The experimental work has been divided into following two parts for the convenience:
Part I - Weight loss studies and Part II - Galvanostatic studies.

PART - I WEIGHT LOSS STUDIES

In order to study a metal or an alloy, it is essential to have a material of uniform and known composition. The stainless steel used in the present investigation was purchased in a single lot directly from its manufacturer, M/s. Hindustan Steel Limited (a Government of India Undertaking), Durgapur, West Bengal (India). The steel used was A.I.S.I. type 304 (S.W.G. 18). The chemical composition as furnished by the manufacturer was as follows:

\[ \begin{align*}
C & = 0.06, \quad Mn = 1.4, \quad P = 0.024, \quad S = 0.013, \\
Si & = 0.41, \quad Ni = 9.54 \text{ and } Cr = 18.54% 
\end{align*} \]

No further information could be obtained regarding to presence of other impurities by qualitative tests in the laboratory.
The metallurgical data supplied by the manufacturer was as follows:

i. The material was first hot rolled to 1.25 mm thickness, annealed and pickled and then cold rolled from 1.25 to 1.0 mm. thickness and again annealed and pickled.

ii. Hot rolling temperature was 1000-1050°C.

iii. Annealing temperature after both hot rolling and cold rolling was 1980°C.

Methods of studying corrosion

The usual and the most convenient method of measuring damage by corrosion is the loss in the weight of the specimen. This criterion may not be satisfactory, when there are chances of redeposition of one of the constituents of an alloy e.g., in the case of dezincification of brass, the weight of the redeposited metal will not be included in the apparent loss in weight. The apparent loss in weight will not obviously be related to damage by corrosion. Likewise, when the attack has been confined to specific points on specimen e.g., along the grain boundaries, or across grains, the
mass of the metal actually removed may be too small to be weighed and yet the strength of the specimen may be completely destroyed. When the corrosion product is an adherent solid, the increase in the weight may give a measure of the non-metallic constituents (e.g., oxygen) which has entered into combination. A specimen when placed in a corrosive medium may lose or gain weight depending upon whether the corrosion product is a soluble one or is a completely adherent solid. Both the phenomena may take place simultaneously. After dissolution, a film may be deposited. In some cases, the products of corrosion are loose and thick layer. They may be removed on washing the specimen. Hence, interpretation of the data on corrosion requires a careful study of the nature of the products of corrosion. The gain in weight criteria is of limited use. The loss in weight of a specimen after a certain interval gives only one point on the corrosion time curve for the specimen tested.

In the present investigation corrosion of stainless steel was evaluated mainly by loss in weight method. This was followed by inhibition studies using various organic compounds containing mainly atoms like sulphur, nitrogen etc. The retardation was calculated
by using the following formula:

\[
\frac{i_0 - i}{i_0} \times 100 = \% \text{ Inhibition}
\]

where \(i_0\) and \(i\) are the losses in weight in absence and presence of an inhibitor respectively (1). The methods followed to study the corrosion in the present investigation were restricted to the available resources of the laboratory.

**PREPARATION OF SPECIMEN**

Specification on corrosion tests, in general, recommends that the dimensions of specimen should not be less than 5x2 cm (2). However, specimens used in the present investigation were 2.54 x 2.54 cm due to limited quantity of the material at hand. A small hole of 2 mm diameter was drilled just near the upper edge in middle of the specimen for suspension. As emphasised by Protevin (3), edge of the specimen may be particularly susceptible to the attack. When disturbing factors are liable to occur at the edges of the specimen, it is advantageous to adopt a size and shape of specimen giving a low edge/area ratio and a reasonably large area. The circular specimens evidently meet these requirements best;
however, in the present case, square specimens were used since they are less troublesome to cut and support.

The specimens of stainless steel were first washed with double distilled water and then dried. They were then polished as follows:

A mirror like finish was obtained on both surfaces by polishing with a white rouge containing aluminium oxide and followed by a green rouge containing chromium oxide\(^{(4,5,6)}\). The use of emery cloth for smoothing and aqueous suspension of \(\text{Cr}_2\text{O}_3\) for brightening the stainless steel specimens has also been recommended\(^{(7)}\). R. Weiner and G. Klein\(^{(8)}\) studied the effect of polishing agent upon corrodibility of metallic surfaces. They tabulated the effect of \(\text{Fe}_2\text{O}_3\), \(\text{Cr}_2\text{O}_3\), \(\text{Al}_2\text{O}_3\), siliceous chalk etc. on Ag, Al, Cu, Zn, brass, Ni, Cr, steel etc.

The specimens were finally degreased by immersion in double distilled, sulphur free carbon tetrachloride. Then the specimens were wrapped with a clean paper and preserved in a desiccator and used next day.
The principal experimental difficulty in total immersion tests is the locally accelerated corrosion due to contact of the specimen with its support in the corrosive medium. The effects may be minimised using point contacts and minimum number of contacts. The specimen was suspended by pyrex glass hook. Here also there are chances of localized corrosion; but by making the hole through which the hook passed as small as possible and nearest to the edge, it is possible to reduce this type of corrosion to a minimum.

Bengouh and coworkers(9) have made an interesting observation on the relation between the corrosion rate and the depths of the immersion. When the specimen is very close to the surface of the liquid, the attack is rapid. As the depth is increased, the velocity falls off, because the oxygen has to diffuse across the thicker layer to reach the metal or the alloy. If diffusion were the only mode of transport available, corrosion would be negligibly slow at larger depths of immersion; but actually when the depth exceeds 1.5 cm, the corrosion rate ceases to fall off further. This suggests that diffusion plays an important part in the oxygen supply with relatively shallow immersion; but
with deeper immersion (about 1.5 cm), the oxygen supply is actually controlled by convection current, so that variation in depth is insignificant.

In the present investigation the specimens were immersed nearly to the same depth viz., 2.0 cm below the surface of the liquid. The volume of the liquid for each specimen was 250 ml in a container. The container was a 'corning' brand beaker of 265 ml capacity. Only one specimen was suspended in each beaker. The beakers were placed in a thermostat-cupboard within which the temperature was at 40±2°C. Duplicate experiments were performed; however, mean values of the results have been recorded.

**ASSESSMENT OF CORROSION**

For satisfactory assessment of corrosion, it is necessary to remove the products of corrosion film formation etc., from the surface of the specimen. At the same time, it is desirable to avoid, as far as possible, further attack on the metal during cleaning of specimen by any method such as: (a) chemical, (b) electrochemical treatment or (c) mechanical treatment. Friend(10) pointed out that mechanical removal of rust or any kind of film formed during corrosion test is the best method since
It gives minimum error. It has, however, one drawback that it cannot remove completely the corroded products formed in pits. In the present investigation, it was found that use of 20 to 30% HNO₃ acid gave satisfactory results (11,12). The corroded specimen was dipped in the acid and, if required, rubbed with a rubber bung attached to a glass rod. It was subsequently washed with distilled water followed by alcohol-ether mixture. Finally they were wrapped with its original wrapper paper after weighing on one pan semimicro balance.

Remarks

Most of the organic compounds studied as inhibitors were those supplied by Fulka (Italy), E. Merck (Germany) or BDH (England). The acids used were of A.R. grade (Analar-quality), while sodium hydroxide and ferric chloride were of C.P. (Chemically pure) grade (BDH).

The strengths of the acids' solutions etc., were checked by following standard analytical procedure.

Duration of the exposure

The concentrations of hydrochloric acid selected were 2.5, 5.0 and 7.5M. The duration of the exposure were 12 and 24 hours. In the case of sulphuric acid, the concentrations selected were 1.25, 2.5 and 3.75M.
so as to keep the concentrations of the acid practically similar to that in hydrochloric acid. However, the durations of the exposure were increased to 24 and 48 hours so that a measurable loss in weight could be obtained.

The ferric chloride solution used in the present investigation was prepared as follows:

A weighed quantity of ferric chloride was dissolved in a calculated volume of 0.5M HCl to prevent the formation of hydrated colloidal iron oxide. This added acid was neutralized by adding an equivalent quantity of sodium hydroxide. The pH of the solution was then adjusted in close vicinity of 1.3. The solution thus obtained was quite clear and stable. The concentration of ferric chloride was checked by estimating iron volumetrically. The concentrations of ferric chloride selected for corrosion studies were 0.5 and 1.0M. As both these solutions contain 0.5M NaCl (approximately), their pitting tendency was considerably increased (13). Durations of the exposure were increased to 48 and 96 hours.

In the entire work, volumetric apparatus such as burette, pipette, micro pipette, measuring flasks, cylinder were of standard quality and were calibrated
before use. The weights, unless otherwise stated, were taken correct to 0.001 mg. The Mettler one pan balanced was used. Distilled water was used for the preparation of solutions. Unless otherwise stated, all experiments were performed in duplicate, however, the mean was taken. Corrosion loss is expressed (i) loss in milligrams (mg) and (ii) loss in milligrams per decimeter square per hour (mg/dm²/hour). The figures of the weight losses and mg/dm²/hr were rounded suitably. The inhibitors were added to the corrosive medium as follows: If the substance was in the form of solid, a weighed quantity of it was added to the medium. In case it was liquid, a measured volume of it was added to the solution with the help of proper burette. The concentrations of the inhibitors are expressed in terms of either grams or ml per litre of the solution.

As described earlier, the corrosion resistance of stainless steels is mostly combated by modifying its chemical alloying components. In literature innumerable data are available on prevention of corrosion of ferrous and nonferrous metals and alloys in various media by adding appropriate inhibitors. However, scanty data are available to decrease corrosion of stainless steels by modifying suitably the corrosive environments.
The scanty data available from chemical abstracts have been grouped in the list of references (pages 375, 382-386, 473-476, 142, etc.).

In the present investigation an attempt has been made to study the extent and nature of inhibition shown by various organic compounds towards corrosion of A.I.S.I. type 304 stainless steel in 2.5, 5.0 and 7.5M HCl, 1.25, 2.5, 3.75M H$_2$SO$_4$ and 0.5 and 1.0M FeCl$_3$ (containing 0.5M NaCl) adjusted to pH 1.3 by adding sodium hydroxide.

Following inhibitors have been studied in all the above three systems:

Urea, thiourea, methyl thiourea, ethyl thiourea, diethyl thiourea, dibutyl thiourea, allyl thiourea, thiourea dioxide, phenyl thiourea, diphenyl thiourea, N-N'-di-o-tolyl thiourea, N-N'-di-p-tolyl thiourea, dodecyl mercaptan, dimethyl sulphoxide, dibutyl sulphoxide, dibenzyl sulphoxide and propargyl alcohol.

Following additional substances were studied in specific medium:

(I) In hydrochloric acid

Carbon disulphide, 2-mercaptobenzothiazole, dithizone, dithio-oxamide, indigo carmine, nitron, phenyl
hydrazine, o- and p-anisidine, benzidine, aniline, N-ethyl aniline, N-N'-diethyl aniline, quinoline, 8-hydroxy quinoline, ferron, acriflavine, rhodamine B, p-benzoquinone, dibenzyl, iso-amyl alcohol, methylene blue, methyl violet.

(II) **In sulphuric acid**

Carbon disulphide, nitron, ferron, 2-mercapto benzothiazole, 2-mercapto thiazoline, 2-benzimidazole thiol, acriflavine, α-nitroso- β-naphthol, dodecyl alcohol, stearyl alcohol, sodium diuranate.

(III) **In ferric chloride**

o-Nitro aniline, p-anisidine, o-anisidine, quinoline, benzaldehyde, ethyl methyl ketone, ethanediol.

The results obtained are given in Tables 1.1, 2.1 and 3.1 on pages i11, i27, i28 respectively for HCl and 4.1, 5.1, 6.1 on pages i62, i62, i319 respectively for H₂SO₄ and Table 7.1 on page 449 for FeCl₃.

In order to signify the efficiency of an inhibitor following terminology has been used in the text instead of stating the per cent (%) inhibition.

<table>
<thead>
<tr>
<th>Percentage inhibition</th>
<th>Type of inhibitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>≥ 89</td>
<td>Excellent inhibitor</td>
</tr>
<tr>
<td>50 to 89</td>
<td>Efficient or good inhibitor</td>
</tr>
<tr>
<td>≤ 50</td>
<td>Poor inhibitor</td>
</tr>
</tbody>
</table>
PART - II GALVANOSTATIC STUDIES

Corrosion is essentially an electrochemical phenomenon.* This view was initiated by Whitney(14) and received support of other workers including Walker(15), Coshman(16) and Tilden(17).

Two dissimilar metals in electrical contact and immersed in a conducting solution form an electrochemical cell in which the less noble metal becomes an anode and other metal becomes a cathode. Even a single metal or an alloy, for example, a zinc rod half immersed in an aqueous solution of sodium chloride, may suffer electrochemical corrosion(18), consisting of a cathodic reaction proceeding just below the water line and the anodic reaction lower down the metal specimen as given below:

\[ 2H^+ + 2e^- \rightleftharpoons H_2 \quad (I) \]
\[ \frac{1}{2}O_2 + H_2O + 2e^- = 2OH^- \quad (IA) \]
\[ \text{(cathodic reaction)} \]
\[ Zn = Zn^{++} + 2e^- \quad (II) \]
\[ \text{(anodic reaction)} \]

* The account given below summarizes the view of H.C.Gatos Corrosion, 12, 23t (1956).
The cathodic reaction uses up electrons and thus makes possible the entry of metal into the liquid as cations. The electrochemical view of corrosion received a firm support from Evans and Hoar (19) and Brown and Mears (20) who proved that the quantity of electricity flowing through a local cell is equivalent to the amount of metallic corrosion in accordance with Faraday’s laws. In acids, impurities, e.g., arsenic or copper in zinc, may cause corrosion, impurities acting as cathode. Cathodic and anodic areas may exist on a metal surface even in the absence of foreign impurities. Distribution of anodic and cathodic areas depends upon the existence of crystal-lattice imperfections, strains, etc.

When an electric current flows through a local cell, the potential of the anode and the potential of the cathode (A and C in Fig. 1, page 22) come closer to each other, i.e., both become polarized, the anodic potential shifting towards the cathodic value and the cathodic potential shifting towards anodic value. Polarization is due to the slowness of one or more processes occurring at the electrodes. The value of 'a' depends upon maximum current which can flow in the circuit and corresponds to maximum steady state corrosion theoretically possible. The conditions which decrease
Polarization curves of corrosion local cells.
the slope of the polarization curve will result in accelerating corrosion and conditions which increased the slope will result in inhibition of corrosion. 'b' and 'c' represent the conditions giving higher current values due to prevention of polarization of cathode and anode respectively. On the other hand, 'd' and 'e' represent decrease of current by increase in polarization of anode and cathode respectively. Thus, increasing the polarization of anode shifts the steady state potential towards the cathodic side and increasing the polarization of cathode shifts the steady state potential towards the anodic side. If polarization of both increases to the same amount, steady state current decreases but the potential remains the same at 'f'.

INHIBITION BY ANODIC POLARIZATION

The corrosion of a metal in an aqueous medium due to anodic dissolution of the metal at the anodic areas is as per the following reaction:

\[ M \rightleftharpoons M^{+x} + xe^- \]

where M represents corroding metal, \( M^{+x} \) represents the metal ions formed during corrosion, and x represents oxidation number of the ions. The electrons released at
the anode are transferred to the cathode through metallic conduction and are consumed there by cations present in the solution. The corrosion inhibitors retarding the anodic reaction cause anodic polarization. Such inhibitors are termed anodic inhibitors (21). If the corrosion current is proportional to the anodic areas, i.e., the corrosion process is anodically controlled, decrease in anodic areas may result in decreasing corrosion current. On the other hand, if corrosion is controlled by the cathodic reaction the corrosion current, and therefore the total amount of corrosion, is not affected by decreasing the anodic areas. In this case the same amount of corrosion must be distributed over a smaller anodic area, resulting in intensified localized attack termed 'Pitting'. The metal salts of chromate, carbonate, phosphate, silicate etc., act as anodic inhibitors. Sometimes all these inhibitors, if used in small concentration, may increase overall corrosion (22), e.g., sodium chromate and potassium permanganate, if present in small quantities, accelerate corrosion whereas large quantities of inhibitors may act as effective inhibitors. In such cases it is likely that the inhibitor if present in small amount may act as cathodic depolarizer; and at higher concentration it may acts as anodic polarizer.
INHIBITION BY CATHODIC POLARIZATION

During the corrosion of common metals in acid, the cathodic reaction is

$$2H^+ + 2e^- \rightarrow H_2$$

In neutral solutions containing oxygen, the main cathodic reaction is the reduction of oxygen to hydroxyl ions,

$$\frac{1}{2}O_2 + H_2O + 2e^- = 2OH^-$$

In environment favouring corrosion, substances other than hydrogen ion and oxygen may be reduced at local cathodes. Inhibitors interfering with the above reaction are called cathodic inhibitors. The cathodic areas are not attacked during corrosion; hence, inhibition by cathodic reaction generally do not lead to a localized attack. If corrosion is controlled by cathodic inhibitors, decrease in cathodic area will result in decreasing overall corrosion. If corrosion is controlled by anodic reaction, decrease in cathodic area may result in increase of cathode current density but will not have any effect on over all corrosion. Arsenic salts which are effective in inhibiting corrosion of steel in mineral acids are cathodic inhibitors. They are termed as 'safe inhibitors' by Evans(21). A number of substances,
on the other hand, interfere both with anodic and cathodic reactions and cause both anodic and polarization. Gelatine, glue and other high molecular weight substances fall in this category. These inhibitors concentrate at the metal liquid interface and because of high viscosity cause decrease in diffusion rates of the corrosive substances towards the metal surface. In addition to anodic, cathodic and mixed polarization, corrosion inhibitors may also alter the open circuit potential and thus lead to decreased corrosion.

**POTENTIAL MEASUREMENTS**

Electrode potential measurements of a metal in aqueous solutions have been widely employed for inhibitor studies and have contributed to the understanding of the corrosion process.

The potential of a metal in the corrosive medium may not be important but change in potential occurring in the presence of inhibitors is usually significant. Corrosion inhibition may take place without any shift of the potential of the metal. Hence, potential measurement must be considered in conjunction with
corrosion rates, chemistry and geometry of the systems etc. Shifting of the potential to more cathodic values accompanied by decrease in corrosion rate may indicate anodic polarization. In the corrosion of steel in aerated neutral or alkaline systems in the presence of an inhibitor, such as sodium silicate, there is inhibition and potential ranges from 0.0 to 0.35 v (standard hydrogen scale) (23). While in deaerated solution, in presence of the same inhibitor, there is no inhibition, the potential remaining less cathodic. On the other hand, in the case of sodium chromate and sodium nitrite potential does not change from aerated to deaerated condition. The potential is more cathodic in the presence of the inhibitor both in aerated or deaerated condition. Potential of steel in sulphuric acid is shifted towards more cathodic value in presence of amines and other nitrogen containing compounds (2+) They are termed as anodic inhibitors. On the other hand, As+++ inhibits the corrosion of iron in sulphuric acid and shifts the potential towards more anodic value, indicating cathodic polarization. Electrode potential changes of metals in aqueous media may indicate the extent and type of adsorption on metal surface. Thus in the case of mild steel in sulphuric acid containing inhibitor like
triethylamine(25), it was found that chemi-adsorption isotherm was obtained by plotting change in potential vs. inhibitor concentration.

**Polarization Studies with Externally Applied EMF**

The electrode potential of corroding metal represents the average potential of the local cells. Direct measurement of polarization of anode or cathode is virtually impossible and hence anodic and cathodic behaviour of corroding metal has been studied by making the metal anode or cathode against auxiliary electrode in the corrosive medium by means of an externally applied emf. Such studies give valuable information. Thus, Chappel, Roetheli and McCarthy(26) found that mild steel showed a little change in potential when made anode in presence of quinoline ethiodide. On the other hand, the specimen when made cathode in the same electrolyte in the presence of quinoline ethiodide showed pronounced polarization. It was concluded that quinoline ethiodide interferes with cathodic reaction. Thus quinoline ethiodide increases hydrogen over-voltage. Corrosion accelerator such as nitrobenzene decreases hydrogen overvoltage. Hence it may be termed cathodic accelerator.
It may be concluded, in general, that inhibitors act by inducing anodic, cathodic or mixed polarization.

INORGANIC INHIBITORS

To account for the action of inorganic anodic inhibitors, Evans advanced a theory of formation of a protective film of a sparingly soluble salt of the metal with the inhibitor. Hoar and Evans(27) proposed that phosphate ions in neutral and alkaline solution react with ferrous ions and precipitate an adherent protective film which contains hydrated ferric oxide. Pryor and Cohen(28) concluded that the protective action of anodic inhibitors is based on the formation of protective films of Fe₂O₃ maintained in constant repair. In the case of nonoxidizing anions the film may consist entirely of dissolved oxygen i.e., the inhibitor does not participate directly in the formation of a protective film but it merely contributes to the repairing discontinuities in the oxide film. In the presence of oxidizing anions, the protective film is formed by dissolved oxygen. In deaerated solutions, the inhibitors, such as potassium chromate, sodium nitrite, etc., may react directly with iron to form protective oxide films. On the other hand, according to Uhlig(29, 30) it is not
necessary to have protective film of stoichiometric chemical compounds. According to him inhibition by potassium chromate is primarily due to physical adsorption and chemisorption due to valence forces of the surface metal atoms.

Hackerman(31) concluded that general adsorption rather than specific adsorption takes place on the metal surface. During adsorption studies with inhibitors in benzene solution it was found that both physical and chemical adsorption takes place, a pair of the inhibitor electrons being shared with the metal. In contrast to inorganic inhibitors, organic inhibitors do not undergo chemical changes during inhibition.

**EXPERIMENTAL**

Studies in polarization of cathode and anode are of great assistance in understanding the mechanism of corrosion and inhibition. It may give information regarding polarization characteristic of the corroding metals. The steady state potential of the specimen is measured against a saturated calomel electrode, this being a potential of the corroding metal in the absence of an external source of emf. The potential of the corroding
metal is made up of the potential of its cathodic and anodic areas. The passage of the current may lead to polarization which is due to slowing down of the processes at the cathode and/or the anode. The shift of the potential towards more positive (or less negative) value may indicate cathode polarization; while shift towards more negative (less positive) value may indicate anode polarization. However, interpretation of the results are rather difficult and it is more useful to measure the current density when the corroding metal is made, the anode or the cathode, when external emf is applied.

Fig. 2 on page 31A represents the system for measuring the potential of the corroding metal and Fig. 3 on page 31A represents the system to measure the shift in the potential when the corroding metal is made the cathode, the arrangement when the corroding metal is made the anode will be of similar type. The stainless steel (type 304) coupon had an effective area of 4 sq. cm (size 2x2 cm), the length of the handle being 4 cm. The handle as well as the back of the coupons was coated with purpex and wax. Polarization studies were made with the stainless steel coupon as cathode or anode, the other electrode being of platinum of the same dimensions. Back and handle of this electrode was also coated with purpex and wax.
**Fig. 2.**

Apparatus for Measuring Corrosion Potentials

**Fig. 3.**

Arrangement of Apparatus for Cathode Polarisation Measurement.
The galvanostatic studies of corrosion of stainless steel were made with and without the inhibitor in 100 ml corning beaker containing corrosive medium. The external current was supplied from a storage battery (90 v, Eveready Battery No. 701) and the change in potential was noted by making the coupon either anode or cathode on a D.C. microvolt meter (Philips India GM 6021) against a saturated calomel electrode. Attempt was made to minimize liquid junction potential by keeping the tip of the salt bridge very near to the metal surface. The specifications regarding experimental conditions were as under:

1. Electrolytes: 2.5, 5.0 and 7.5M hydrochloric acid and 1.25, 2.5 and 3.75M sulphuric acid.
2. Temperature: Room temperature ($30\pm 2^\circ$, constant for the experiment).
3. Concentration of inhibitors used was one which gave maximum protection.

The results of (i) change of potential with or without inhibitor in HCl solutions are given in Tables 2.1 to 2.21 on pages 207 to 227 and for sulphuric acid solutions in Tables 5.1 to 5.15 on pages 242 to 256 (ii) Galvanostatic
measurements for HCl solutions are given in Tables 3.1 to 3.3 on pages 283 to 312.
and for H₂SO₄ solutions in Tables 6.1 to 6.21 on pages 319 to 339.

4. When no current is passed, the potential registered fluctuated almost continuously.
The fluctuations, however, slowed down with time and the potential was taken as steady after 20 minutes. The current density in the galvanostatic experiments was varied from 2.5 × 10⁻⁵ to 25 × 10⁻⁴ Amp/cm².
REFERENCES


