

# Pitting corrosion inhibition of 316 stainless steel in phosphoric acid-chloride solutions

## Part I *Potentiodynamic and potentiostatic polarization studies*

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The electrochemical behaviour of 316 stainless steel in  $\text{H}_3\text{PO}_4\text{-Cl}^-$  solutions containing nitrate, dichromate, tungstate, and molybdate anions as inhibitors are presented and discussed using potentiodynamic and potentiostatic polarization techniques. The results showed that most additives improve the corrosion resistance of the alloy. The additives retard both active and pitting attack to an extent depending on the type and concentration of the additive. Results were correlated with the beneficial action of the corresponding alloying elements. © 1999 Kluwer Academic Publishers

### 1. Introduction

Austenitic stainless steels are widely used in several industries such as acid production, storage, and shipping, due to the stability of the passive film which form on their surfaces [1, 2–4]. In spite of their wide use, corrosion failures are often reported [2, 3]. Localized corrosion is the main cause of the failure of stainless steel structures in industry.

Pitting corrosion is one of the most dangerous forms of local attack for steels specially in chloride media. The major efforts to prevent this type of attack were undertaken by metallurgists developing new high resistant alloy to chloride environments. The major disadvantage of these new alloys is their high cost compared with conventional stainless steels, due to the higher percentage of the alloying elements such as Cr, Ni and Mo, as well as the complexity of the fabrication process. The favourable effect of these alloying elements on the pitting resistance is attributed either to the formation of a protective passive surface film containing these elements, or to the adsorption of soluble products of these elements (e.g.,  $\text{MoO}_4^{2-}$  in case of alloyed Mo) [5–7]. These assumptions have been confirmed by experiments in which the addition of  $\text{MoO}_4^{2-}$  to the corrosive medium was shown to inhibit pitting of austenitic alloys with and without alloyed molybdenum [6, 7].

Therefore, it is of interest to investigate the possibility of increasing the corrosion resistance of one of the most common and widely applied stainless steel, namely 316, by the addition of oxyanions of the alloying elements Cr, Mo, W and N to the electrolyte solution. In this work, the effect of addition of nitrate, dichromate, molybdate and tungstate on the electrochemical behaviour of the alloy in phosphoric acid/chloride solutions has been studied using potentiodynamic and potentiostatic polarization techniques. The efficiency of these additives will be discussed in relation to the effects of the corresponding alloying elements: nitrogen,

chromium, molybdenum and tungsten. In attempting to explain the mechanism whereby corrosion resistance is improved, an AES investigation will also be carried out in part II of this study.

### 2. Experimental method

#### 2.1. Chemicals and materials

The inhibitors used, phosphoric acid and NaCl were chemically pure grade of BDH chemicals and were used as supplied. All solutions were prepared using double distilled water.

Each experiment was carried out by using 30%  $\text{H}_3\text{PO}_4$  (pH = 1.4) containing 15000 ppm NaCl (higher than the level at which pitting is observed). The results were obtained in the absence and presence of increasing amounts of nitrate, tungstate, dichromate, and molybdate as additives at  $25 \pm 2^\circ\text{C}$ .

The working electrode ( $0.5 \times 0.5 \times 0.2$  cm) was made from a commercially produced 316 stainless steel of analysis given in Table I.

#### 2.2. Electrochemical tests

The polarization measurements were recorded using a Wenking potentiostat (model POS 73) with an x-y recorder. The test electrodes were first polished with emery paper, degreased with acetone, and washed with distilled water before immersion in the test solution. The anodic polarization scans were conducted in the test solutions using Pt as the counter electrode and all potentials applied were referred to the calomel electrode (SCE) interfaced to the test solution via a salt bridge assembly and luggin capillary. Prior to commencing the anodic scan, a cathodic potential of  $-600$  mV was applied to the working electrode for 15 min to reduce any oxide films, after which the anodic polarization scan was performed. All scan rates were

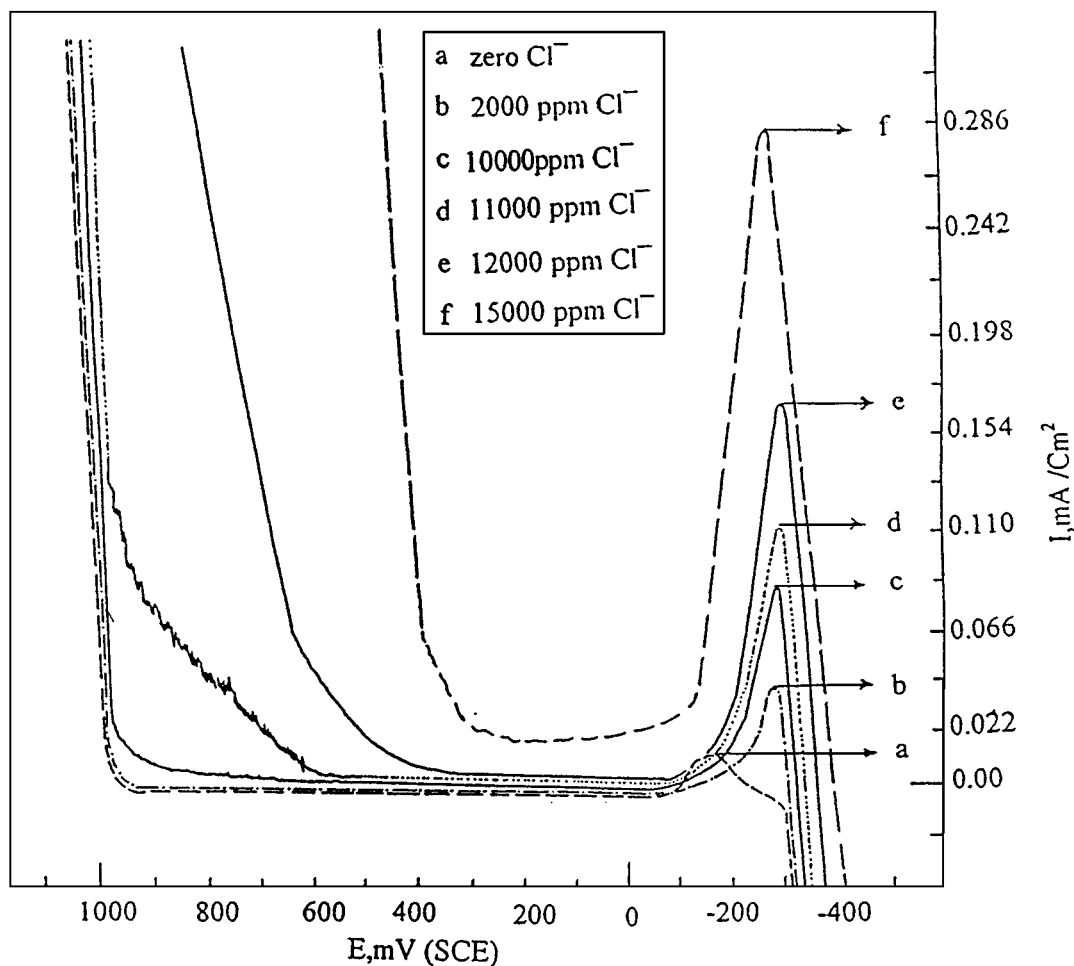


Figure 1 Potentiodynamic anodic polarization curves for 316 stainless steel in 30%  $H_3PO_4$  with given chloride ion concentrations.

TABLE I Composition of stainless steel (wt %)

C	Cr	Ni	Mo	Mn	Cu	Si	S	P
0.06	17.20	11.80	2.80	1.50	0.25	0.50	0.02	0.03

1 mV/s. Potentiostatic polarization measurements (i-t curves) were also conducted at 50 mV above the breakdown potential at selected additive concentrations.

### 3. Results and discussion

#### 3.1. Potentiodynamic polarization measurements

The effect of NaCl on the polarization behaviour of 316 stainless steel in 30%  $H_3PO_4$  is shown in Fig. 1. It can be seen that curve a shows a slight hump at  $\sim -0.2$  V followed by a passive region extending till oxygen evolution. The addition of the aggressive ion (from 2000 to 15000 ppm – curves b–f) causes an increase in the peak current density in the active region with increase in chloride content in solution. This is followed by a passivation region then breakdown potential where an abrupt increase in current is recorded. At higher concentrations of chloride there is a shift in the breakdown potential towards more negative values indicating an increased tendency of pitting attack. At the higher concentration examined, very small pits on the surface of

the alloy could be distinguished by the optical microscope.

The effects of sodium nitrate, molybdate, tungstate, and potassium dichromate were investigated. The measurements were conducted in 30%  $H_3PO_4 + 15000$  ppm  $Cl^-$  solutions. Fig. 2 shows the potentiodynamic polarization behaviour in the presence of 0–1500 ppm  $NO_3^-$ . Similar curves were obtained with the other additives tested show that both active and pitting attack of the alloy are retarded to an extent depending on inhibitor type and concentration.

The variations in active current  $I_c$ , passive current  $I_p$ , and pitting potential  $E_p$  with anion concentration [8] are shown in Figs 3–5, respectively. These figures show that:

(a) In most cases  $I_c$  decreases with additive concentration (Fig. 3).

(b) The current diminishes near zero, indicating complete inhibition of active dissolution, in presence of  $\sim 1500$  ppm  $NO_3^-$ ,  $\sim 5700$  ppm  $Cr_2O_7^{2-}$ , 5500 ppm  $WO_4^{2-}$  and 5800 ppm  $MoO_4^{2-}$ .

(c) The passive current decreases with increasing additive concentration, attaining minimum values in the range  $8\text{--}12 \mu A/cm^2$  in all cases (Fig. 4).

(d) The pitting potential shifts progressively to more noble values with increasing anion additions (Fig. 5).

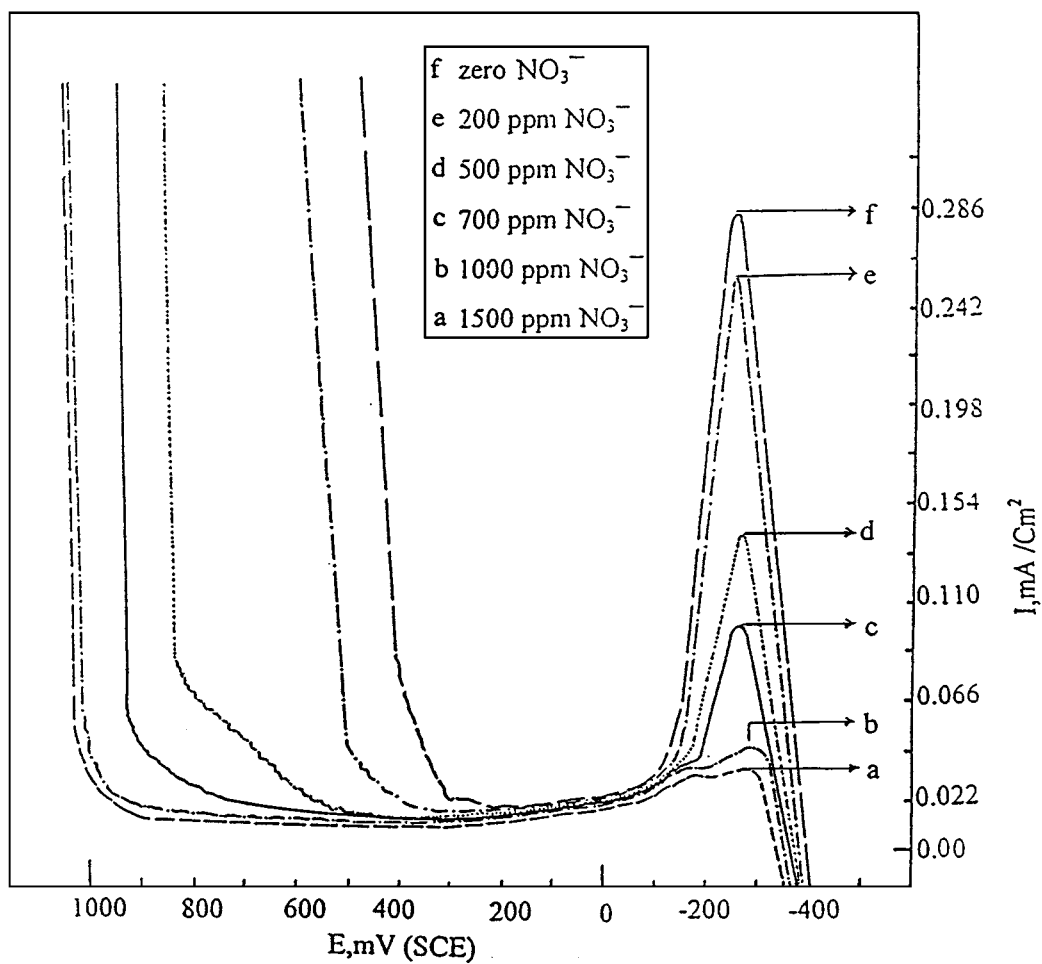


Figure 2 Potentiodynamic anodic polarization curves for 316 stainless steel in 30%  $H_3PO_4$  containing 15000 ppm  $Cl^-$  and given concentrations of  $NaNO_3$ .

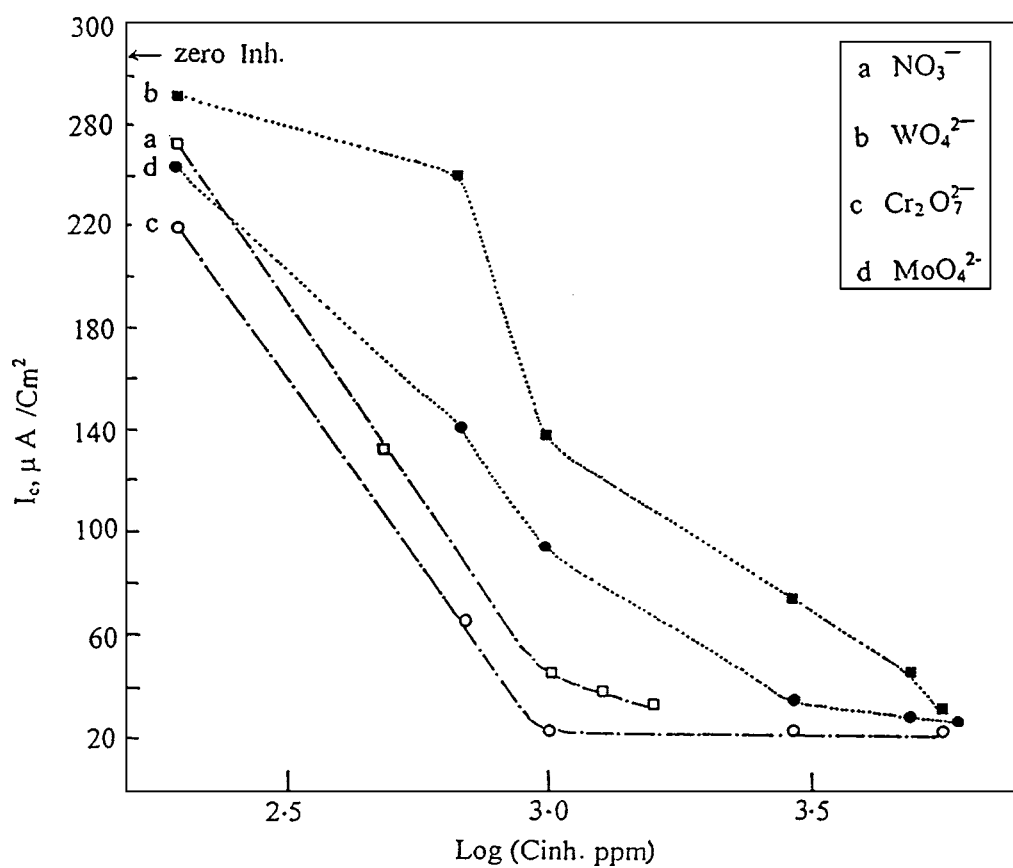


Figure 3 Variation of active current ( $I_c$ ) with inhibitor concentration ( $C_{inh}$ ) for 316 stainless steel in 30%  $H_3PO_4$  containing 15000 ppm  $Cl^-$ .

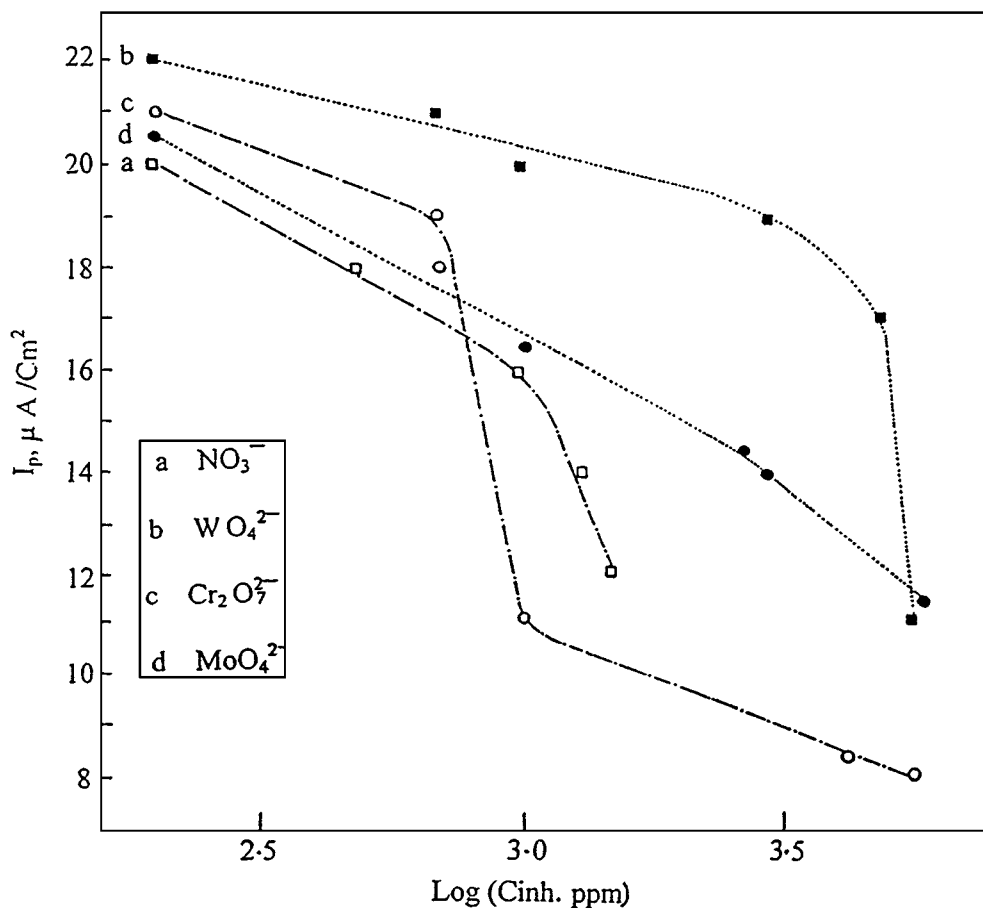


Figure 4 Variation of passive current ( $I_p$ ) with inhibitor concentration ( $C_{inh}$ ) for 316 stainless steel in 30%  $H_3PO_4$  containing 15000 ppm  $Cl^-$ .

(e) Dichromate, tungstate and molybdate behave similarly. Low concentration (~1000 ppm) produce a change of +150 to 200 mV in  $E_p$ , which increase with increasing additive concentration.

### 3.2. Potentiostatic measurements

For the sake of comparison of the effect of the used inhibitor on behaviour of 316 stainless steel, the  $i-t$  curves were constructed by addition of  $NO_3^-$ ,  $Cr_2O_7^{2-}$ ,  $WO_4^{2-}$  and  $MoO_4^{2-}$  anions to 30%  $H_3PO_4$  containing 15000 ppm NaCl. The potential was fixed at 450 mV which is chosen to be 50 mV higher than that of pitting potential. The variation of current is followed with time for the different inhibitors and curves are displayed in Fig. 6. It can be seen that in inhibitor free electrolyte there is a relatively slight decrease in the current values during the first two minutes then attaining a constant value (curve a). In the presence of the tested inhibitors (curves b-e), there is a higher decrease in the current values in the first few minutes which then decreases gradually with time. This behaviour depends on the type and concentration of the inhibitor added. Within the experimental concentrations examined, the efficiencies of additives can be arranged in the following order  $NO_3^- > WO_4^{2-} > Cr_2O_7^{2-} > MoO_4^{2-}$ .

The results of the present study indicate that the oxyanions  $NO_3^-$ ,  $Cr_2O_7^{2-}$ ,  $WO_4^{2-}$  and  $MoO_4^{2-}$  inhibit both active and pitting corrosion of 316 stainless steel in 30%  $H_3PO_4-Cl^-$  solution. The application of these

inhibitors in controlling uniform active corrosion has become common and the inhibiting mechanism are known [9] but this not so in the case of localized attack.

The effect of inhibitors on pitting has been discussed on the basis of two mechanisms [9–15].

(a) Competitive adsorption between the inhibitor and the aggressive ion where adsorption of inhibitor predominates leading to protective layer;

(b) Incorporation of the inhibitor molecules or ions into the passive layer to provide enhanced stability against aggressive ion attack.

The four inhibitors examined are nearly of comparable results, while nitrate is the most effective.

**Nitrate.** Although nitrate ions [16] are far less oxidizing than chromates, they have more inhibitive effect indicating no direct relation between the oxidation properties and the protective ability. From this, it is clear that inhibition is not caused by the ability of anion to heal the oxide film, but its ability to be adsorbed on the electrode and to displace the aggressive ions from the surface [17].

The curve representing the variation of  $E_p$  with  $NO_3^-$  concentration (curve a in Fig. 5) reveals that the nitrate anion produces a significant reduction in pitting corrosion. This curve is characterised by a sharp rise in  $E_p$  at ~500 ppm of inhibitor.

Above this threshold concentration  $E_p$  approaches the value recorded for chloride free solutions, indicating

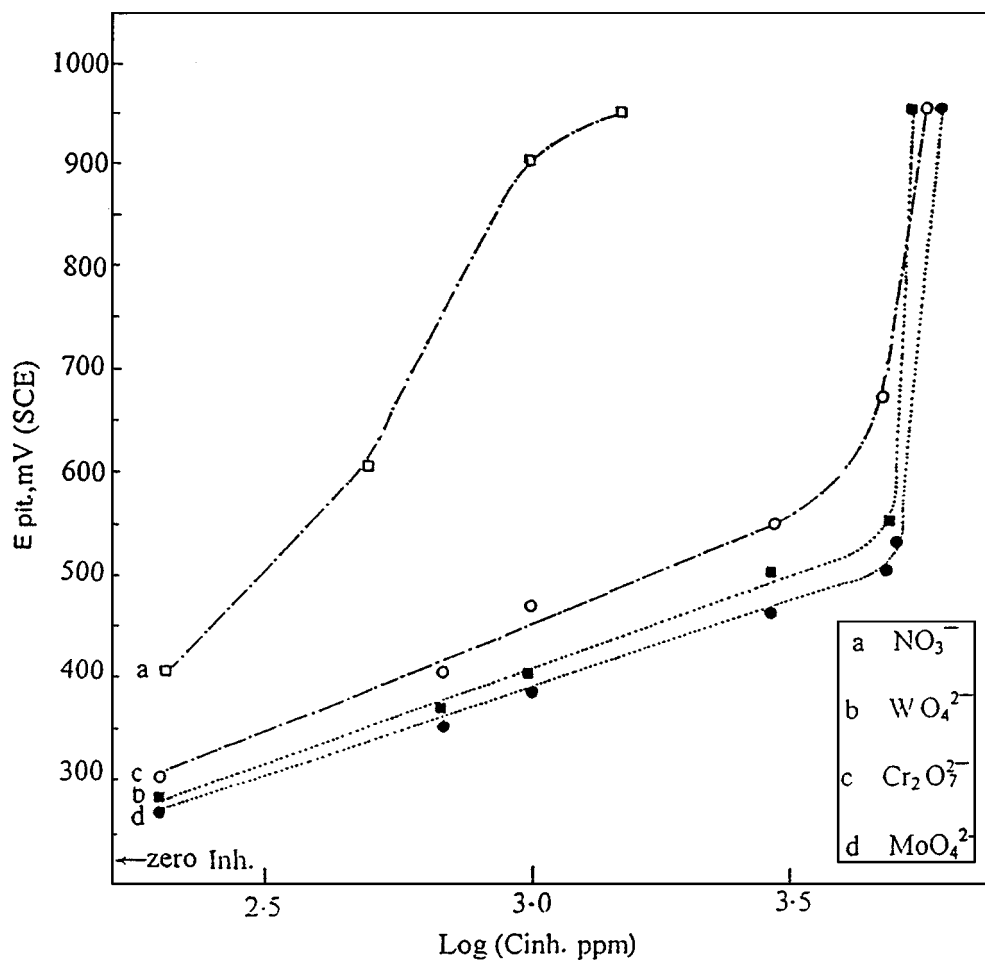


Figure 5 Variation of pitting potential ( $E_{pit}$ ) with inhibitor concentration ( $C_{inh}$ ) for 316 stainless steel in 30%  $H_3PO_4$  containing 15000 ppm  $Cl^-$ .

complete inhibition of pitting corrosion. These results suggest that additive adsorption and build-up of a protective passive layer seems to occur. Similar beneficial effects have been reported when nitrogen was added in solution or as alloying element to various stainless steels and nickel based alloys [18–21] and the role of this element in enhancing corrosion resistance has been widely discussed before [20, 22, 23]. Streicher [24] found that nitrogen increases the pitting corrosion resistance of austenitic stainless steel. This was explained by passivation of micro pits before they can grow as ordinary pits. The effect of nitrogen was also found to be greater if the elements with high passivating ability, e.g., chromium, molybdenum and nickel are present in steel. Clayton *et al.* [25] suggested that the effect in N-bearing alloys results from segregation of N to the metal surface during preferential dissolution of metal atoms, rather than its incorporation into oxide film. Truman *et al.* [20] proposed that increased availability of atomic nitrogen at the surface could favour the formation of nitrides that coexist with chromium-rich oxide film.

Herbsleb *et al.* [21, 26] stated that addition of  $NaNO_3$  as inhibitor for 18Cr-8Ni-2Mo steel in acid chloride solution shifts  $E_p$  in the more positive direction than in case of Mo-free steels. This agrees with the data of other authors [9, 20] and with ours, Fig. 5 (curve a). Therefore effect of addition of  $NO_3^-$  ions to an acidic chloride environment in improving the pitting corrosion

resistance may be due to an adsorbed layer of nitrogen on the oxide film [23] such that it is competing with chloride ions for adsorption sites.

**Dichromate.** The adsorption of dichromate, tungstate and molybdate appears to be not as strong as nitrate. The potentiodynamic measurements on  $Cr_2O_7^{2-}$  anion illustrate that the anion provides adequate protection on 316 stainless steel when present at  $\sim 5700$  ppm  $Cr_2O_7^{2-}$  in the solution. This behaviour can be explained in terms of the existence of sufficient concentration to make complete adsorbed or incorporated species for inducing passivity on the film.

Szklarska-Smialowska [27] proposed that the development of pits, and areas of localized attack, is controlled by solubility of the oxidizing alloying elements in acid solutions. She found a strong correlation between the solubility of the oxidized species in acid solutions and pitting potentials of Metal-Cr and Metal-Mo alloys.

Dichromate solutions, in acidic conditions are powerful oxidizing agent [28]. The role of chromate has been noted before elsewhere [29, 30] and was suggested to occur through the reduction of Cr(VI) to Cr(III) producing oxide ions which help repair defects in the oxide film and aid oxide growth, such that pitting is avoided. The surface-charge-adsorption theory advanced by McCafferty *et al.* [31–33] may account for the ability of dichromate species to displace chloride from the interface. This may also be consistent with the

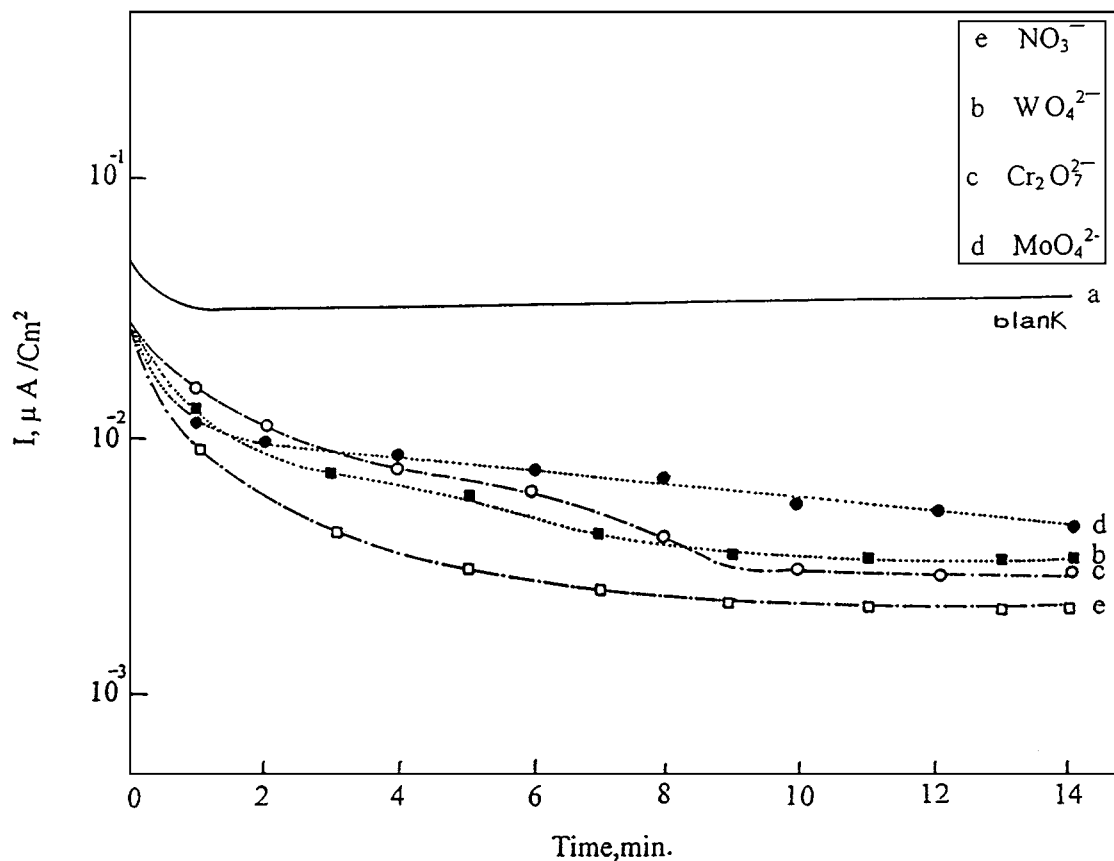


Figure 6 Potentiostatic polarization (i-t) curves for 316 stainless steel in 30%  $\text{H}_3\text{PO}_4$  containing 15000 ppm  $\text{Cl}^-$  and given concentrations of  $\text{NaNO}_3$ ,  $\text{Na}_2\text{WO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{Na}_2\text{MoO}_4$ .

views of MacMullen and Pryor [34] which showed that  $\text{CrO}_4^{2-}$  ion is adsorbed strongly on the oxide surface and prevents the penetration of aggressive anions such as  $\text{Cl}^-$  ions, into the oxide. Moreover, Kawano *et al.* [35] reported that  $\text{CrO}_4^{2-}$  ions penetrate into the imperfections of the oxide film and react with the Metal-substrate to form  $\text{Cr}_2\text{O}_3$  and  $\text{M}_2\text{O}_3$  repairing the films, and at the same time  $\text{CrO}_4^{2-}$  ions prevent the formation of soluble metal species by adsorption on the oxide. Therefore, the data obtained in Figs 3–5 may be explained in the following way; improvement of the pitting corrosion resistance of stainless steel 316 in  $\text{H}_3\text{PO}_4\text{-Cl}^-$  environment is observed in the presence of dichromate species because of its ability as a strong oxidizing agent and therefore may be adsorbed strongly and incorporated as  $\text{Cr}_2\text{O}_3$  to heal the developing pits and repair the films.

**Tungstate.** Tungstate anions produced a slow decrease in  $I_c$  (Fig. 3 – curve b) and  $I_p$  (Fig. 4 – curve b), but had a greater effect on the pitting potential (Fig. 5 – curve b). Similar findings have been reported by Osozawa and Okato [36] who found that, tungsten was a very beneficial alloying element to pitting corrosion resistance of the stable austenitic stainless steel if added with molybdenum. Very little is known about the effect of tungstate on the corrosion resistance of stainless steels in acid media. The literature contains great controversy about the  $\text{WO}_4^{2-}$  inhibitor. The results obtained by El Hosary *et al.* [9] on the effect of tungstate as inhibitor for corrosion of 304 stainless steel (Mo-free) in  $\text{H}_3\text{PO}_4\text{-Cl}^-$  solution show that tungstate ion has a limited protective action if it is present in higher con-

centrations. Similar findings have been reported by Bui *et al.* [37] who examined the effect of tungstate on the inhibition of stainless steels in 0.1 M HCl solution. They observed yellow precipitates of sparingly soluble tungstic acid ( $\text{H}_3\text{WO}_4$ ). In the presence of this inactive precipitates suppression of the pitting was not noted. The role of tungsten in improving the passivity of austenitic stainless steels in acid chloride and  $\text{H}_3\text{PO}_4\text{-Cl}^-$  solutions has been also discussed by Bui *et al.* [37]. It was concluded that, in acid solutions, tungsten probably passes directly from the metal into the passive film by interaction with water and formation of insoluble  $\text{WO}_3$  rather than through dissolution followed by adsorption.

The role of tungstate as inhibitor still requires clarification to explain the mechanism whereby corrosion resistance is improved. This may be achieved through the analysis of the oxide film formed.

**Molybdate.** Although many studies have been carried out on the effect of molybdenum on pitting corrosion resistance, the literature contains great controversy about the precise benefits of molybdenum, since negative effects of this element have also been observed for Fe-Cr-Ni alloys [38–41]. The present results of potentiodynamic measurements illustrate that the  $\text{MoO}_4^{2-}$  anion provides adequate protection when present at 5800 ppm concentration. Its effect on  $I_c$  and  $I_p$  is lower than that of  $\text{NO}_3^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  (Fig. 3 – curve d, Fig. 4 – curve d), while its effect on  $E_p$  comes lower after the other three additives (Fig. 5 – curve d). Should these findings be compared with previous results in literature, it will appear that  $\text{MoO}_4^{2-}$

ions were detected [42, 43] in all passive films formed on molybdenum-bearing alloys in acidic solutions. It was suggested that  $\text{MoO}_4^{2-}$  anions are responsible for the production in 0.1 M HCl of a bipolar film consisting of a cation selective outer layer and an intrinsically selective inner layer. The bipolarity of the duplex film was considered to be largely responsible for the development of an interfacial barrier layer. The same effect was observed by introducing  $\text{MoO}_4^{2-}$  to the passive film formed on stainless steels from solution [44]. Ogawa *et al.* [45] in his study assume that molybdate ions absorb on the fresh metal surface and act as anodic inhibitor in acid chloride solutions. This conclusion is based on the observation that Mo contained in the alloy exerts a similar effect as molybdate in the surrounding electrolyte [6, 45]. According to Pourbaix [46] molybdate ions are thermodynamically unstable in acid solution. The thermodynamically stable species is  $\text{MoO}_3$ . Szklarska-Smialowska [27] attributed the noble pitting potentials observed for M-Molybdenum systems to the solubility of the oxidized species,  $\text{MoO}_3$ . The author points to the fact that the solubility of the  $\text{MoO}_3$  oxide decreases with increasing acidity. Thus, acidity increases the stability of oxidized molybdenum species and superior pitting resistance is observed. This agrees with the observations of experimental data here, which are showed in Fig. 5 (curve d).

The role of these additives may still require clarification and further work will be needed to determine the nature and composition of the passive films. It is also important to determine the distribution and chemical state of inhibitive species across the depth of the films (These will be the subject of part II.)

#### 4. Conclusion

From the above discussion, electrochemical measurements showed that, nitrate, dichromate, tungstate, and molybdate anions are reasonably successful inhibitors. These reduce the corrosion rate of 316 stainless steel in  $\text{H}_3\text{PO}_4\text{-Cl}^-$  solutions. The additives retard both active and pitting attack to an extent depending on the type and concentration of the additives. This could be due to improved film repair conditions. Within the experimental concentrations examined the potentiostatic (i-t curves) results showed that the efficiencies of the additives can be arranged in the following order  $\text{NO}_3^- > \text{WO}_4^{2-} > \text{Cr}_2\text{O}_7^{2-} > \text{MoO}_4^{2-}$ ; with complete inhibition of the pitting corrosion.

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