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Synthesis of hydrazide derivatives and study their application as corrosion inhibitors for carbon steel in acidic solution

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ABSTRACT

The inhibition efficiency of two novels ethoxylated (10 and 20 ethylene oxide units) streayl hydrazides against corrosion of carbon steel in 1 M HCl was investigated at different temperature ranges (25 – 55 °C) by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods. The carbon steel surface morphology was investigated by scanning electron microscopy (SEM). The obtained results showed that the prepared inhibitors have good inhibition in 1 M HCl, and the inhibition efficiency increases with the inhibitor concentration at 25 °C. At 600 ppm the corrosion rates increase with increasing the temperature. Polarization curves show that the inhibitors in hydrochloric acid act as mixed type inhibitors.

Keywords: Hydrazide Derivatives; Carbon Steel; Potentiodynamic Polarization; EIS; SEM.

INTRODUCTION

The use of hydrochloric acid in pickling of metals, acidization of the oil wells and cleaning of scales is more economical, efficient and trouble-free, than other mineral acids [1,2]. Inhibition is used to prevent metal dissolution as well as acid consumption [3,4]. One of such methods is the use of the organic inhibitors [5–10]. Most organic inhibitors are substances with at least one functional group, which considered as the reaction center in the adsorption process. The adsorption of inhibitors is related to the presence of heteroatom as nitrogen [11-17] phosphorus and sulfur [19-20]. Surfactants are a special type of organic compounds and exhibit unique properties due to their amphiphilic molecule. The surfactant inhibitors have many advantages, for example, high inhibition efficiency, low price, low toxicity, and easy production [21-26]. In particular nonionic surfactants (where the polar head group is without charge) have been shown to possess high inhibition efficiency for metal corrosion in different solutions [27,28]. The adsorption of the surfactant on the metal surface can markedly change the corrosion resisting property of the metal, so the study of the relationship between the adsorption and corrosion inhibition is of great importance. The aim of the present work is to investigate the corrosion inhibition and the inhibition mechanism of the prepared hydrazide derivatives for carbon steel in 1 M hydrochloric acid, and the effect of temperature in their corrosion.

MATERIALS AND METHODS

2.1. Materials

All tests were performed on carbon steel, the chemical composition is listed in Table 1.

Table 1: Chemical composition of carbon steel sample

Element	C	Si	Mn	P	S	Fe
Weight (%)	0.19	0.05	0.94	0.09	0.04	Reminder

2.2. Inhibitors

The used inhibitors were prepared through two steps: Synthesis of Streyalhydrazide Streyalhydrazide were prepared according to previous the method [29].

2.2.2. Ethoxylation of streyalhydrazide

Streyalhydrazide was charged into a high pressure stainless steel autoclave with sodium metal (0.3 wt. %) as a catalyst at 150 °C with continuous stirring. While passing a stream of nitrogen gas through the system for 10 min to flush out the air. The nitrogen stream was then replaced by three different molar ratios 10 and 20 units of ethylene oxide (e.o.) [30]. The reaction completion was established when the pressure reached to its minimum value. At this stage, heating was stopped and the contents were cooled. After cooling, the product obtained was neutralized with HCl (37 %). Then dissolved in isopropanol and salted out with a supersaturated NaCl solution. The ethoxylated products I and II obtained are equivalent to the addition of 10 and 20 e.o., respectively (Fig. 1).

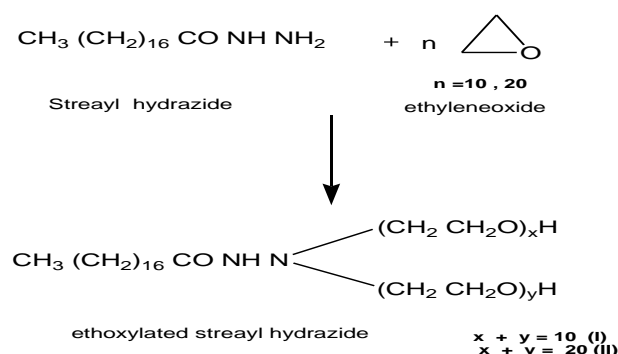


Fig. 1: Scheme for the synthesized compounds

2.3. Solutions

The aggressive solution, 1 M HCl, were prepared by dilution of analytical grade 37% HCl with distilled water. The concentration range of the prepared surfactants used from 100 ppm to 600 ppm.

2.4. Polarization measurements

Potentiodynamic and electrochemical impedance spectroscopy (EIS) measurements were carried out in a conventional three- electrode cell with a platinum electrode as an auxiliary electrode and a saturated calomel electrode as a reference electrode. The working electrode was in the form of rod from carbon steel embedded in epoxy resin of polytetra fluoro ethylene. The exposed area to the corrosive solution was 0.5 cm². The carbon steel rod was abraded with a series of emery paper (grade 320 - 500 - 800 - 1200) and then washed with distilled water and acetone. Before measurements, the electrode was immersed in the test solution at the natural potential for 1h until a steady state was reached. Potentiodynamic and EIS measurements were recorded by a volta lab 40 potentiostat PGZ 301 attached with to software program (voltmaster 4). The measurements were carried out using AC signal (10 mv) peak at the open circuit potential in the frequency range of 100-50 kHz.

2.5. Scanning electron microscopy

The surface examination was carried out using scanning electron microscope (Jeol 5400, Japan), the energy of the accelerated beam employed was 30 kV.

RESULTS AND DISCUSSION

3.1. Chemical structure

The chemical structures of the synthesized inhibitors were confirmed By the FTIR, Mass and ¹HNMR spectra.

3.1.1. FTIR

FTIR spectrum of the synthesized compounds before and after ethoxylation (Fig. 2 a and b) showed the following absorption bands at 1630cm⁻¹ (C=O), 2894 cm⁻¹ (CH asymmetric stretching) and 3183, 3319 cm⁻¹ for -NH₂. The

disappearance of $-\text{NH}_2$ band and appearance of the broad band that corresponding to $-\text{OH}$ at 3378 cm^{-1} was revealed in Fig 2b. FTIR spectrum confirmed the formation of the prepared functional groups of the synthesized ethoxylated stearylhydrazide.

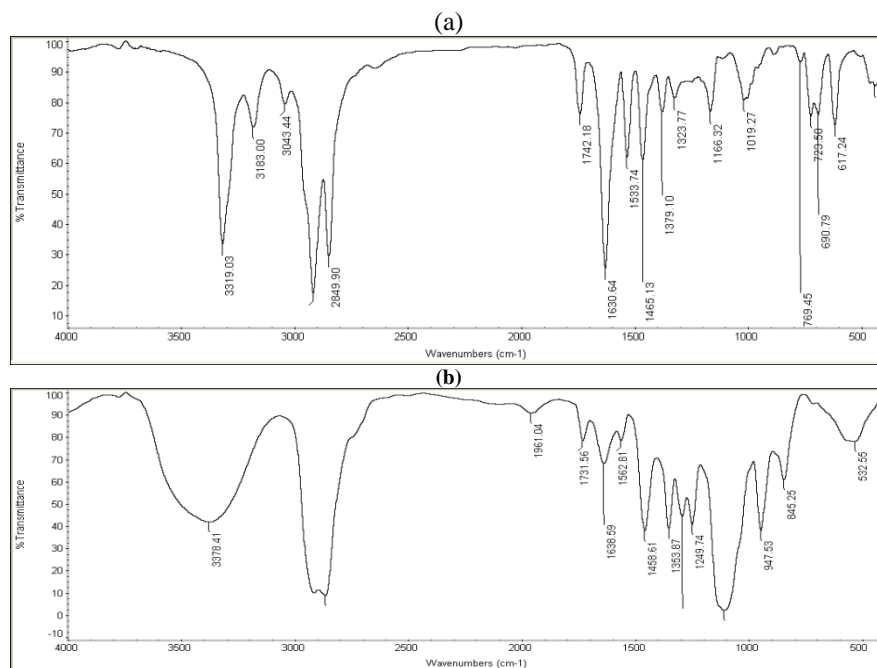


Fig. 2: FTIR charts of inhibitor I (a) before ethoxylation (b) after ethoxylation

3.1.2. Mass spectroscopy

The mass spectrum of the synthesized ethoxylated stearylhydrazide (I) illustrated a molecular ion peak at m/z 738(26%) together with a base peak at 87 (100% , $\text{CH}_3\text{CH}_2\text{C}=\text{ONHNH}-$). Fragmentation were obtained as : 722 (13 $(\text{CH}_2)_{16}\text{C}=\text{O NH-N}(\text{CH}_2\text{CH}_2\text{-O})_{10}\text{H}$), 635(21 $(\text{CH}_2)_{16}\text{C}=\text{O NH-NH}(\text{CH}_2\text{CH}_2\text{-O})_8\text{H}$), 591(19 $(\text{CH}_2)_{16}\text{C}=\text{O NH-NH}(\text{CH}_2\text{CH}_2\text{-O})_7\text{H}$) and 563 (21 $(\text{CH}_2)_{14}\text{C}=\text{O NH-NH}(\text{CH}_2\text{CH}_2\text{-O})_7\text{H}$). The results of mass spectrum confirmed the chemical structure of the synthesized ethoxylated stearylhydrazide.

3.1.3. ^1H NMR Spectroscopy

The ^1H NMR (CDCl_3 , 300 MHz, δ ppm) spectrum of the synthesized ethoxylated stearylhydrazide I showed different peaks at $\delta = 0.77$ (t, 3H, $-\text{CH}_3$), 1.23 (m, 28H, $\text{CH}_3-(\text{CH}_2)_{14}-$), 1.53 (m, 2H, $\text{CH}_3-(\text{CH}_2)_{14}-\text{CH}_2-$), 2.23 (t, 2H, $\text{CH}_3-(\text{CH}_2)_{15}-\text{CH}_2-\text{C}=\text{O}$), 3.02 (s, 1H, $-\text{NH}-\text{CH}_2$), 3.62 (t, 20H, $-\text{NH}-(\text{CH}_2-\text{CH}_2-\text{O})_{10}$), 4.13 (s, 1H, OH) and 7.27 (s, 1H, $\text{C}=\text{O NH}-$). The data of ^1H NMR spectrum confirmed the expected hydrogen proton distribution in the synthesized ethoxylated stearylhydrazide.

3.2. Potentiodynamic polarization

The potentiodynamic polarization curves of steel in 1 M HCl solution in the absence and presence of prepared surfactants are shown in Fig. (3,4), the values of related electrochemical parameters i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic tafel slope β_a , cathodic tafel slope β_c , the degree of surface coverage and the corrosion inhibition efficiencies η_p were calculated and given in Table 2.

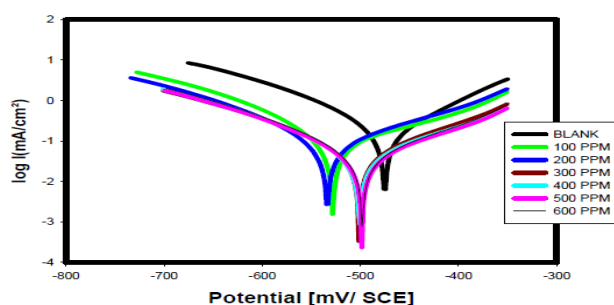


Fig. 3: Polarization plots of carbon steel electrode obtained in 1 M HCl solution and containing various concentrations of the inhibitor (I) at $25\text{ }^\circ\text{C}$.

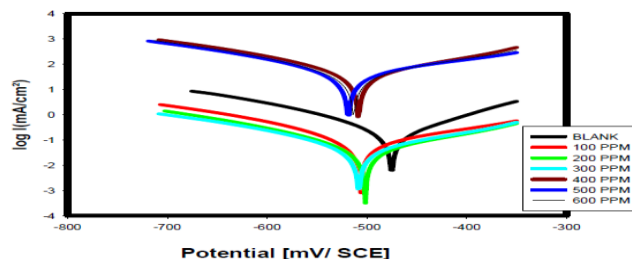


Fig. 4: Polarization plots of carbon steel electrode obtained in 1 M HCl solution and containing various concentrations of the inhibitor (II) at 25 °C

The percentage of inhibition efficiency, η_p , was calculated from polarization measurements according to the following relationship and listed in Table 2 [31,32]:

$$\eta_p = \frac{i_{\text{corr}}(\text{uninh}) - i_{\text{corr}}(\text{inh})}{i_{\text{corr}}(\text{uninh})} \times 100 \quad (1)$$

where, $i_{\text{corr}}(\text{uninh})$ and $i_{\text{corr}}(\text{inh})$ are uninhibited and inhibited corrosion current densities, respectively.

The polarization resistance was calculated using the stern-Geary equation [33]:

$$R_p = \frac{\beta_a \beta_c}{2.303 i_{\text{corr}}(\beta_a + \beta_c)} \quad (2)$$

Where, β_a and β_c the slopes of the anodic and the cathodic tafel lines, respectively.

Table 2: Electrochemical parameters for the corrosion of steel in 1 M HCl solution in the absence and presence of synthesized surfactants at 25 °C

Inhibitors	C, ppm	-E _{corr} (mV)	i _{corr} (μA/cm ²)	β _a (mV)	-β _c (mV)	R _p Ω/cm ²	θ	η%
Absence	---	475.30	369.5	131.1	139.8	117.50	--	--
I	100	528.00	351.9	253.5	173.0	253.46	0.633	63.30
	200	533.70	183.3	182.8	151.2	285.14	0.688	68.80
	300	501.30	109.1	191.1	165.9	508.03	0.705	70.48
	400	500.50	14.0-	207.5	158.1	547.61	0.722	72.22
	500	498.10	80.1	173.9	141.0	537.23	0.783	78.30
	600	498.10	80.1	173.9	141.0	537.23	0.783	78.30
II	100	506.30	190.1	329.6	197.7	360.86	0.320	32.0
	200	501.70	91.9	222.9	169.7	617.63	0.751	75.10
	300	508.30	89.2	233.0	184.1	608.64	0.758	75.80
	400	508.40	84.99	218.6	192.8	668.76	0.770	77.00
	500	518.70	73.59	293.6	191.3	745.04	0.800	80.00
	600	513.20	77.56	243.1	184.4	755.64	0.808	80.75

The decrease in corrosion current densities i_{corr} and the increase in the degree of surface coverage θ with increasing inhibitor concentration (Table 2) shown that the synthesized inhibitors are efficient corrosion inhibitors for carbon steel dissolution in 1 M HCl solution. Concerning Fig. (3,4), one can conclude that the addition of inhibitors to the corrosive solution reduces both anodic and cathodic reactions as would be expected. This may be described by the adsorption of the inhibitor molecules over the steel surface. The anodic and cathodic tafel slope changes with the increase of ethylene oxide e.o. units in the surfactants. Therefore, the synthesized nonionic surfactants can be classified as a mixed type inhibitor in HCl solution [34]. According to η_p values represented in Table 2., inhibitor II declared more inhibition efficiency than inhibitor I. That is, the inhibition efficiency increased by increasing e. o. units, this can be due the increase in e.o. units lead to increasing the surface coverage of the inhibitor and hence increase the adsorption on the steel surface [27,32].

3.3. EIS measurements

Results obtained from EIS can be interpreted in terms of the equivalent circuit of the electrical double layer shown in Fig. 5 which was used previously to model the metal / acid interface [35,36, 32].

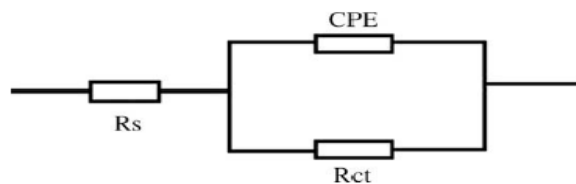


Fig. 5: Equivalent circuit used to fit the impedance spectra

The effects of the synthesized inhibitors on the impedance behavior for carbon steel in 1 M HCl in the absence and presence of different concentration of inhibitors are represented in Fig. (6,7).

It is clear from Fig. (6,7) that inhibited solution show a semicircular shape, their diameter increased after the addition of inhibitors to the corrosive solution. This increased was more and more pronounced with increasing the ethylene oxide units (e.o.) of the synthesized surfactants which indicates the adsorption of surfactant molecules on the metal surface increased by increasing e. o. units of surfactants [37]. The deviation from the ideal semicircle is generally attributed to the frequency dispersion as well as to the in homogeneities of surface and mass transport resistant [38].

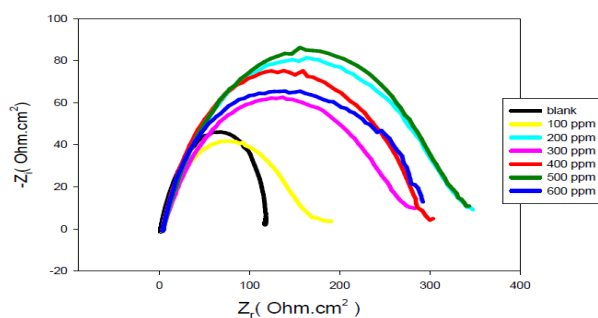


Fig. 6 : Nyquist plots for carbon steel electrode in 1 M HCl solutions in absence and presence inhibitor I at 25 °C.

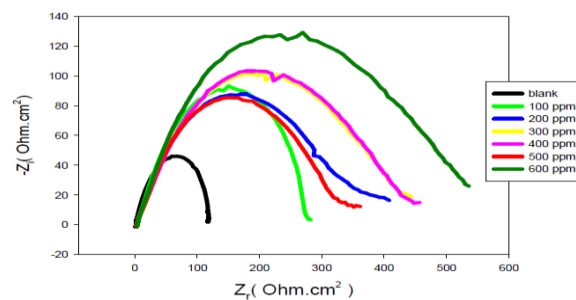


Fig. 7 : Nyquist plots for carbon steel electrode in 1 M HCl solutions in absence and presence inhibitor II at 25 °C

The electrochemical impedance parameters of carbon steel in 1 M HCl solution in the presence and absence of inhibitor additive were calculated. The charge-transfer resistance R_{ct} was given by subtracting the high frequency impedance from the low frequency one as follow [39] and the values are listed in Table 3:

$$R_{ct} = \dot{Z}_{re} \text{ (at low frequency)} - \dot{Z}_{re} \text{ (at high frequency)} \quad (3)$$

The values of electrochemical double layer capacitance C_{dl} were calculated at the frequency f_{max} at which the imaginary component of the impedance is maximal ($-Z_{max}$) by the following equation [40,41]

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (4)$$

The inhibition efficiency η_i were calculated from the values of R_{ct} according to the following equation [42,43]:

$$\eta_i = \frac{R_{ct}(inh) - R_{ct}(uninh)}{R_{ct}(inh)} \times 100 \quad (5)$$

where, $R_{ct(inh)}$ and $R_{ct(uninh)}$ are the values of charge transfer resistance in the presence and the absence of the inhibitor, respectively.

As can be seen from Table 3, the impedance parameter values are increased with increasing the inhibitor concentrations at 25 °C. the decrease in the values of the electrochemical double layer capacitance (C_{dl}) of the inhibitor I by increasing the concentration may be attributed to the replacement of the water molecules at the electrode surface of the inhibitor molecules at the electrode surface by the inhibitor molecules of lower dielectric constant through the adsorption process [44 -46].

Table 3 : Impedance electrochemical parameters derived from the Nyquist plot for carbon steel in 1 M HCl in the absence and presence of the synthesized inhibitors at 25 °C

Inhibitor	C, ppm	R_{ct} , ohm cm^2	C_{dl} , $\mu F cm^2$	Θ	$\eta_p\%$
Blank	--	117.5	121	--	--
I	100	275.0	129.6	0.573	57.27
	200	375.4	133.9	0.687	68.70
	300	432.5	82.41	0.728	72.83
	400	437.6	72.73	0.731	73.14
	500	337.1	105.7	0.651	65.14
	600	530.9	83.93	0.779	77.86
II	100	169.6	210.1	0.307	30.72
	200	337.0	132.2	0.651	65.13
	300	274.3	162.4	0.572	57.16
	400	292.3	121.9	0.598	59.80
	500	335.2	150.0	0.649	64.94
	600	299.0	133.0	0.607	60.70

3.4. Effect of temperature

Temperature is an important parameter in studies on metal dissolution. The corrosion rate in acid solutions, for example, increases exponentially with a temperature increase because the hydrogen evolution over potential decreases [47].

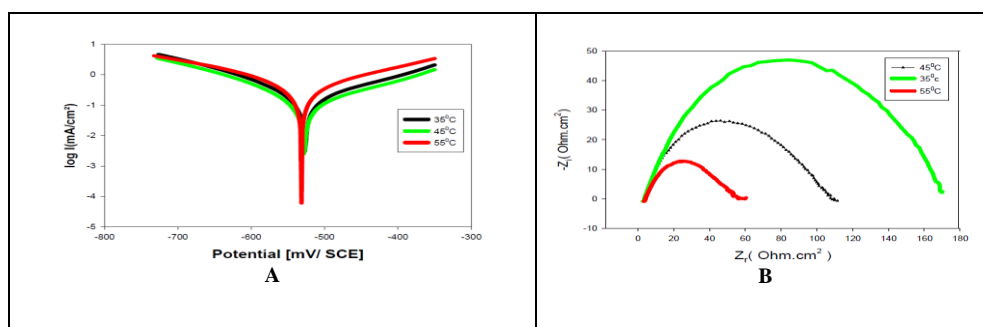


Fig.8 : Carbon steel in 1 M HCl in absence and presence of 600 ppm of II (a) Potentiodynamic polarization and (b) impedance curves at different temperature

The influence of temperature on the polarization in 1 M HCl in absence and presence of the investigated surfactants are represented in Fig. 8. Corrosion parameters of the investigated synthesized inhibitors I and II at 600 ppm are listed in Table 4 at different temperature. The listed data revealed that the corrosion inhibition efficiencies of the investigated compounds I and II decrease with increasing the temperature where the adsorption of the compounds on the metal surface are decreased.

Table 4: Electrochemical parameters for the corrosion of steel in 1 M HCl solution in the absence and presence of 600 ppm at different temperature.

Inhibitor	T °C	$-E_{corr}$ (mV)	i_{corr} ($\mu A/cm^2$)	β_a (mV)	$-\beta_c$ (mV)	R_p Ω/cm^2	$\eta_p\%$
I	35	527.9	270.5	246.3	180.2	219.66	26.79
	45	526.6	279.5	242.9	183.6	153.91	24.36
	55	531.3	291.3	242.3	236.2	87.70	21.16
II	35	508.6	218.3	178.0	206.7	226.40	44.92
	45	514.5	235.0	191.6	211.7	205.14	40.70
	55	534.6	271.2	145.4	194.7	145.44	31.57

3.5. Surface examination by SEM

Fig. 9 (a and b) show the SEM images of the steel surface after immersion in 1M HCl, for a period of 4hrs, in the absence and presence of inhibitor II. The SEM micrographs show that the surface of steel is highly damaged in the uninhibited solution (Fig. 9a). However smoother surface is seen in the presence of the inhibitor molecules (Fig. 9b) hinder the dissolution of steel by formation of a protective film on the steel surface [48].

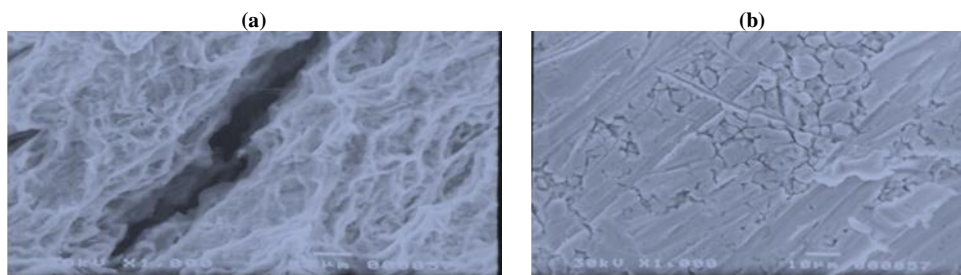


Fig. 9: The SEM image of carbon steel surface after immersion period, (a) absence of inhibitor (b) presence of inhibitor II

CONCLUSION

1. Ethoxylated streaylhydrazide (I and II) were characterized by FTIR, Mass and ¹HNMR.
- 2- Polarization and Impedance measurements results are matched.
- 3- The corrosion efficiencies of I and II increases as the e.o. units increase.
- 4- Polarization measurements declared the corrosion mechanism achieved by blocking active sites of the metal surface.
- 5- As the temperature increase the corrosion rate increase, and inhibitor II stilled more efficient than inhibitor I.

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