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Corrosion Inhibition and Adsorption Behaviour of Janumet for Mild Steel in 0.1 M HCl

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Abstract: **Inhibitive and adsorption properties of Janumet for inhibition of corrosion of mild steel in HCl was studied using weight loss and hydrogen evolution methods at 303 and 333 K. It was found that the studied drug inhibited the corrosion of mild steel in this acid induced condition The inhibition efficiency increases with increase in inhibitors concentration and decreases at a higher temperature. The adsorption of inhibitor on the mild steel follows Langmuir isotherm at two temperatures studied. Results obtained by these two techniques are in good agreement. Mechanism of physical adsorption is proposed from the apparent activation energy (Ea) and thermodynamic parameters obtained. The adsorption of the Janumet on the mild steel surface was also found to be spontaneous.**

Keywords: **Corrosion inhibition, Mild steel, Acid, weight loss, Janumet.**

1. INTRODUCTION

In an attempt to find corrosion inhibitors which are environmentally safe and readily available, there has been a growing trend in the use of drugs as corrosion inhibitors for metals in acid cleaning process1. A lot of works have been reported using drugs such as such as quinine [1] norfloxacin [2], Ciprofloxacin [3] Streptomycin [4] and Cefazolin [5] and Cefuroxime [6] for the acid corrosion inhibition of mild steel.

In this study, the inhibitory action of Janumet on the corrosion of mild steel in hydrochloric acid solution has been investigated at two different temperatures (303 and 333K) using weight loss and hydrogen evolution method. Janumet is a prescription drug that belongs to a group of Type 2 diabetes drugs called incretin therapies. The tablets of this drug contain two oral antidiabetic drugs (sitagliptin and metformin hydrochloride) used in the management of type 2 diabetes only. Sitagliptin (marketed under the trade name Januvia) is an orally-active inhibitor of the dipeptidyl peptidase-4 (DPP-4) enzyme and is present in Janumet tablets in the form of sitagliptin phosphate monohydrate. Metformin hydrochloride (marketed under the trade name Glucophage) is not chemically related to any other classes of oral antidiabetic agents. There are two prescription drugs: Janumet tablets and Janumet XR tablets (extended-release) and both are used along with meals. The main difference between the two is that Janumet tablet is taken twice daily, while that of Janumet XR is taken once daily. It was Janumet tablets that were used in this study. Each tablet of Janumet used contains 50 mg sitagliptin as free base and 1000 mg metformin hydrochloride and the tablets are red, capsule-shaped, film-coated tablets with "577" debossed on one side. The chemical structures of sitagliptin phosphate monohydrate and metformin hydrochloride are shown below.[7]

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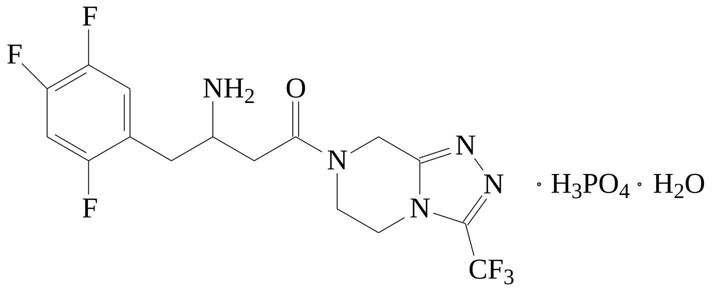
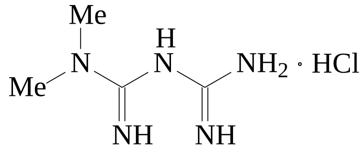


Sitagliptin phosphate monohydrate



Metformin hydrochloride

Metformin can cause a rare but serious side effect called lactic acidosis (a buildup of lactic acid in the blood), which can cause death. There also have been several post marketing reports of pancreatitis in people treated with sitagliptin and other DPP-4 inhibitors as a result of which the U.S. package insert carries a warning to this effect [7].

Janumet drug contains heteroatoms (ten nitrogen, seven fluorine and one oxygen atom) as reactive centers through which they can adsorb readily on the metal surface hence their suitability for the study.

2. MATERIALS AND METHODS

2.1 Weight loss method

A previously weighed metal (mild steel sheet) was completely immersed in 250 ml of the test solution in an open beaker. The beaker was inserted into a water bath maintained at a temperature of 30 °C. Similar experiments were repeated at 60°C. In each case, the weight of the sample before immersion was measured using Scaltec high precision balance (Model SPB31) After every 24 hours, each sample was removed from the test solution, washed in a solution of NaOH containing zinc dust and dried in acetone before re-weighing. The difference in weight for a period of 168 hours was taken as total weight loss. The inhibition efficiency (% I) for the inhibitor was calculated using equation 1 [8]

$$\%I = \left(1 - \frac{W_1}{W_2}\right) \times 100 \qquad 1$$

where W_1 and W_2 are the weight losses (g/dm^3) for mild steel in the presence and absence of inhibitor in HCl solution respectively. The degree of surface coverage θ is given by the equation 2 [9]:

$$\theta = \left(1 - \frac{W_1}{W_2}\right) \qquad 2$$

The corrosion rates for mild steel corrosion in different concentrations of the acid was determined for 168 h immersion period from weight loss using equation 3 [6]

$$Corrosion\ rate(mpy) = \frac{534W}{DAT} \qquad 3$$

where W = weight loss (mg); D = density of specimen (g/cm^3), A = area of specimen (square inches) and T = period of immersion (hour).

2.2 Gasometry method

The method used for hydrogen evolution measurement is as described elsewhere [9]. The test solution (different concentrations of acid, inhibitor or their mixtures) was poured into the reaction vessel (gasometer). Upon the introduction of mild steel, the flask was quickly corked and the rise in volume of the paraffin due to hydrogen evolution was noted after every minute until a steady volume was observed. From the results obtained, the corrosion inhibition efficiency was calculated using the following equation,

$$\%IE = \frac{V_b - V_t}{V_b} \times 100 \qquad 4$$

whereV_b is the volume of hydrogen gas evolved by the blank and V_t is the volume of hydrogen gas evolved in the presence of the inhibitor, after time, t.

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3. RESULTS AND DISCUSSIONS

3.1 Gasometric Study

Figure 1 shows the variation of the volume of hydrogen gas evolved with time for the corrosion of mild steel in various concentration of HCl.. Figure. 2 represents the variation of volume of hydrogen gas evolved with time for the corrosion of mild steel in HCl containing various concentrations of Janumet at 303 and 333 K. The figures clearly indicated that the volume of hydrogen gas evolved increased with increase in period of contact and with increase in temperature indicating that the rate of corrosion of mild steel in HCl increased with increase in temperature and the period of contact. However, in the presence of Janumet, the rates of corrosion (as indicated by the volume of hydrogen gas evolved) were seen to decreased with increase in the concentration of Janumet indicating that Janumet inhibited the corrosion of mild steel in HCl and that the inhibition efficiency of Janumet increased with increase in its concentration. Calculated inhibition efficiencies of various concentrations of Janumet in HCl is presented in Table 1. The inhibition efficiency was found to increases with increase in the concentration of the inhibitor but decreases with increase in temperature indicating that the mechanism of physical adsorption favours the adsorption of Janumet on mild steel surface.

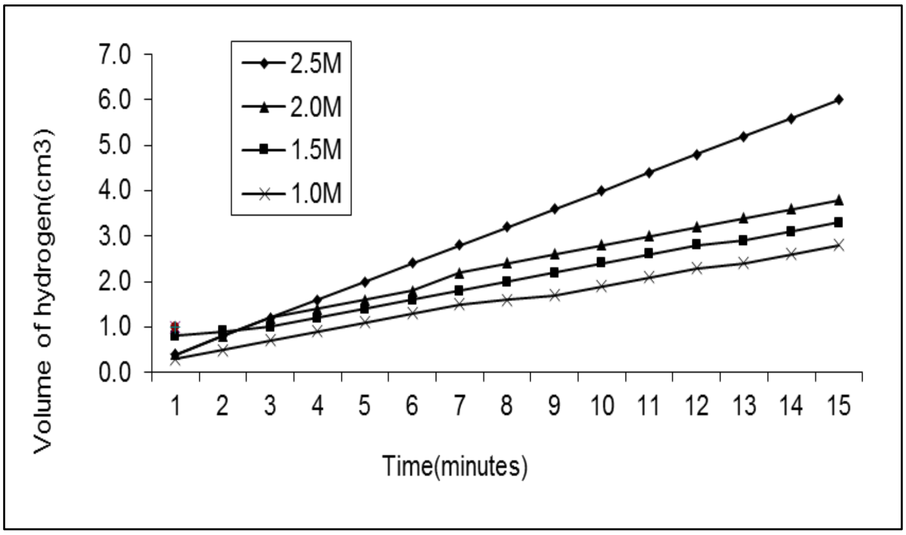

Fig 1: Variation of hydrogen gas evolved with time for the corrosion of mild steel at various concentrations of HCl at 303K

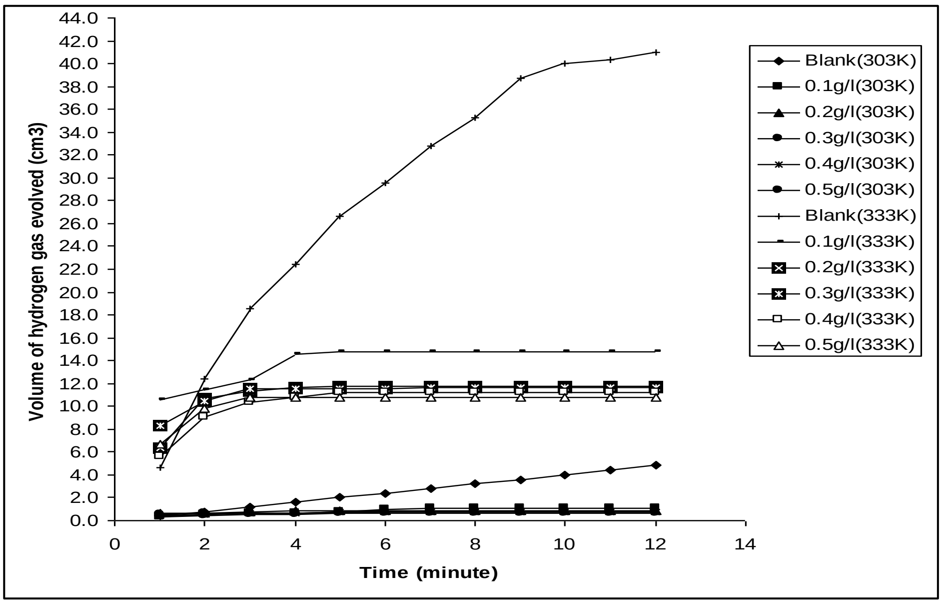

FIG. 2: Variation of volume of hydrogen gas evolved with time for the corrosion of mild steel in 2.5 M HCl containing various concentrations of Janumetat 303 and 333 K

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TABLE 1: Inhibition efficiencies of Janumet

C (g/L)	Volume of H_2 evolved (cm^3)		%I (333 K)	%I (303 K)
0.1	7.4	5.4	24.49	45.00
0.2	4.9	4.9	50.00	50.00
0.3	4.2	4.0	57.14	59.18
0.4	3.7	3.4	62.25	65.31
0.5	2.9	2.5	70.41	74.39

3.2 Gravimetric Study

Figures 3 and 4 present variation of weight loss with time for the corrosion of mild steel in 0.1 M HCl containing various concentrations of Janumet at 303 and 333 K respectively. From the plots obtained, it can be deduced that Janumet is indeed a corrosion inhibitor for mild steel in hydrochloric acid solution since there was a general decrease in weight loss at the end of the corrosion-monitoring process at the temperatures studied. Also a remarkable decrease in weight loss of the metal in the presence of inhibitor as compared to mild steel alone in acid signifying corrosion inhibition. Values of corrosion rates of mild steel in the absence and presence of various concentrations of Janumet are recorded in Table 2 while Table 3 present the values of inhibition efficiencies of Janumet for the corrosion of mild steel in HCl. As expected, the corrosion rates of mild steel in the presence of HCl were lower than the value for the blank. In addition, the corrosion rates were found to decrease as the concentration of Janumet increases while the inhibition efficiencies increased with increase in the concentration of Janumet. The result that the inhibition efficiency of Janumet increases with increase in inhibitor concentration suggests that some of the molecules of the inhibitor are adsorbed on the metal surface thereby protecting the “covered” surface from further corrodent attack [10].

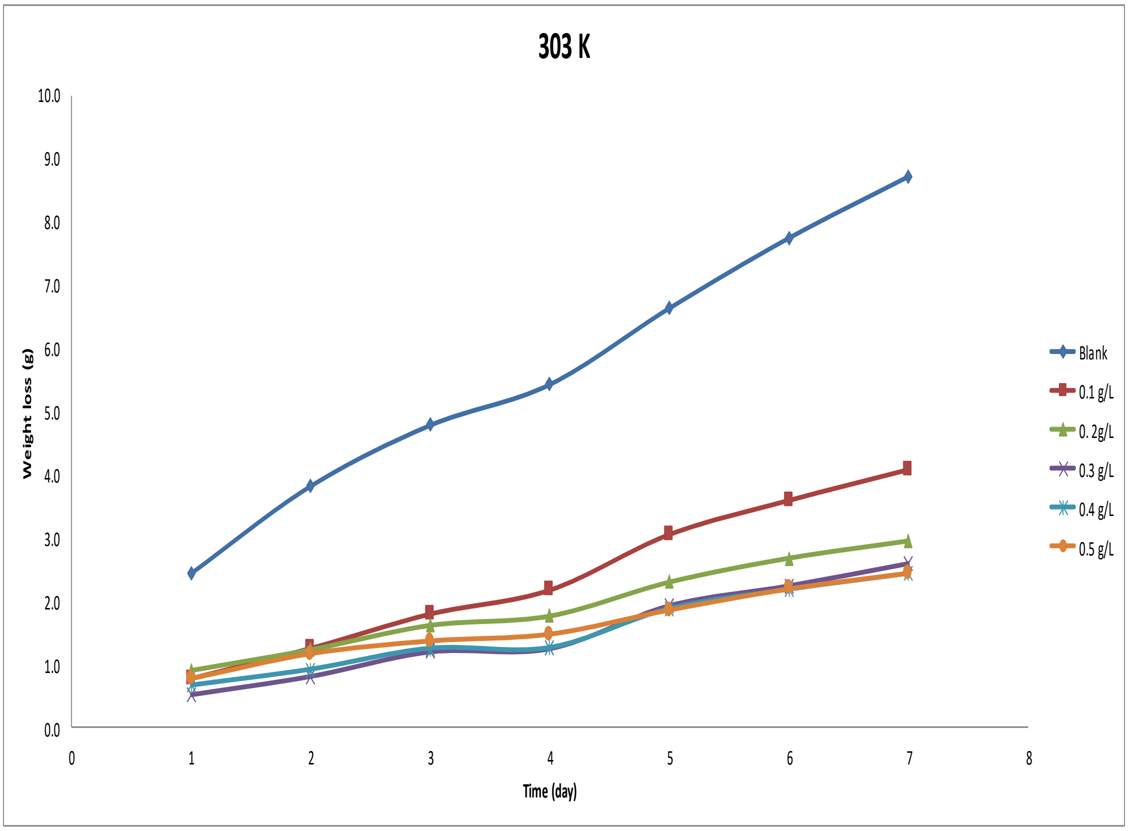

FIG. 3: Variation of weight loss with time for the corrosion of mild steel in 0.1 M HCl containing various concentrations of Janumet at 303 K

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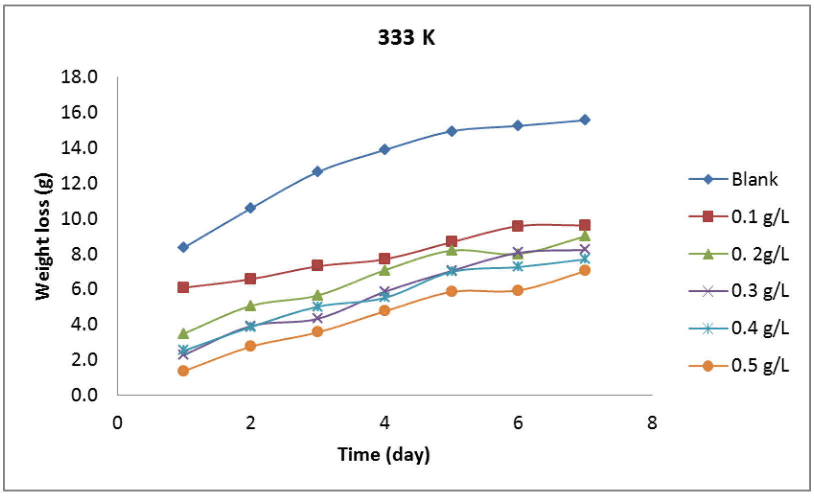

FIG. 4: Variation of weight loss with time for the corrosion of mild steel in 0.1 M HCl containing various concentrations of Janumet at 333 K

TABLE 2: Corrosion rate of mild steel in solutions of HCl and Janumet

C (g/L)	Corrosion rate ($g/h^{-1}cm^{-2}$) x 0.0001	
	303 K	**333 K**
Blank	2.61	4.60
0.1	1.21	2.84
0.2	0.88	2.65
0.3	0.77	2.44
0.4	0.71	2.28
0.5	0.69	2.07

TABLE 3: Inhibition efficiencies of Janumet for mild steel in 0.1 M HCl

C (g/L)	**Inhibition efficiency (%)**	
	303 K	**333 K**
Blank	-	-
0.1	53.5	41.2
0.2	66.4	47.4
0.3	70.5	55.3
0.4	72.5	60.1
0.5	72.7	64.0

3.3 Thermodynamic Considerations

The dependence of the rate of corrosion of mild steel on temperature was studied using the condensed form of Arrhenius equation (Equation 5) [10].

$$\log(CR_2/CR_1) = E_a/2.303(1/T_1 - 1/T_2) \qquad 5$$

where E_a is the activation energy, CR_1 and CR_2 are the corrosion rates at the temperatures T_1 (303 K) and T_2 (333 K) respectively. Values of E_a calculated from equation 7 are recorded in Table 4. These values were found to range from 41.10 to 47.54 kJ/mol. The observed results indicated that the adsorption of the drug is consistent with the mechanism of physical adsorption. For a physical adsorption mechanism, the activation energy should be less than 80 kJ/mol as observed in the present study [10]. Also, the values of E_a obtained in the presence of Janumet were higher than the value obtained for the blank indicating that the drug retarded the corrosion of mild steel in HCl.

The heat of adsorption of the inhibitor unto mild steel surface was calculated using the following equations [11].

$$Q_{ads} = 2.303R\left(\frac{\theta_2}{1-\theta_2} - \frac{\theta_1}{1-\theta_1}\right) \times \left(\frac{T_1T_2}{T_2-T_2}\right) \qquad 6$$

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where Q_{ads} is the heat of adsorption, R is the gas constant, θ_1 and θ_2 are the degrees of surface coverage of the inhibitor at the lower and higher temperatures (T_1 and T_2) respectively. Calculated values of Q_{ads} are also presented in Table 4. These values are low and negative, indicating that the adsorption of the inhibitors is exothermic and that the mechanism of physical adsorption is favoured. Physical adsorption is characterized by low values of heat of adsorption, as found in the present study. Values of Q_{ads} calculated from equation 6 are also seen to decrease with increase in the concentration of the inhibitor indicating that the adsorption becomes more exothermic with increasing concentration of the inhibitor.

Table 4: Thermodynamic parameters for the adsorption of Janumet on mild steel surface

C (g l^{-1})	E_a (kJmol^{-1})	Q_{ads} (kJmol^{-1})
Blank	29.50	-
0.1	47.54	-39.22
0.2	46.10	-28.54
0.3	43.23	-26.25
0.4	41.45	-24.26
0.5	41.10	-23.54

3.4 Adsorption considerations

The adsorption characteristics of Janumet was also studied by fitting curves for different adsorption isotherms including Langmuir, Freundlich, Temkin, Florry Huggins, Frumkin and Bockris Swinkel adsorption isotherms. The test indicated that Langmuir adsorption isotherm best described the adsorption characteristics of Janumet. The assumptions of Langmuir isotherms is expressed by Equation 7 [11].

$$ln\left(\frac{C}{\theta}\right) = lnb_{ads} - lnC \qquad 7$$

From equation 7, a plot of $ln\left(\frac{C}{\theta}\right)$ versus ln (C) should be a straight line with slope and intercept equal to unity and lnb_{ads} respectively. Figure 5 show the Langmuir shows Langmuir isotherm for the adsorption of Janumet on the surface of mild steel. Values of adsorption parameter deduced from Langmuir isotherms are recorded in Table 5. Results in the Table indicate that b_{ads} values whose values indicate the binding power of the inhibitor to the metal surface are seen to increase with increasing temperature. Such behaviour can be interpreted on the basis that an increase in temperature results in the adsorption of more components of the Janumet on the metal surface and is consistent with the proposed physically mechanism [10, 12]. These results confirm the suggestion that this inhibitor is physically adsorbed and the strength of adsorption decreases with temperature.

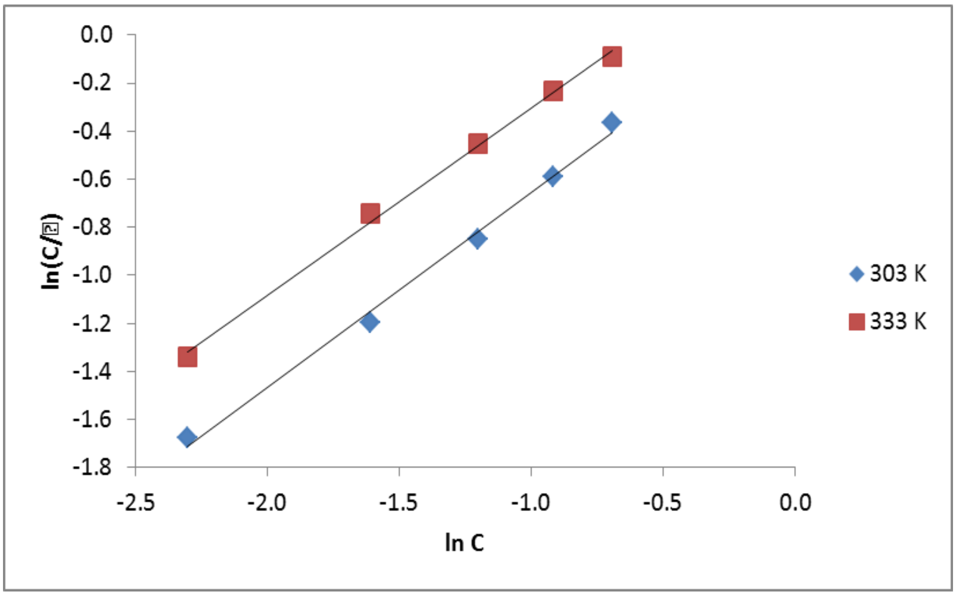

FIG. 5: Langmuir isotherm for the adsorption of Janumet on the surface of mild steel.

TABLE 5: Langmuir parameters for the adsorption of Janumet on mild steel surface

T (K)	slope	$\ln b_{abs}$	ΔG^0_{ads} $(kJ/mol$	R^2
303	0.809	0.153	-24.19	0.9953
333	0.777	0.474	-26.05	0.9962

From values of the equilibrium constant of adsorption, the free energy of adsorption was calculated using Equation 8[2, 3]

$$b_{ads} = \frac{1}{55.5} exp\left(\frac{\Delta G^0_{ads}}{RT}\right) \qquad 8$$

Calculated values of ΔG_{ads} are recorded in Table 5. These values are negative and are less than the threshold value of -40kJ/mol required for chemical adsorption hence the adsorption of Janumet on the surface of mild steel is spontaneous and occurred according to the mechanism of physical adsorption. [12- 14].

4. CONCLUSIONS

Janumet is a good inhibitor for mild steel corrosion. The inhibitor functions by being adsorbed on mild steel surface. Janumet is a better inhibitor at lower temperature. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters. The experimental data fit the Langmuir adsorption isotherm.

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