JOURNAL OF APPLIED ELECTROCHEMISTRY 10 (1980) 587–592

Inhibitive effects of isatin, thiosemicarbazide and isatin-3-(3-thiosemicarbazone) on the corrosion of aluminium alloys in nitric acid

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Received 26 July 1979

The inhibitive efficiencies of isatin, thiosemicarbazide and their condensation product, i.e. isatin-3-(3-thiosemicarbazone) are studied at different concentrations in relation to corrosion of aluminium alloys (1060, 1100, 3003) in 20% nitric acid at 30, 40 and 50° C using the weight loss method. Polarization experiments have been performed at 0.05, 0.2 and 0.3% concentrations of the inhibitors at 30° C. It is found that isatin-3-(3-thiosemicarbazone) is a more effective inhibitor as compared to the parent compounds for the three alloys at all the experimental temperatures. The effectiveness of the inhibitors increases with increase in temperature from 30° C to 50° C. The inhibitors are found to retard the corrosion by predominantly acting on local cathodes although they are also partially effective on the anodes. The critical current density for the passivation of aluminium decreases almost in the same order as the inhibition efficiency of the inhibitors increases.

1. Introduction

An extensive review of the literature has shown that very little attention has been paid to inhibition studies on aluminium alloys in nitric acid. Use of the organic compounds as corrosion inhibitors in nitric acid, especially at higher concentrations of the acid, has been scarcely attempted because of the presumption that organic compounds would not be stable in the acid and would show very poor inhibition [1]. In the case of corrosion of aluminium in nitric acid, N-containing compounds like amines have been found to be not very effective [2]. Sulphur-containing compounds like thioureas have shown satisfactory inhibition for the system and their inhibitive performances were enhanced if aromatic rings were attached to these molecules [3–7]. Thiosemicarbazide has been reported to be a better inhibitor than thiourea for the iron–sulphuric acid system [8]. Therefore, this compound was chosen to study the inhibition of aluminium alloys in nitric acid. In order to improve the inhibitive performance of the compound, the isatin molecule which has nitrogen and oxygen atoms and an aromatic ring was condensed with thiosemicarbazide (synthesis given elsewhere [9]).

2. Experimental

2.1. *Materials*

All the chemicals used in the present investigation were of AR grade except isatin-3-(3-thiosemicarbazone) which was synthesized in the laboratory, with very good yield [9], and recrystlized; m.pt., observed 253° C, reported 255° C [9]. The experimental electrolyte was 20% nitric acid which was prepared by diluting 69.5% (sp. gr. 1.42) pure nitric acid with double distilled water. The aluminium alloys supplied by M/s Hindustan Aluminium Corporation Ltd had the composition shown in Table 1.

Table 1

Grade	*% alloying elements*				
	Si	*Fe*	*Mn*	*Mg*	*Cu*
1060	0.12	0.02	0.04	–	–
1100	0.13	0.52	0.068	0.021	0.01
3003	0.16	0.58	0.78	–	–

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2.2. *Procedure*

For weight loss experiments, the specimens of size 75 mm x 50 mm polished with 1/0 to 5/0 grade of emery papers and washed successively with benzene, soap, distilled water and finally with acetone, were kept dipped in 300 ml test solution for 24 h and the loss in weight was determined after the specimen had been cleaned in 70% nitric acid. Inhibition efficiencies were calculated from the weight loss data using the relation:

$$E = \frac{a-b}{a} \times 100$$

where E is the percentage inhibition efficiency, a the weight loss in uninhibited solution, and b the weight loss in inhibited solution. Triplicate experiments were performed to ascertain the reproducibility of data.

Working electrodes for polarization experiments were 'flag-shaped', 10 mm x 10 mm, with a side tag of length 40 mm. Part of the tag and one surface of the electrode were blocked off with Araldite. The steady-state corrosion potentials were measured with the help of a high precision potentiometer. Polarization experiments were performed using a Wenking (laboratory model) potentiostat. Duplicate and, in some cases, triplicate trials were run for confirmation of the results. All the potentials were measured against saturated calomel electrode.

3. Results and discussion

In Figs. 1–3, the percentage inhibition efficiencies evaluated by the weight loss method are plotted against logarithm of percentage concentrations of the inhibitors at 30, 40 and 50° C for 1060, 1100, 3003 alloys. It is found that in all cases, the inhibitors show maximum inhibition at the concentration of 0.2%. With increase in temperature from 30° C to 50° C, the efficiencies of the compounds are gradually increased. This tendency is most pronounced in the case of isatin inhibiting 1060 alloy. The maximum inhibition by the inhibitors is exhibited for 1060 alloy followed by 1100 and 3003 alloys at all the three temperatures.

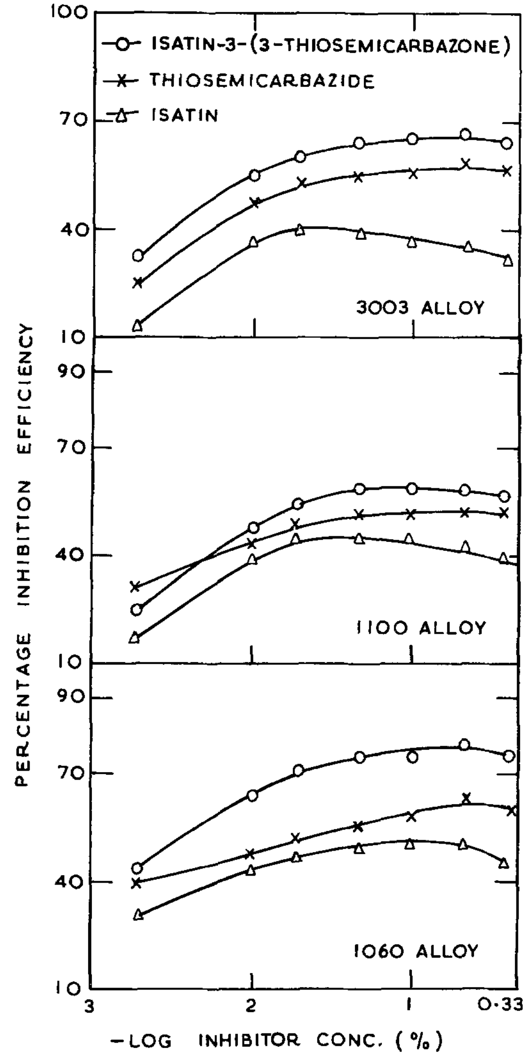
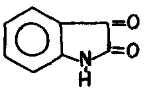
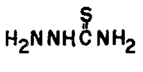


Fig. 1. Variation of the percentage inhibition efficiency with concentrations of the inhibitors at 30° C.

Isatin-3-(3-thiosemicarbazone) shows very satisfactory inhibition for the three alloys at all three experimental temperatures. It is more effective than the parent compounds. The enhanced effectiveness can be explained by considering the structure of the inhibitors and electron densities on the active centres. Isatin molecule may become adsorbed on the metal surface through oxygen

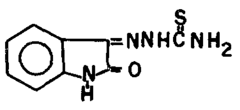


ISATIN



$H_2NNH\overset{S}{\overset{\|}{C}}NH_2$

THIOSEMICARBAZIDE



ISATIN 3-(3-THIOSEMICARBAZONE)

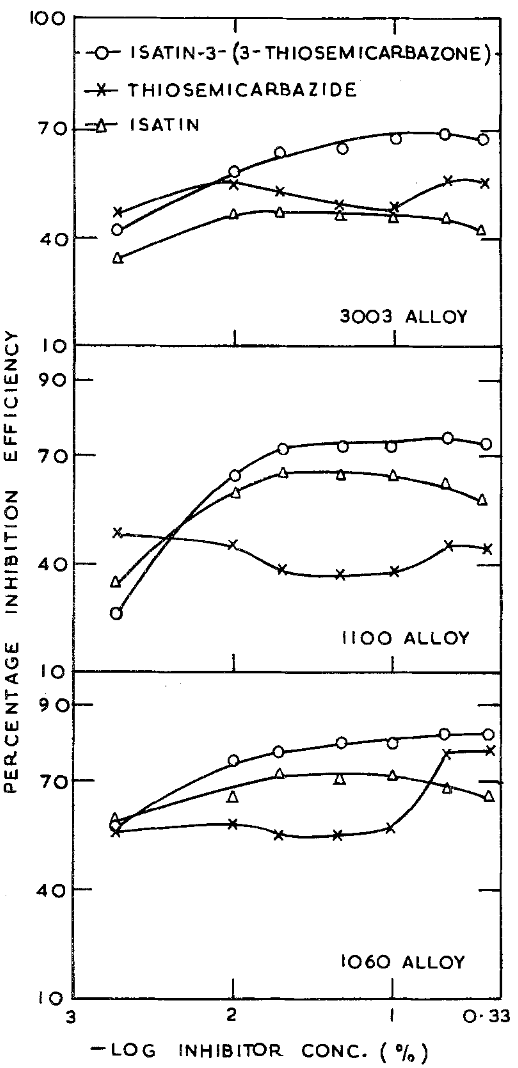


Fig. 2. Variation of the percentage inhibition efficiency with concentations of the inhibitors at 40° C.

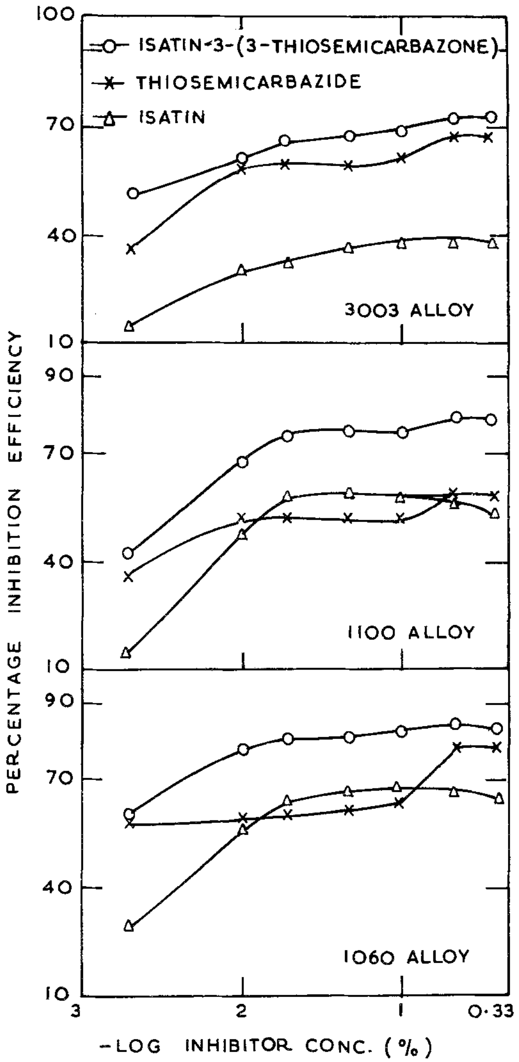


Fig. 3. Variation of the percentage inhibition efficiency with concentrations of the inhibitors at 50° C.

atoms present in the molecule and/or through the delocalized π electrons of the benzene ring.

Thiosemicarbazide has N and S as key atoms for the process of adsorption whereas in isatin-3-(3-thiosemicarbazone), there are N, O and S atoms in addition to the delocalized π electrons of benzene ring through which it may become adsorbed on the metal surface. Therefore, the enhanced efficiency of the latter compound may be due to the presence of a greater number of active centres for adsorption and a greater surface area projected by the compound on the metal surface.

Anodic and cathodic polarization studies have been carried out in the presence of 0.05, 0.2 and 0.3% concentrations of the compounds for the three alloys at 30° C. However, Figs. 4 and 5 show polarization behaviours in the presence of 0.2% of the compounds only, the concentration at which the inhibitors showed maximum inhibition. Other parameters, such as critical current density (i_c), passivation potential (E_p), cathodic Tafel slope (b_c) and steady state corrosion potential ($E_{corr.}$) are summarized in Tables 2 and 3. During the anodic polarization of the alloys, it was observed that after a particular applied potential, the current slowly decreased indicating formation of some surface-protecting barrier on the metal surfaces. In the presence of the inhibitors, the nature of the curves was similar but shifted towards lower current density region. The potentials at which the

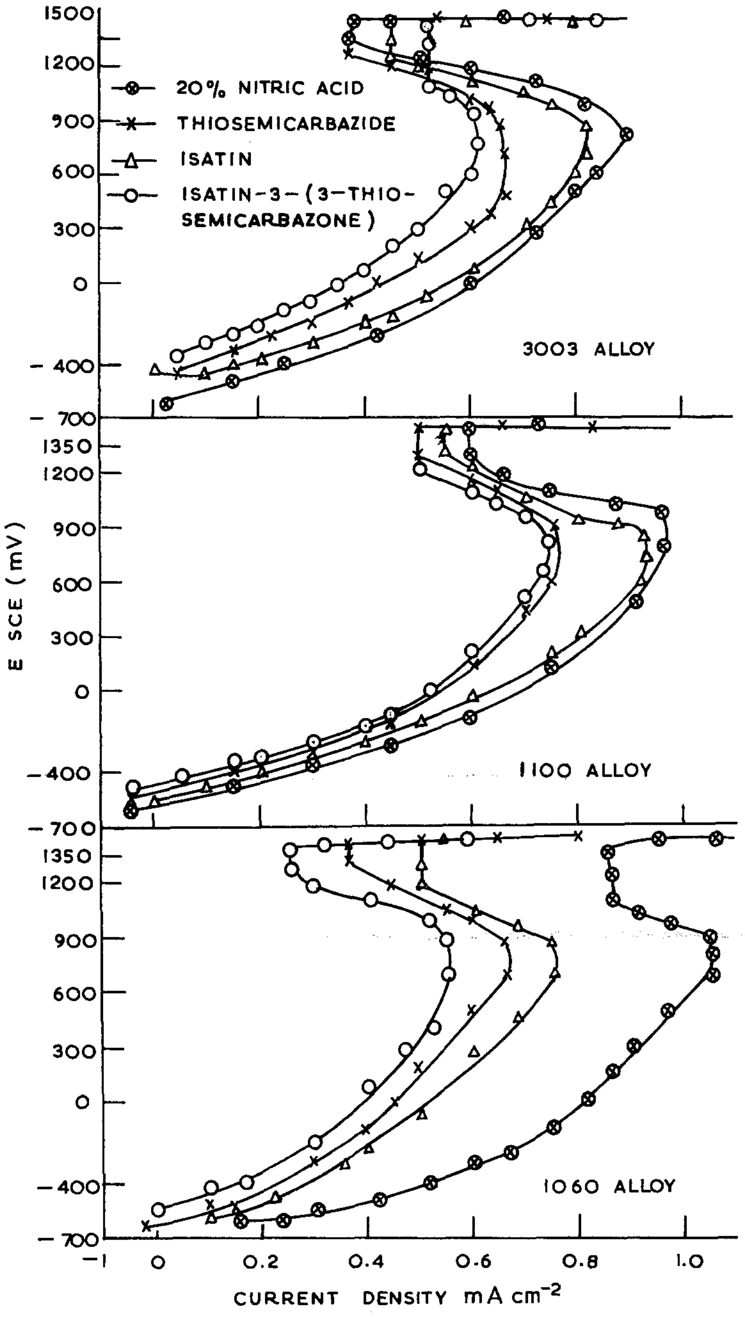


Fig. 4. Anodic polarization of 1060, 1100 and 3003 alloys in the presence of 0.2% concentration of the inhibitors.

decrease in current was observed, were taken as passivation potentials (E_p) and corresponding currents as the critical currents (i_c).

The anodic polarization curves in the absence and in the presence of the inhibitors have been shown in Fig. 4. It is seen from the figure that although the curves in the presence of all the inhibitors have been shifted towards the lower current density region, it is most pronounced in the presence of isatin-3-(3-thiosemicarbazone) which appears as the best inhibitor. This indicates that very strong and poorly conducting film is formed on the metal surface in the presence of this compound. The values of critical current densities, passivation potentials and inhibition efficiencies recorded in Table 2 show that the

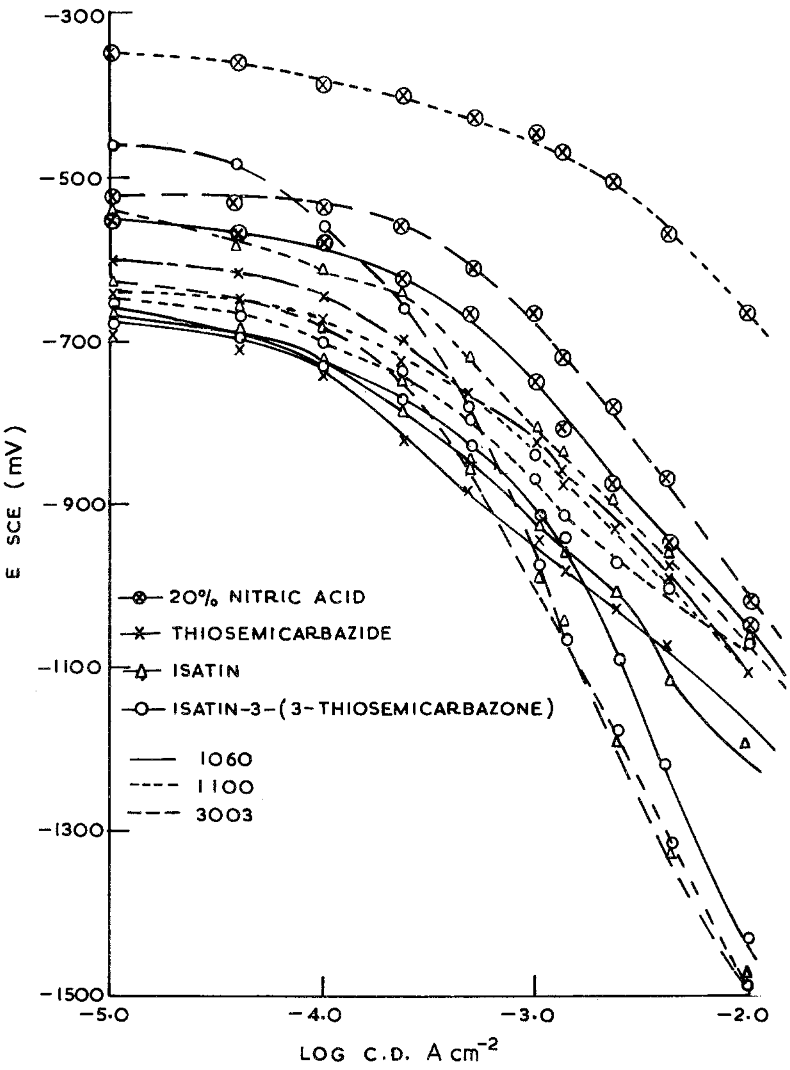


Fig. 5. Cathodic polarization of 1060, 1100 and 3003 alloys in the presence of 0.2% concentration of the inhibitors.

inhibitors which are most effective at the concentration of 0.2% have lower i_c values at this concentration as compared to the other concentrations. Moreover, the critical current densities in the presence of the inhibitors for the different alloys are almost in the same order as their effectiveness. The values of i_c/i_{c_0} (critical current density ratio) for the compounds for different alloys and for different concentrations show that their order of decrease is almost the same as the effectiveness of the inhibitors increases. Here i_c and i_{c_0} represent the critical current densities in the presence and the absence of the inhibitors, respectively.

The steady state corrosion potentials in the presence of the inhibitors for all the alloys shifted towards more active direction as compared to the values in their absence (Table 3). This indicates that the inhibitors are predominantly effective on the local cathodes. This was further complemented by the cathodic polarization studies shown in Fig. 5. It is evident from this figure and the cathodic Tafel slopes summarized in Table 3 that the inhibitors have polarized cathodic reactions. Thus from Figs. 4 and 5, one can conclude that the compounds are effective on both local cathodes and anodes.

A comparison of the percentage inhibition

Table 2. Critical current density (i_c), passivation potential (E_p), critical current density ratio (i_c/i_{c_0}) and percentage inhibition efficiency (p_i) of the inhibitors at their different concentrations. Temperature 30° C*

Inhibitors and their concentrations (%)		*1060*				*1100*				*3003*			
		i_c (mA cm^{-2})	E_p (V)	i_c/i_{c_0}	p_i	i_c (mA cm^{-2})	E_p (V)	i_c/i_{c_0}	p_i	i_c (mA cm^{-2})	E_p (V)	i_c/i_{c_0}	p_i
Uninhibited solution		1.05	0.70	–	–	0.99	0.80	–	–	0.90	0.80	–	–
Thiosemi-carbazide	0.05	0.75	0.70	0.71	56	0.75	0.70	0.77	52	0.90	0.70	1.00	52
	0.20	0.67	0.70	0.63	62	0.77	0.70	0.79	52	0.67	0.50	0.74	58
	0.30	0.82	0.80	0.78	56	0.92	0.80	0.94	50	0.87	0.70	0.97	57
Isatin	0.05	0.82	0.80	0.78	48	0.92	0.60	0.94	45	0.90	0.70	1.00	40
	0.20	0.75	0.70	0.71	51	0.92	0.60	0.94	42	0.82	0.70	0.91	35
	0.30	0.90	0.80	0.85	44	0.90	0.80	0.92	40	0.87	0.80	0.97	32
Isatin 3-(3-thiosemi-carbazone)	0.05	0.72	0.80	0.68	73	0.92	0.80	0.94	56	0.85	0.70	0.94	63
	0.20	0.55	0.70	0.52	77	0.75	0.70	0.77	58	0.60	0.60	0.67	68
	0.30	0.67	0.70	0.63	75	0.82	0.70	0.84	55	0.75	0.80	0.83	65

* i_{c_0} = critical current density in the absence of the inhibitors.

Table 3. Corrosion potential (E_{corr}) and cathodic Tafel slopes (b_c) in the absence and in the presence of 0.2% compounds at 30° C

Inhibitors	*1060*		*1100*		*3003*	
	$-E_{corr}$ (mV)	b_c (V/dec)	$-E_{corr}$ (mV)	b_c (V/dec)	$-E_{corr}$ (mV)	b_c (V/dec)
No inhibitors	552	0.076	536	0.180	450	0.098
Thiosemcarbazide	669	0.207	578	0.203	631	0.178
Isatin	668	0.193	628	0.199	545	0.230
Isatin-3-(3-thiosemicarbazone)	679	0.211	636	0.339	643	0.138

efficiencies afforded by different inhibitors for nitric acid/aluminium system reported earlier [2–7] show that the investigated inhibitor, i.e. isatin-3-(3-thiosemicarbazone), is comparatively more effective.

Acknowledgements

We are grateful to Hindustan Aluminium Corporation Ltd, Renukoot, Mirzapur, India for the gift of aluminium sheets, One of us (D.D.N. Singh) wishes to thank CSIR, New Delhi for the award of a research fellowship.

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