

SYNERGISM IN THE INHIBITION OF AISI 304 STAINLESS STEEL CORROSION

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Abstract

The stainless steel, studied in the present scheme was AISI 304 stainless steel. The AISI 304 stainless steel is an austenitic stainless steel. This stainless steel is essentially a non-magnetic and cannot be hardened by heat treatment. This stainless steel is hardenable only by cold-working. This stainless steel is a continuous 18-8 steel. The chemical composition of AISI 304 stainless steel was as follows: 0.08% C, 2.00% Mn, 0.045% P, 0.03% S, 1.00% Si, 18.00-20.00% Cr, 8.00-10.50% Ni and the remainder is Fe. The density of the AISI 304 stainless steel was reported as 7.94 g/cm.

Keywords: *Synergistic Corrosion, Potentiostatic Polarisation*

Introduction

Stainless steels are iron-base alloys containing at least 10.5% Cr. With increasing chromium content and the presence or absence of some ten to fifteen other elements, stainless steels can provide an extraordinary range of corrosion resistance. Various grades have been used for many years in environments as mild as open air in architectural applications and as severe as the chemically active product streams in the chemical processing industries. Stainless steels are categorized in five distinct families according to their crystal structure and strengthening precipitates. Each family exhibits its own general characteristics in terms of mechanical properties and corrosion resistance [1]. With each family, there is a range of grades that varies in composition, corrosion resistance and cost.

Stainless steels are susceptible to several forms of localized corrosive attack. The avoidance of such localized corrosion is the focus of most of the effort involved in selecting stainless steels. Furthermore, the corrosion performance of stainless steels can be strongly affected by practices of design, fabrication, surface conditioning and maintenance. The selection of a grade of stainless steel for a particular application involves the consideration of many factors, but always begins with corrosion resistance [2]. It is first necessary to characterize the probable service environment. It is not enough to consider only the design conditions. It is also necessary to consider the reasonably anticipated excursions or upsets in service conditions. The suitability of various grades can be estimated from laboratory tests or from documentation of field experience in comparable environments [3]. Once the grades with adequate corrosion resistance have been identified, it is then appropriate to consider mechanical properties, ease of fabrication, the types and degree of risk present in the application, the availability of the necessary product forms and cost. The mechanism of corrosion protection for stainless steels differs from that for carbon steels, alloy steels and most other metals. In these other cases, the formation of a barrier of pure oxide separates the metal from the surrounding atmosphere. The degree of protection afforded by such an oxide is a function of the thickness of the oxide layer, its continuity, its coherence and adhesion to the metal and the diffusivities of oxygen and metal in the oxide. In high-temperature oxidation, stainless steels use a generally similar model for corrosion protection. However, at low temperatures, stainless steels do not form a layer of pure oxide. Instead, a passive film is formed. One mechanism that has been suggested is the formation of a film of hydrated oxide, but there is not total agreement on the nature of the oxide complex on the metal surface. However, the oxide film should be continuous, nonporous, insoluble and self-healing if broken in the presence of oxygen [4].

The presence of oxygen is essential to the corrosion resistance of a stainless steel. The corrosion resistance of stainless steel is at its maximum when the steel is boldly exposed and the surface is maintained free of deposits by a flowing bulk environment. Covering a portion of the surface for example, by biofouling, painting, or installing a gasket produces an oxygen-depleted region under the covered region. The oxygen-depleted region is anodic relative to the well-aerated boldly exposed surface, and a higher level of alloy content in the stainless steel is required to prevent corrosion with appropriate grade selection, stainless steel will perform for very long times with minimal corrosion, but an inadequate grade can corrode and perforate more rapidly than a plain carbon steel will fail by uniform corrosion. Selection of the appropriate grade of stainless steel is then a balancing of the desire to minimize cost and the risk of corrosion damage by excursions of environmental conditions during operation or downtime [5].

The stainless steel, studied in the present scheme was AISI 304 stainless steel. The AISI 304 stainless steel is an austenitic stainless steel. This stainless steel is essentially a non-magnetic and cannot be hardened by heat treatment [6]. This stainless steel is hardenable only by cold-working. This stainless steel is a continuous 18-8 steel. The chemical composition of AISI 304 stainless steel was as follows: 0.08% C, 2.00% Mn, 0.045% P, 0.03% S, 1.00% Si, 18.00-20.00% Cr, 8.00-10.50% Ni and the remainder is Fe. The density of the AISI 304 stainless steel was reported as 7.94 g/cm.

Weight-loss Experiments

Square specimens (20 mm x20 mmx3 mm) of AISI 304 stainless steel were cut from the sheet and a small hole of 1.5 mm diameter was drilled near the upper edge in each specimen for mounting the specimen into the corrosive medium. The specimens were prepared, cleaned and evaluated as per ASTM G1-81 [7]. The specimens were not stored in the desiccator and were immersed in the corrosive medium just after the preparation. The surface area and mass of the test specimens were 10.00-11.00 cm² and 9.00-10.00 g respectively. The corrosive medium (test solution) for the static immersion studies was 5N H₂SO₄. The test solution was prepared by proper dilution of AR grade sulphuric acid [7664-93-9] in deionized water. The inhibitors used were of AR grade quinoline [91-22-5] and methyl methacrylate [80-62-6] (stabilized with 5% hydroquinone) in one set and aniline [62-53-3] and potassium iodide [7681-11-0] in another set. The concentrations of inhibitors studied ranged from 0.01-0.08N each of quinoline and methyl methacrylate in the first set and 0.05-0.50M/L of aniline and 0.02-0.45 M/L of potassium iodide in the second set. Five specimens were used for each corrosive medium for studying the corrosion rate at five different time intervals. The testing periods were 72, 96, 120, 144 and 168 hours. The temperature throughout the experiment was maintained at 30 ± 2°C. The specimens were cleaned by the following method after the test:

The specimens were dipped in:

Ammonium hydroxide (NH ₄ OH, sp gr 0.90)	100 ml
Water to make	1 litre
Temperature	60°C (140°F)
Time	20 minutes

The specimens were rinsed following cleaning and scrubbed lightly with a bristle brush and running water. After the final rinse, specimens were air dried and weighed to an accuracy of at least 1 mg. The mass lost during the test was determined and corrosion rate in mils per year (mpy) was calculated as per ASTM G31-72 [7]. The results of first set of studies are depicted in Figure 1-4.

Potentiostatic Polarisation Measurements

For polarisation studies, rectangular specimens (20 mm×10 mm×1.5 mm) with a narrow strip (15 mm×3 mm×1.5 mm) at one end were cut from the sheet of AISI 304 stainless steel. Within one hour of the experiment the working electrodes (test electrodes) were prepared. Each working electrode was drilled, tapped and mounted onto the electrode holder. The back and sides of the test electrode were coated with a mixture of Perspex and wax from chloroform solution, leaving only the 1 cm² portion of the test electrode exposed to the test solution (5N H₂SO₄). The volume of the test solution was 300 ml in the polarisation 1 cell (test cell or corrosion cell). The auxiliary electrode (platinum electrode) salt-bridge probe and other components were placed in the corrosion cell and the salt-

bridge was filled with the test solution (5N H_2SO_4). The working electrode was transferred to the test cell and the salt-bridge probe tip was adjusted in the manner that it was about 2 mm away from the test electrode. The open-circuit potential E_{corr} (corrosion potential) of the test specimen, after 5 and 55 min immersion was recorded and E_{corr} was suppressed. After this the potentiostatic potential scan was started at a constant step rate of 10 mV/min and the corresponding current densities were recorded. The cathodic polarisation scan was performed first and after one minute the anodic polarisation scan was performed. The polarisation curve was plotted as a linear potential-current density curve and the cathodic and anodic potentiostatic polarisation data were plotted on semi logarithmic paper in accordance with practice G3-74 [7], (potential-ordinate, current density-abscissa). The polarisation resistance, R_p , has been determined graphically as the tangent of the linear polarisation curve at the origin of the plot (AE) (anodic and cathodic Tafel slopes) were obtained from Evan's diagram. Each step was performed as per ASTM G3-74, G5-87 and G59-78 [7]. The corrosion current density I_{corr} was calculated and the same has also been evaluated from Evan's diagram.

Results and Discussions

Methyl methacrylate-Quinoline System

Weight-loss Kinetics

A perusal of Figures 1 clearly shows that the corrosion rate of AISI 304 stainless steel is very high in 5N H_2SO_4 being 980 mpy to 1006 mpy between 72 hours of immersion to 120 hours. It decreases fast with time beyond 120 hours which must be due to decrease in concentration of sulphuric acid. The addition of quinoline decreases corrosion rates and this confirms that it acts like an inhibitor. As the concentration of quinoline increases from 0.01N to 0.06N in 5N H_2SO_4 the corrosion rates decrease during immersion period from 72 hours to 120 hours but show an increase at 144 hours up to 0.02N quinoline concentration but at higher concentration the rates decrease continuously. Corrosion rates at 168 hours with quinoline increase and decrease and do not show any regular

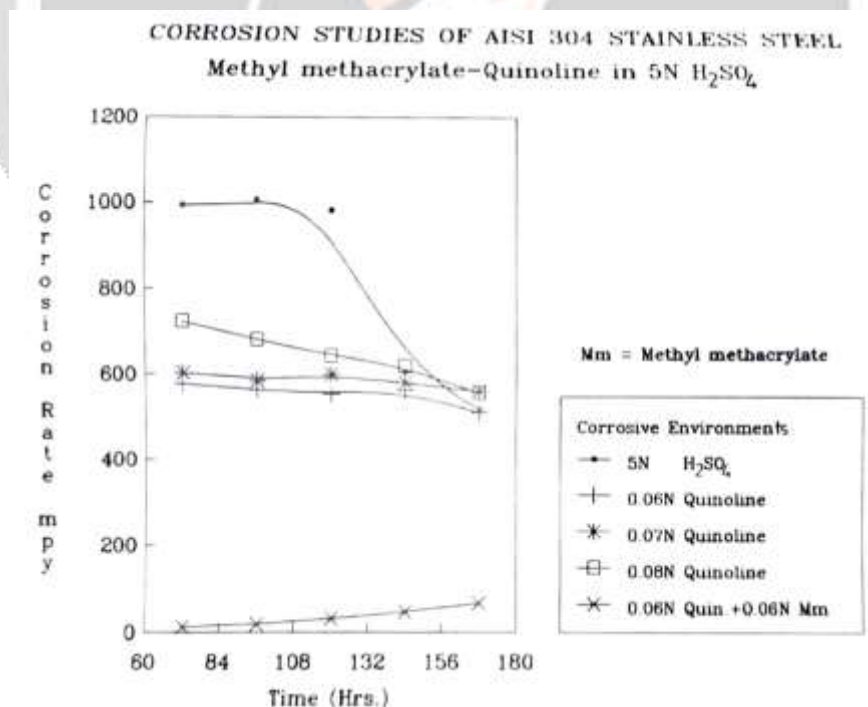


Figure 1. Corrosion studied (Corrosion rate) of AISI 304 Stainless Steel Methyl metaacrylte-Quinoline in 0.5N H_2SO_4 .

trend. At higher concentrations of quinoline i.e. 0.07N and 0.08N, the rates again increase indicating reactivation process. However, rates with synergistic combination are very low as compared to rates with 0.06N quinoline concentration.

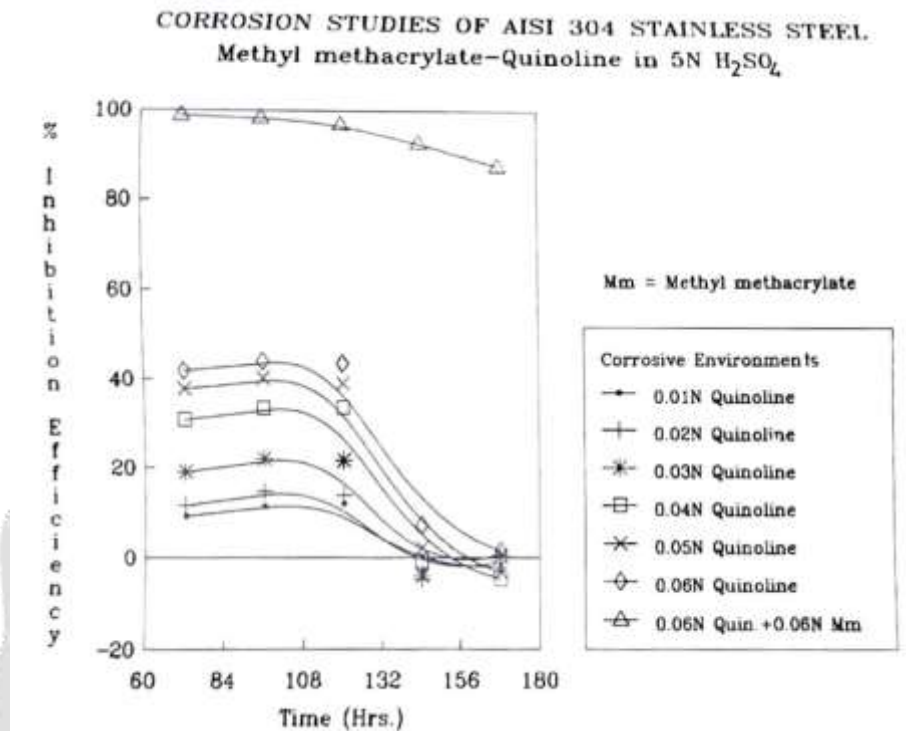


Figure 2. Corrosion studied (Inhibition Efficiency) of AISI 304 Stainless Steel Methyl metaacrylte-Quinoline in 0.5N H₂SO₄.

The low rates of corrosion or better protection of the AISI304 stainless steel is especially useful for their use as pickling inhibitor. Results of my studies with methyl methacrylate as inhibitor in the above AISI 304 stainless steel in 5N H₂SO₄ system are recorded and expressed graphically in Figures 4. The decrease in corrosion rates with 0.01N methyl methacrylate is not so much as observed with higher concentration i.e. from 0.02N to 0.06N. The corrosion rate again decreases with time up to 0.05N concentration of methyl methacrylate but show an increasing trend from 144 hours onwards at 0.06N, 0.07N and 0.08N concentration of methyl methacrylate. A perusal of corrosion rates show that methyl methacrylate is a better inhibitor than quinoline. The inhibitor also shows reactivation as with quinoline beyond 0.06N concentration but corrosion rates do not exceed the rates without inhibitor at any stage of my study. These facts indicate that with both quinoline and methyl methacrylate, the mechanism of reactivation is by desorption of inhibitor from the metal surface permitting acid to react with more surface resulting in higher corrosion rates. The maximum inhibition efficiency seen with methyl methacrylate is 61.94% with 0.06N concentration at 96 hours. The percent inhibition efficiency is also much less than inhibition efficiency observed with synergistic combination which is 98.78% at 72 hours.

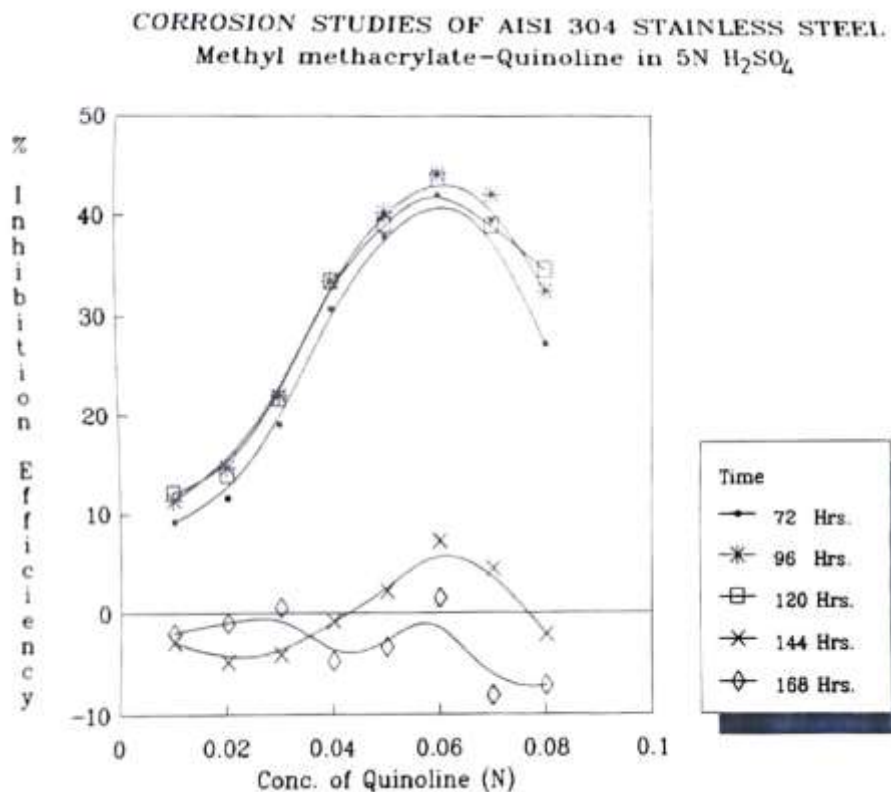


Figure 3. Corrosion studied (Inhibition Efficiency) of AISI 304 Stainless Steel Methyl metaacrylte-Quinoline in 0.5N H₂SO₄.

Potentiostatic Polarisation Studies

The studies with weight-loss experiments are at a later stages of corrosion but my study of electrochemical methods gives the corrosion behaviour of the sample in the first few hours in the highly corrosive medium. It will be seen that dissolution of AISI 304 stainless steel in 5N H₂SO₄ is predominantly under cathodic control. Addition of quinoline reduces the corrosion rate. Polarisation curves in 0.06N quinoline indicate that the reaction is initially under mixed control but at later stages becomes under cathodic control. Polarisation studies also show that methyl methacrylate stifles the anodic current density more than the cathodic current density and hence it is mainly covering anodic active sites on the metal surface. An interesting fact is that the E_{corr} values of uninhibited sample is -505 mV which changes to -490 mV after 55 minutes. Likewise, E_{corr} of metal in 5N H₂SO₄ with 0.06Nquinoline is -498 mV initially which changes to 491 mV after 55 minutes but E_{corr} with methyl methacrylate is initially -485mV in corrosive acid medium which shows a jump in the anodic direction and it becomes -405 mV after 55 minutes.

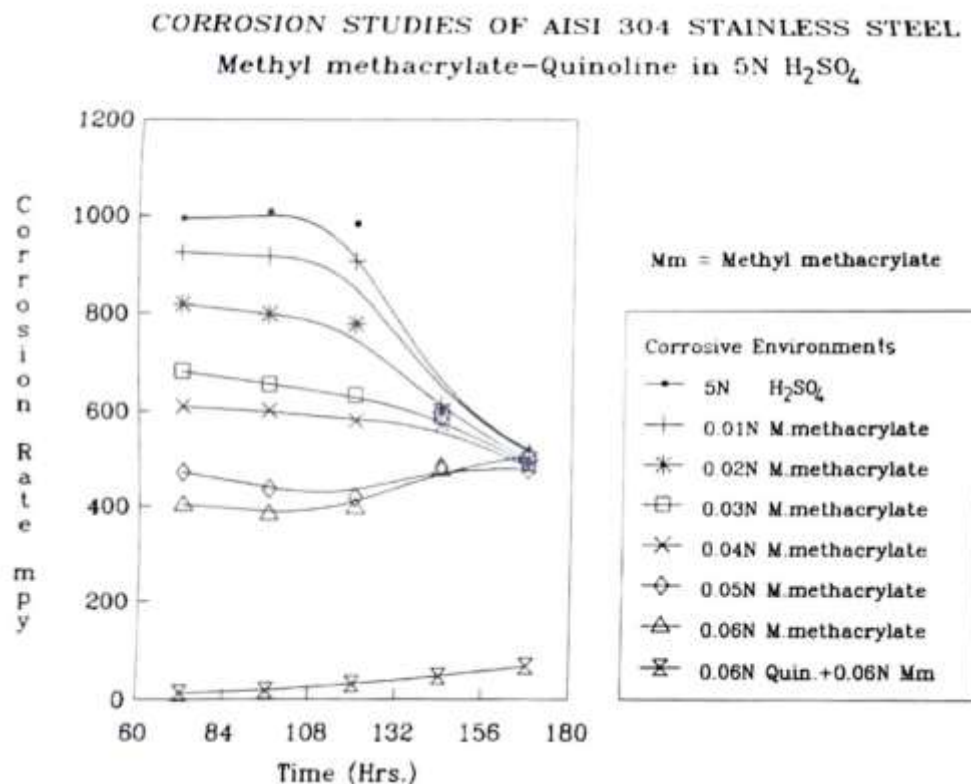


Figure 4. Corrosion studied (Corrosion rate) of AISI 304 Stainless Steel Methyl metaacrylyte-Quinoline in 0.5N H₂SO₄.

This large shift is associated with the anodic polarisation of the corrosion process. Addition of 0.04N methyl methacrylate to 0.06N quinoline is under cathodic control but this combination is showing better protective action than either of the two inhibitors alone. An increase in concentration of methyl methacrylate makes the reaction under anodic control and the maximum protection of the metal could be achieved by the synergistic combination with 0.06N each of the inhibitor in the highly corrosive acid medium. A further increase in concentration of methyl methacrylate in 0.06N quinoline+5N H₂SO₄, increases the corrosion rate though the combination has better protective action than the individual inhibitor. As seen earlier, the E_{corr} values after 55 minutes show higher shifts with methyl methacrylate even in the presence of quinoline.

The inhibiting action seems to be under anodic control and the protective action increases till 0.06N quinoline concentration from 0.04N onwards but then the inhibiting action decreases on further increasing the quinoline concentration i.e. 0.07N and 0.08N. The reaction also becomes under cathodic control at 0.08N quinoline concentration. It is also interesting to note that E_{corr} values of the metal do not differ much initially when the concentration of quinoline is changing but shift after 55 minutes is reduced at higher concentration of quinoline i.e. 0.07N and 0.08N. These results point to the fact that the shift of potential towards anodic direction with time is mainly due to methyl methacrylate. The shift due to quinoline is very slight but at higher concentration of quinoline in 0.06N methyl methacrylate + 5N H₂SO₄ reduces the shift towards anodic direction.

In the present study also, quinoline acts as an inhibitor by getting adsorbed on the metal surface reducing both anodic and cathodic processes by blocking metal surface for hydrogen ions. Beyond a critical concentration the protonated quinolinium ion itself gets reduced at the cathode by accepting electron and Fe along with an electron of the quinoline adsorbed at the anodic area leave the surface as the products, the corrosion rate increases. The increase in corrosion current densities I_{corr} is seen even in the presence of methyl methacrylate at higher concentration of quinoline.

Conclusion

The following conclusions can be drawn from the results of my study by weight-loss kinetics and polarisation studies: Both KI and aniline acts as stimulator at low concentrations in 5N H₂SO₄ in corrosion of AISI 304 stainless steel. The corrosion rate decreases with increase in concentration of these substances and the corrosion rate is minimum at some concentration of each inhibitor. The corrosion rates again increase with both inhibitors when they exceed beyond some critical concentration. Potassium iodide acts as an anodic inhibitor while aniline acts as a cathodic inhibitor. The combination of 0.25 M/L KI+0.40 M/L aniline gives the best synergistic inhibition providing 97% inhibition. The inhibition efficiency decreases with time.

Acknowledgment

Authors gratefully acknowledge the Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University.

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