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Z.A. EL-HADI

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ORGANIC CORROSION INHIBITORS FOR TA6V ALLOY IN NON-OXIDIZING ACID SOLUTIONS

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Z.A. EL-HADI

Chemistry Department, University College For Girls, Ain-Shams University, Heliopolis, Cairo, Egypt.

SUMMARY

The efficiency of the azo compounds as corrosion inhibitors for TA6V alloy in areated 10, 15 and 25N H_2SO_4 has been investigated. It was found that these compounds are good passivators. An interesting peculiarity of these inhibitors should be noted that their inhibiting influence starts at once at the moment of their contact with the metal surface, this behaviour takes place only in the presence of the naturally occuring oxide layer. A mechanism for the corrosion inhibition is prosed based on the reduction of the azo compounds on the surface of the alloy, as a result the corrosion potential becomes positive, its value falling in the range which the alloy is completely passive. Potentiostatic measurements have made it possible to establish the limits of stability of the passive state. The results of the corrosion tests agree fully with the results of the electrochemical measurements.

INTRODUCTION:

The inhibition of titanium corrosion in non-oxidizing acid solutions has been the subject of a number of investigators [1–8]. A good survey for all the type of inhibitors is reported by Petit et al [9]. Many of these investigations have studied the effect of oxidizing agents. As has been shown by our studies, the corrosion rate of titanium in sulfuric acid may be diminished considerably by oxidizing anions [10], as well as some azoic compounds [11]. TA6V is one of the most important titanium alloys which have been widely used in the commercial industrial applications especially in the domain of the aerospace industry due to their high specific strength and excellent mechanical properties. However, it appeared of interest to extend the study to TA6V alloy in a trial to find a wide range of effective organic corrosion inhibitors in sulfuric

acid solutions. A limited amount of work on TA6V from this standpoint has been published [12,13] as far as we are aware.

EXPERIMENTAL TECHNIQUE:

The tests electrode were prepared from TA6V sheets (chemical analysis is given in Table 1), cut into 1 cm^2 surface area pieces and then annealed in vacuum at 800 °C for 1 hour. A thin copper wire was tightly wrapped around one end of the electrode, which was squezed inside a clean glass tube, and the glass was sealed over the copper wire by Araldite. Each electrode was mechanically polished with 600 emery paper under water, followed by ultra-sonic cleaning, rinsing throughly with distilled water ana then dried with compressed air. Each experiment was carried out with a newly polished electrode and with a fresh portion of the test solution.

Table (1): Chemical composition of TA6V alloy (wt.%)

Al	V	Fe	C	O	N	H
5.7	3.85	0.18	0.038	0.106	0.035	0.0053

Anodic measurements are potentiostatically. The reference electrode to which all potentials are referred, is a saturated calomel electrode and the counter electrode is in the form of a 1 cm^2 platinum sheet. The cell used is made of pyrex glass. Experimental details have been given elsewhere [14].

Determination of the corrosion rate is also carried out using the weight loss technique.

Experiments were performed on alloy specimens measuring 3 x 2 cm and 2 mm thick. The test piece surface is treated as discussed above and the corrosion tests are carried out in 200 ml beaker, in which the specimen is suspended by means of glass hooks in the test solution. After a limited time, the specimen is removed, washed with water, dried and finally weighted. All corrossion testwere carried out in aerated, unstirred solution at room temperature. All solutions are prepared from the purest available chemicals. Results are duplicated and the average was computed.

RESULTS AND DISCUSSION:

In order to examine the inhibition efficiency of the azoic derivatives on the retardation of TA6V alloy dissolution in 10, 15 and 25 N

H_2SO_4, the loss in weight and the corrosion potential were followed as a function of exposure time.

I.a. Weight Loss Measurements:

Weight loss was followed as a function of time in the absence and in the presence of 0.5 g/L of the different azo compounds. Table (2)

Table (2): Comparison between the inhibitor efficiences of azo compounds using the weight loss measurements (mg/cm²).

Inhibitors 0.5 g/L Time in days	10 N H_2SO_4			15 N H_2SO_4			25 N H_2SO_4		
	7	15	30	7	15	30	7	15	30
1. Without inhibitor	5.2	29.4	60.00	140.00	0000	00000	200.0	0000	00
2. Azo benzen	000	1.0	7.20	0.02	4.00	19.90	0.8	1.50	00
3. P. Oxiazobenzen	000	1.0	6.90	0.03	3.90	10.00	0.5	1.60	00
4. Methyl oxiazobenzen	000	000	0.01	0.01	0.09	9.01	0.39	0.85	00
5. Dimethyl a-minoazo benzen	000	000	0000	0000	0.05	9.00	0.10	0.82	00
6. Methyl orange	000	000	0000	0000	0.05	8.70	0.079	0.83	00
7. Methyl red	000	000	0000	0000	0.04	8.30	0.07	0.80	00
8. Chrysoidine	000	000	0000	0000	0.04	9.30	0.06	0.80	30

shows the weight loss change expressed in mg/cm² during the period of 30 days. In this table, the azo compounds examined are arranged in the order of increasing inhibition efficiency. For instance, the experimental results obtained suggest that azobenzen and p. oxiazobenzen are the less effective inhibitors. The common feature of all the azo compounds examined shows that, after a long period their inhibiting property decrease with increase of acid concentration, chrysoidin for example is active in 25N H_2SO_4 over a period of 15 days, the loss in weight being 0.8 mg/cm² (it is 0.04 in the case of 15N and zero for 10N H_2SO_4). This means that the critical inhibitor concentration varing with acid concentration. These results suggest that the additives studied belong to the class of passivators, when added in sufficient amounts, reduce corrosion rates [6]. It is worthy to remark that the colour of the solutions change during the experiment (for example in the case of methyl red, the colour changes from red to yellow after about 19 days and finally it turned colouress after 70 days in 10N H_2SO_4, the change in colour does not take place suddenly. After this period, the loss in weight increases as in the absence of the inhibitors and no corossion inhibition was observed. Hence, our observations have shown that the azo compounds, when present

in an acid solution contact with the metal surface, undergo a number of transformations. In this respect, the azo groups seems to be involved in the corrosion inhibition process like the nitro groups [13], and the film formation reaction on the electrode surface plays an important role for the attainment of the passivity.

I.b. Dissolution Rate and Stability of Protective Film:

In order to examine the resistance of the film formed on the electrode surface in the presence of inhibitors after a certain period of immersion, the test electrode which has been passivated in inhibited 10N H_2SO_4 solution for 20 days, is transfered into a 10N H_2SO_4 in the absence of inhibitors, the electrode become active after a period depends on the type of the inhibitor as shown in Table (3). From the experimen-

Table (3): Loss in weight in 10 N H_2SO_2 in presence of a protective film formed in different inhibitors.

Inhibitors 0.5 g/L Time in days	Loss in weight mg/cm²						
	1	3	5	8	10	12	15
— Azo benzen	3.2	4.5	5.09	9.20	12.00	15.00	0000
— Methyl oxiazobenzen	000	000	0000	0.09	0.300	1.00	2.30
— Methyl orange	000	000	0000	0000	0.020	0.08	0.12
— Methyl red	000	000	0000	0000	0.030	0.10	0.12
— Chrysoidine	000	000	0000	0000	00000	0000	0.01

tal results obtained, we can therefore assume that the surface of the alloy is oxidized in presence of the inhibitor, and that when the concentration of the inhibitor is decreased or in the absence on inhibitors as described above, the oxides are dissolved and the surface becomes less oxidized, consequently the hibitive action of the oxide decrease with the immersion time till the oxide film is completely dissolved. This process is essentially chemical in nature, and the dissolution of the oxide is apparently the reduction of TiO_2 to oxides of a lower valency, which are more readily soluble in the acid medium. From all the above tests, it seems that the azoic derivatives have only a low oxidizing capacity which depends not only on the —N=N— group but also on the functional groups for each compound. These views were confirmed by the electrochemical measurements.

II.a. Corrosion Potential:

The open circuit potentials of the TA6V electrode were followed as a function of time in sulfuric acid solutions containing the different

azo compounds until steady state values were attained. The results obtained, Table 4, shows that the potential values measured at the moment of immersion are positive. This suggests that the inhibitive action of these compound promote the resistance of the air formed pre-immersion oxide film against acid attack.

After certain time dependent on the type of inhibitor, a sudden drop in the potential was observed; which indicates that the electrode becomes in the active state. The shift of potential to the active range ($\sim$—600 mV), when no current is supplied, shows that only the active state is then stable. After that, when adding the same amount of the inhibitor 0.5 g/L, the potential remains active, this confirm that the azo compounds maintain the passive state of the alloy only in the presence of the film formed naturally in air, and the shift of the potential from passive to active values denotes the reduction of the azo compounds.

II.b. Potentiostatic Measurements:

Potentiostatic current density-potential curves $I = f(E)$ were determined for TA6V alloy in 10 and 25N H_2SO_4 solutions in the presence and absence of inhibitors starting from the corrosion potential. Some representative curves are shown in Figs.(1–2). In the absence of inhibitors an active to passive transition is observed, each value of the potential on the anodic curves has a corresponding steady current density, the maximum current density value I_m is 0.26 mA/cm² for 10N H_2SO_4 and 2.65 mA/cm² for 25N H_2SO_4. In the presence of the different inhibititors a shift in corrosion potential to a value at which the alloy is completely passivated is observed, and there is no anodic dissolution section on the curve as shown in Figs. (1–2 curves 2–8); and the current density in the passive state Ip remains unchanged, being 0.02 mA/cm² in 10N H_2SO_4 and 0.03 mA/cm² in 25N H_2SO_4. The curves for this alloy resemble those for the unalloyed titanium in the same solutions [10]. The results obtained reveal that the latter corrodes much faster than the former. The above results suggest that the mechanism of the azo compounds inhibition is based on its capability of achieving a more noble potential than the critical potential of passivity of TA6V.

II.c. Effect of Cathodic Reduction:

In order to find more about the stability of the protective film and the mechanism by which organic inhibitors containing azo group reduce

Table (4): Variation of TA6V electrode potential with exposure time in sulfuric acid solutions containing the different azo compounds.

| Inhibitors Expos.time	10N H$_2$SO$_4$				15N H$_2$SO$_4$				25N H$_2$SO$_4$			
	1 min.	7 days	15 days	30 days	1 min.	7 days	15 days	30 days	1 min.	7 days	15 days	30 days
1. Without inhibitor	—510	—640	—640	—610	—600	—640	—640	—640	—600	—630	—620	—620
2. Azobenzen	—100	+ 75	—480	—600	—180	—400	—610	—610	—170	—360	—600	—600
3. P. Oxiazobenzen	— 80	— 10	—420	—610	—170	—400	—600	—600	—100	—380	—610	—600
4. Methyl-oxiazo-benzen	— 10	+ 30	—100	+ 10	— 70	+ 10	—420	—620	— 10	—410	—600	—590
5. Dimethyl-amino-azo-benzen	+ 20	+ 80	+100	+100	— 15	— 10	—390	—600	— 10	—380	—600	0000
6. Methylorange	+ 50	+100	+120	+120	— 10	— 10	—380	—600	— 15	—360	—600	0000
7. Methylred	+100	+120	+120	+125	+ 15	+ 20	—390	—610	+ 10	—380	—610	0000
8. Chrysoidine	+100	+110	+120	+110	+ 20	+ 20	—390	—600	+ 90	—360	—600	0000
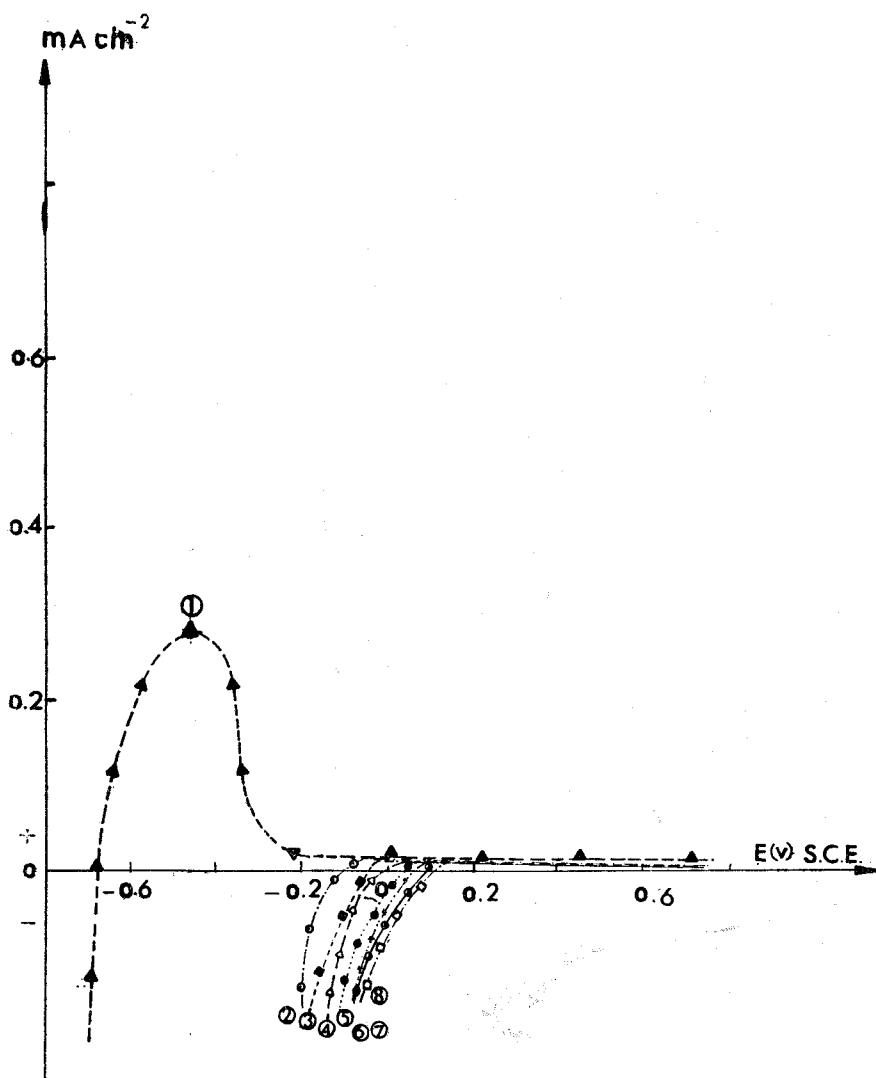
Fig. 1

Fig.(1): Anodic potentiostatic polarization curves recorded in 10 N H_2SO_4 containing 0.5 g/L of the different azo compounds:

1. Without inhibitor, 2. Azo benzen, 3. P. Oxiazobenzen, 4. methyl oxiazobenzen, 5. Dimethyl aminoazobenzen, 6. Methyl orange, 7. Methyl red, 8. Chrysoidine.
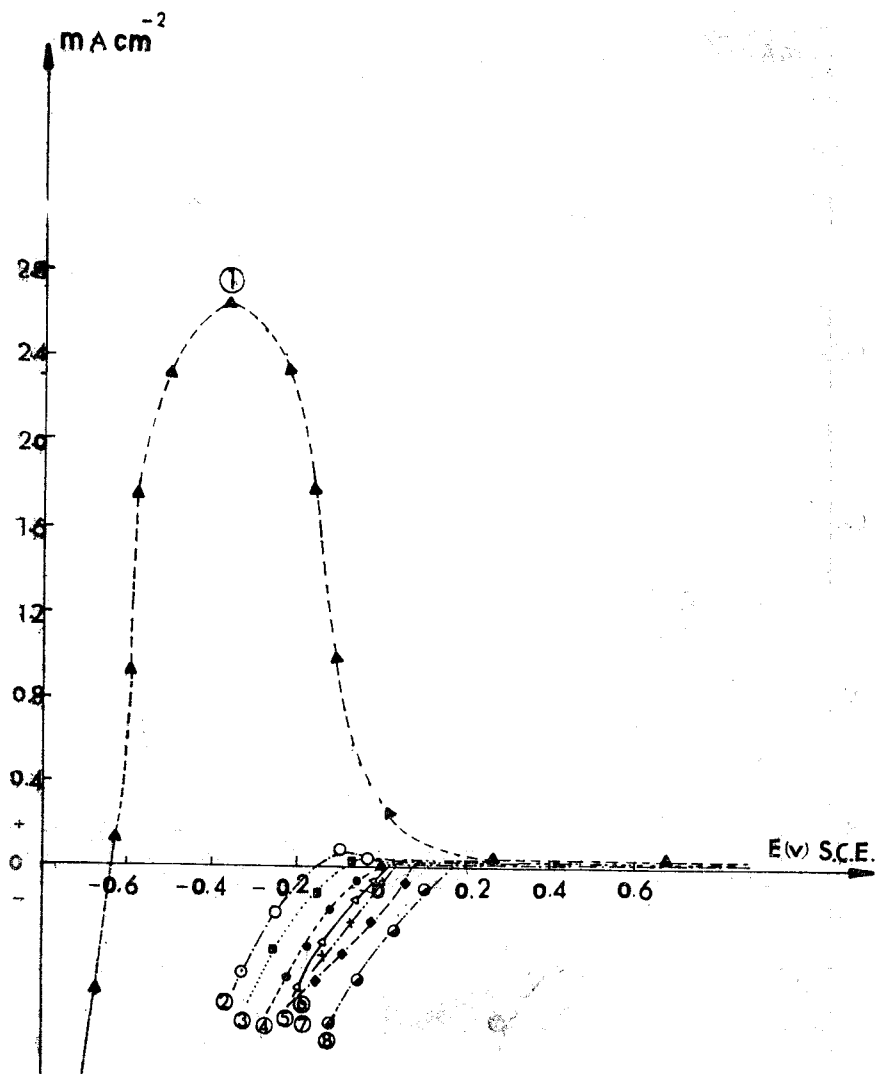
Fig 2

Fig.(2): Anodic potentiostatic polarization curves recorded in 25N H_2SO_4 containing 0.5 g/L
of the different azo compounds:

1. Without inhibitor, 2. Azo benzen, 3. P. Oxiazobenzen, 4. Methyl oxiazobenzen, 5. Di-
methyl aminoazobenzen, 6. Methyl orange, 7. Methyl red, 8. Chrysoidine.
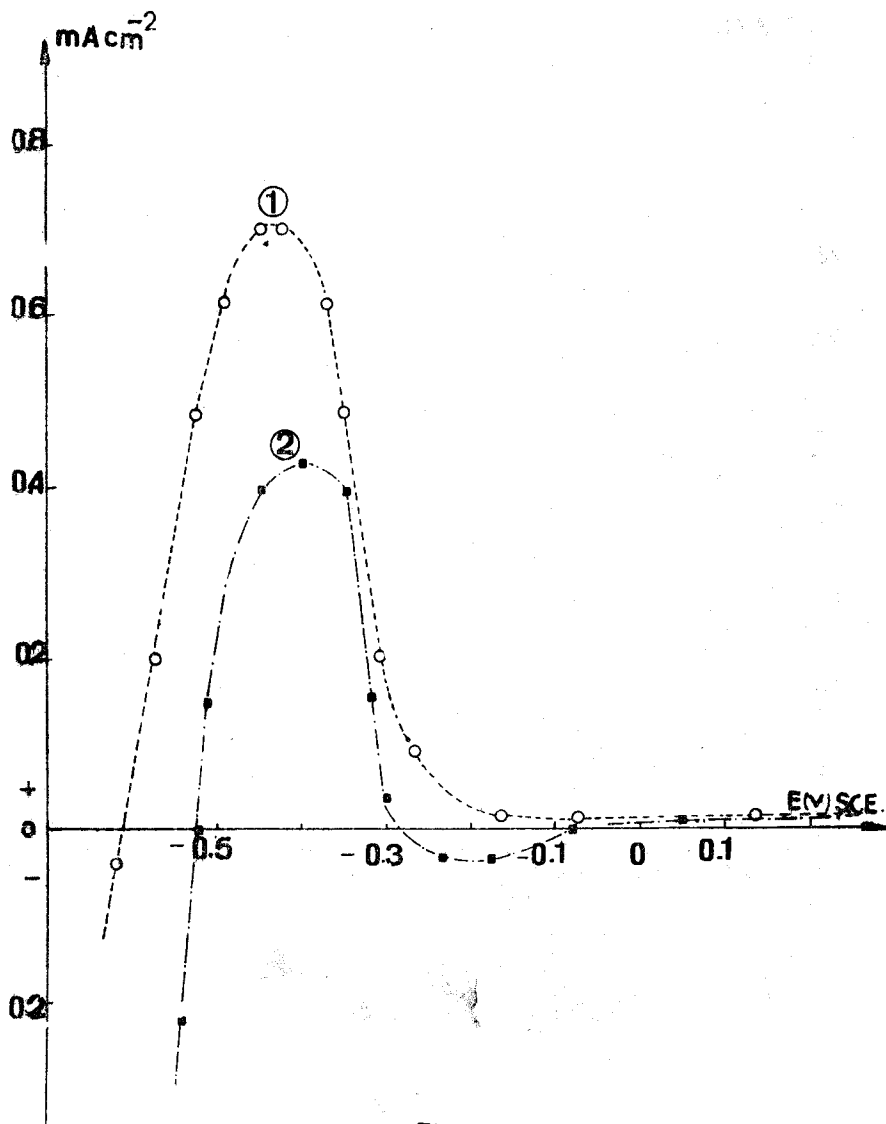
Fig. 3

Fig.(3): Effect of the cathodic reduction at —1 V /S.C.E. on the potentiostatic curve of TA6V electrode in 10 N H_2SO_4:

1. Without inhibitor, 2. + 0.5 g/L chrysoidine.

corrosion rates of TA6V alloy, the test electrode is activated by holding at a cathodic potential of —1 V/S.C.E. for 15 minutes without inhibitors, after that the inhibitor is added and the electrode is anodically polarized as described before. The results obtained in the presence of Methyl red is shown in Fig.(3). It is clear that an active to passive transition is still observed even in the presence of 0.5 g/L of Methyl red indicating that the electrode is in the active state. The presence of the inhibitor is manifested by the decrease in the maximum current density IM, the appearance of a small cathodic loop as shown in Fig. (3 curve 2), and the corrosion potential becomes slightly more noble. Such behaviour is due to the reduction of the organic compounds according to reactions of the type [15]:

$$Ph—N=N—Ph + 2H^+ + 2e \longrightarrow Ph—NH—NH—Ph$$

$$Ph—NH—NH—Ph + 2H^+ + 2e \longrightarrow 2PhNH_2$$
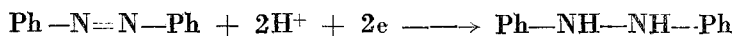
The above experiment confirmes that the azo compounds are effective inhibitors only if the alloy is previously protected by a naturally air formed film, the inhibitor can maintain the passive state of the metal and the inhibition of the metal dissolution occurs through the reduction of the azo compounds on the alloy surface which leads to passivation of the alloy.

The chemical composition of the formed protective films was not investigated in this study but from our results on pure titanium using Auger electron spectroscopy analysis [16], it was found that the passive layers are formed of TiO_2 only and the inhibitor does not seem to be participate in the building of the passive film.

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