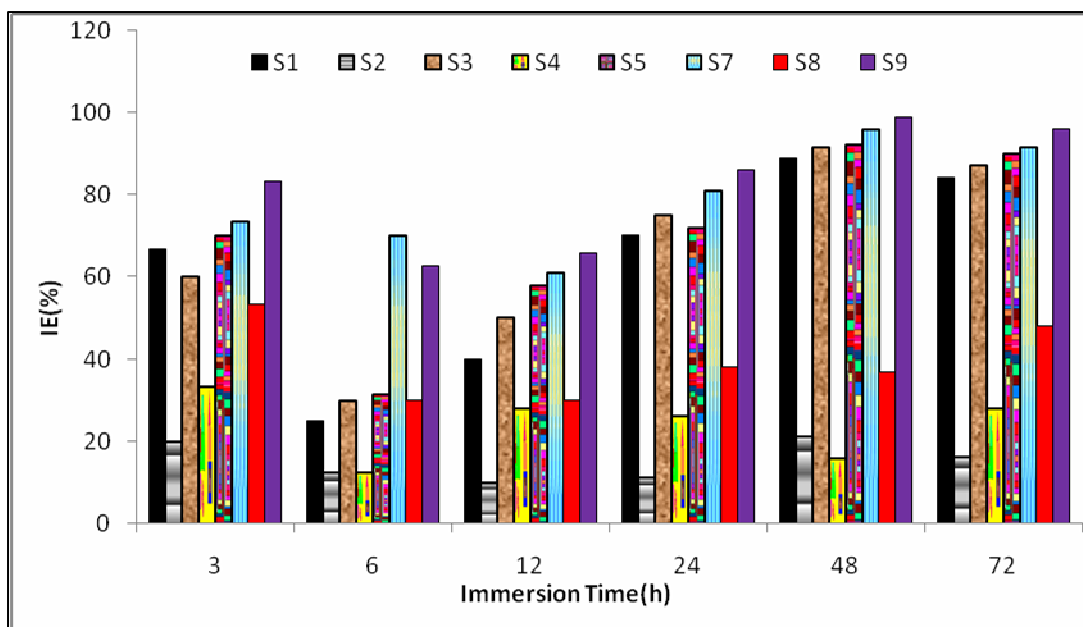


Fig.-3: Inhibition efficiency Vs. immersion time (h)
{ with EETfgS (1.056g/L) (S1); with ion-additives (0.5 g/100 ml) (Cl^- S2 / Br^- S4 / I^- S6 and Zn^{2+} S8) and with [EETfgS + ion-additives] (S3, S5, S7, and S9)}

Table-1: Corrosion parameters for corrosion of AA6063 in 0.5N HCl in absence and presence of EETfgS /and ion-additives at different immersion periods (h).

Immersion period (h)	0.5 N HCl Test Solution without or with extract / ion-additives	Beaker label	Weight loss (mg)	Corrosion rate (ρ_{corro}) (mmy^{-1})	IE (%)	Fractional surface coverage (θ)
3	Corrodent (blank)	S0	3.0	2.0117		
	EETfgS	S1	1.0	0.6706	66.67	0.6667
	KI	S2	2.4	1.6093	20.00	0.2000
	EETfgS+KI	S3	1.2	0.8047	60.00	0.6000
	KCl	S4	2.0	1.3411	33.33	0.3333
	EETfgS+KCl	S5	0.9	0.6035	70.00	0.7000
	KBr	S6	1.5	1.0058	50.00	0.5000
	EETfgS+KBr	S7	0.8	0.5364	73.33	0.7333
	Zn^{2+}	S8	1.4	0.9388	53.33	0.5333
	EETfgS+ Zn^{2+}	S9	0.5	0.3353	83.33	0.8333
6	Corrodent (blank)	S0	4.0	1.3411		
	EETfgS	S1	3.0	1.0058	25.00	0.2500
	KI	S2	3.5	1.1735	12.50	0.1250
	EETfgS+KI	S3	2.8	0.9388	30.00	0.3000
	KCl	S4	3.5	1.1735	12.50	0.1250
	EETfgS+KCl	S5	2.4	0.8047	31.43	0.3143
	KBr	S6	2.7	0.9053	32.50	0.3250
	EETfgS+KBr	S7	1.2	0.4023	70.00	0.7000
	Zn^{2+}	S8	2.8	0.9388	30.00	0.3000
	EETfgS+ Zn^{2+}	S9	1.5	0.5029	62.50	0.6250
	Corrodent (blank)	S0	5.0	0.8382		

12	EETfgS	S1	3.0	0.5029	40.00	0.4000
	KI	S2	4.5	0.7544	10.00	0.1000
	EETfgS+KI	S3	2.5	0.4191	50.00	0.5000
	KCl	S4	3.6	0.6035	28.00	0.2800
	EETfgS+KCl	S5	2.1	0.3520	58.00	0.5800
	KBr	S6	4.1	0.6873	18.00	0.1800
	EETfgS+KBr	S7	1.6	0.2682	60.98	0.6098
	Zn ²⁺	S8	3.5	0.5867	30.00	0.3000
	EETfgS+ Zn ²⁺	S9	1.2	0.2012	65.71	0.6571
24	Corrodent (blank)	S0	10.0	0.8382		
	EETfgS	S1	3.0	0.2515	70.00	0.7000
	KI	S2	8.9	0.7460	11.00	0.1100
	EETfgS+KI	S3	2.5	0.2096	75.00	0.7500
	KCl	S4	7.4	0.6203	26.00	0.2600
	EETfgS+KCl	S5	2.8	0.2347	72.00	0.7200
	KBr	S6	8.4	0.7041	16.00	0.1600
	EETfgS+KBr	S7	1.9	0.1593	81.00	0.8100
	Zn ²⁺	S8	6.2	0.5197	38.00	0.3800
48	Corrodent (blank)	S0	19	0.7963		
	EETfgS	S1	2.1	0.0880	88.95	0.8895
	KI	S2	15	0.6287	21.05	0.2105
	EETfgS+KI	S3	1.6	0.0671	91.58	0.9158
	KCl	S4	16	0.6706	15.79	0.1579
	EETfgS+KCl	S5	1.5	0.0629	92.11	0.9211
	KBr	S6	11	0.4610	42.11	0.4211
	EETfgS+KBr	S7	0.8	0.0335	95.79	0.9579
	Zn ²⁺	S8	12	0.5029	36.84	0.3684
72	Corrodent (blank)	S0	25.0	0.6985		
	EETfgS	S1	4.0	0.1118	84.00	0.8400
	KI	S2	21.0	0.5867	16.00	0.1600
	EETfgS+KI	S3	3.2	0.0894	87.20	0.8720
	KCl	S4	18.0	0.5029	28.00	0.2800
	EETfgS+KCl	S5	2.5	0.0699	90.00	0.9000
	KBr	S6	14.0	0.3912	44.00	0.4400
	EETfgS+KBr	S7	2.1	0.0587	91.60	0.9160
	Zn ²⁺	S8	13.0	0.3632	48.00	0.4800
12	EETfgS+ Zn ²⁺	S9	1.0	0.0279	96.00	0.9600

Table-2: Synergistic parameter (S) for [EETfgS + ion-additives] for AA6063 for various immersion periods (h) in 0.5 N HCl at room temperature.

Immersion period (h)	EETfgS + Ion-additives	Synergistic Parameter (S)
3	I ⁻	2.484
	Cl ⁻	2.329
	Br ⁻	2.438
	Zn ²⁺	2.678
6	I ⁻	2.738
	Cl ⁻	2.864
	Br ⁻	2.595
	Zn ²⁺	2.843
12	I ⁻	2.747

	Cl^-	2.779
	Br^-	2.451
	Zn^{2+}	2.767
24	I^-	2.454
	Cl^-	2.582
	Br^-	2.459
	Zn^{2+}	2.552
48	I^-	1.999
	Cl^-	1.903
	Br^-	3.268
	Zn^{2+}	2.607
72	I^-	3.398
	Cl^-	7.078
	Br^-	5.176
	Zn^{2+}	3.103

CONCLUSIONS

On analyzing the investigations on the inhibition efficiency of co-employment of the two inhibitors, EETfgS and ion-additives, following conclusions can be drawn:

1. The co-employment of the two inhibitors [EETfgS + ion-additives] produced promising results.
2. Inhibition efficiency (% IE) was seen synergistically increased on addition of ion-additives.
3. IE for EETfgS (88.95 %) was found to increase significantly on adding ion-additives, viz. I^- (91.58 %); Cl^- (92.11 %); Br^- (95.79 %) and Zn^{2+} (98.95 %).
4. Of all ion-additives, EETfgS when co-employed with Zn^{2+} ions, show significant rise in inhibitory action for almost all immersion periods.
5. Distinctive synergism has been seen between the two inhibitors, EETfgS and ion-additives, with S values > unity.
6. The synergism vary on addition of ion-additives to EETfgS in the order $\text{Zn}^{2+} > \text{Br}^- > \text{Cl}^- > \text{I}^-$
7. These environmentally friendly inhibitors could find possible applications in metal surface anodizing and surface coating in industries.

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