

CORROSION INHIBITION OF ALPHA BRASS BY 1-PHENYL-3-METHYL-PYRAZOL-5-ONE IN ACIDIC MEDIA AT DIFFERENT TEMPERATURES

F. H. TOBINS, N. C. OFORKA and R. C. ELUAGU

(Received 5 April 2001; Revision accepted 29 August 2002)

ABSTRACT

Corrosion inhibition of alpha – brass (70% Cu/30% Zn) by 1 – phenyl –3 – methyl – pyrazol –5- one (HPMP) in different acidic media using the weight loss method at room temperature, 40°C, 50°C and 60°C has been investigated. At room temperature, maximum weight losses of about 0.1454g, 2.7396g and 0.0517g in HCl, HNO₃ and HClO₄ respectively were recorded without the inhibitor. However, weight losses of 0.0265g, 0.0212g and 0.0089g in HCl, HNO₃ and HClO₄ respectively were recorded when the inhibitor was used at room temperature. At higher temperatures higher weight losses were recorded even when higher concentrations of the inhibitor were used. The results obtained showed that HPMP is an effective inhibitor of alpha brass in these media. The corrosion inhibition efficiency (C.I.E.) of the alpha brass was 99.83%, using the condition of 3.0M HNO₃ for the uninhibited experiment and 0.03M HPMP for the inhibited experiment at 29°C after the 7th day, and the rate constant (K) was $4.03 \times 10^{-6}(\text{s}^{-1})$.

KEYWORDS: Corrosion inhibition, Acidic Media, Alpha Brass, inhibition efficiency, Rate constants.

INTRODUCTION

Copper/zinc alloys are important engineering materials because of their ease of working, range of mechanical properties and good corrosion resistance. Initially, zinc dissolves in copper to form the α - solid solution, thus strengthening the copper. The α solid solution has an f.c.c. structure and is soft and ductile, thus making it suitable for cold working. An interesting feature is that the ductility of the alloys increases with zinc content up to a maximum value at 30% zinc. The ductility then decreases with further addition of zinc until at 38% zinc, the limit of the α phase (Davies and Oelmann, 1983).

Corrosion control involves stopping the electrochemical reaction or at least slowing down the rate of the reaction. Chemical inhibition is one of the numerous measures taken to control corrosion. Dinnappa and Mayanna (1982) studied the dezincification of brass and its inhibition in acidic chloride and sulphate solution. They used weight loss and polarisation measurement in the presence of various surface-active compounds such as haloacetic acid, thio compounds and amines and found that the corrosion was controlled significantly by the concentrations of SO₄²⁻ and Cl⁻ ions present in dilute HNO₃. It has been found also that the mechanism of metallic surface (brass) inhibition using the inhibitor

LAN-5 for nitric acid pickling solution involves formation of adsorption–condensation polymer film from the three components of LAN-5 (Shikai and Yufen, 1994).

Phenothiazines as corrosion inhibitors for zinc in NH₄Cl solution has been investigated also (Abdel. Aal et al; 1994). From this study, it has been found that all the investigated compounds are inhibitors of a mixed type and inhibition occurs by a simple blocking of the electrode surface through chemisorption. Work on halogen substituted acetic acid as corrosion inhibitors for copper (as in brass) in nitric acid has been carried out (Subbramanyan and Mayanna, 1994). A considerable decrease in the corrosion rate was observed in the inhibited miconitrate (V) acid. It was concluded therefore that haloacetic acid acts as efficient cathodic inhibitors for copper in HNO₃. The corrosion inhibitive effects of amygdalina (bitter leaf) solution extract on the corrosion of mild steel test specimen immersed in 0.5M hydrochloric and tetraoxosulphate (VI) acids was investigated at ambient temperature of 28°C (Loto, 1998). The results obtained show that the solution extract of the leaves could serve as effective inhibitor only in the 0.5M HCl at 28°C which also has a high inhibitor efficiency. Ebenso (1998) also worked on the inhibition of aluminium (AA3105) corrosion in hydrochloric acid by acetamide and thiourea. For both inhibitors

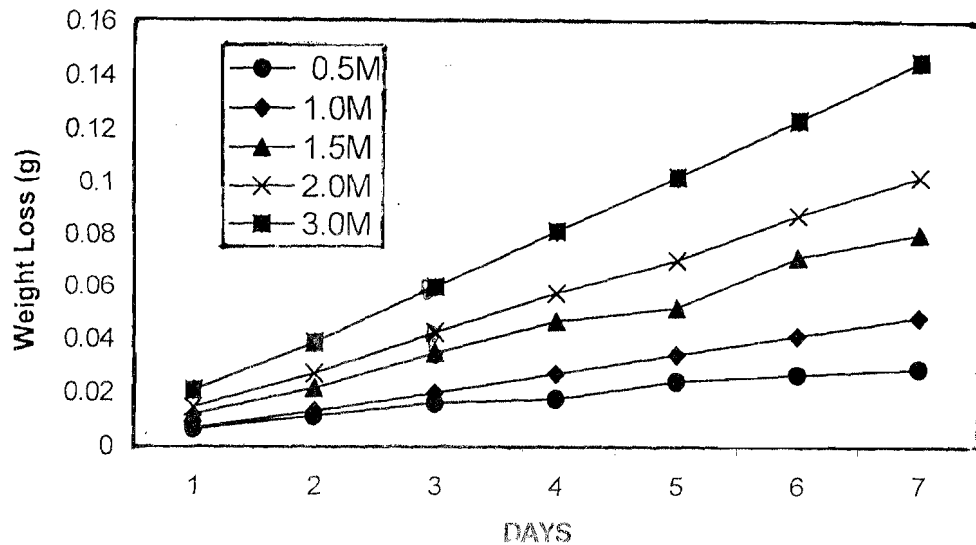


Figure 1: Corrosion of α -brass in HCl solutions without inhibitor at 29°C for seven days.

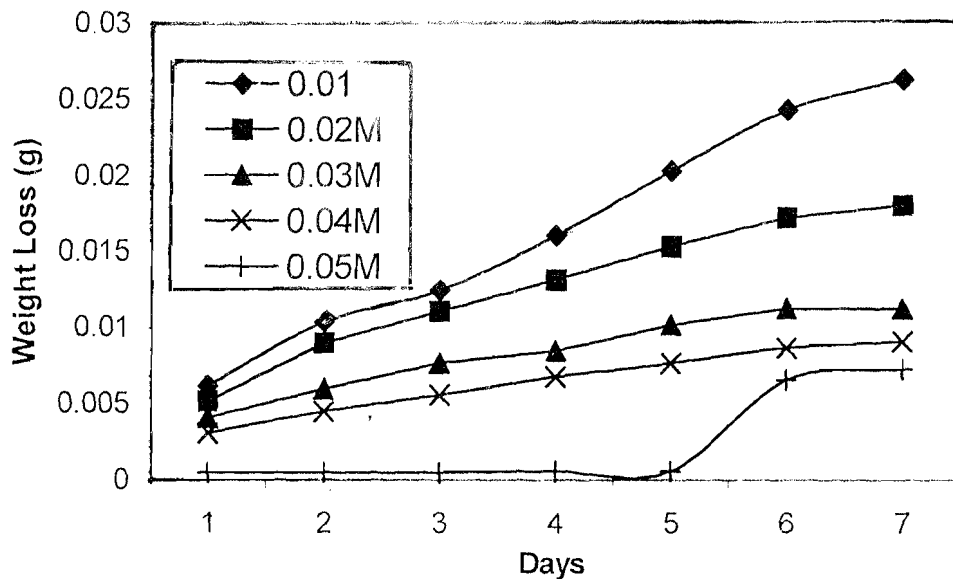


Figure 2: The inhibition of α -brass by HPMP in 3.0M HCl at 29°C.

studied, the inhibition efficiency decreases with increase in concentration and temperature.

Corrosion inhibition of alpha brass in HCl, HNO_3 and HClO_4 acids using HPMP has not been fully studied. The use of brass in the manufacture of propeller of ships, valves, bolts gauges, etc. makes it pertinent that brass should be protected from corrosion attack. In this present work the corrosion inhibition by 1- phenyl - 3 - methyl - pyrazole - 5 - one (HPMP) on alpha brass in HCl, HNO_3 and HClO_4 at 29°C, 40°C, 50°C and 60°C has been investigated.

MATERIALS AND METHOD

Square corrosion coupons of dimension

10mmX 10mm were cut out from alpha brass sheet of thickness 4mm. A hole of about 2.5mm in diameter was bored at the centre of each coupon. The surface of each coupon was cleaned chemically by immersing the entire coupons in 250ml of 10% HCl and left for 12 hours. Each coupon was then thoroughly rinsed in a stream of distilled water and allowed to dry for 30 minutes and then put in a dessicator to remove any trace of moisture. Five different concentrations 0.5M, 1.0M, 1.5M, 2.0M and 3.0M of each of the acids were prepared for this study. Also prepared were five different concentrations of 1- phenyl-3-Methyl - Pyrazol -5-one (HPMP), 0.01M, 0.02M, 0.03M, 0.04M and 0.05M using the three acids.

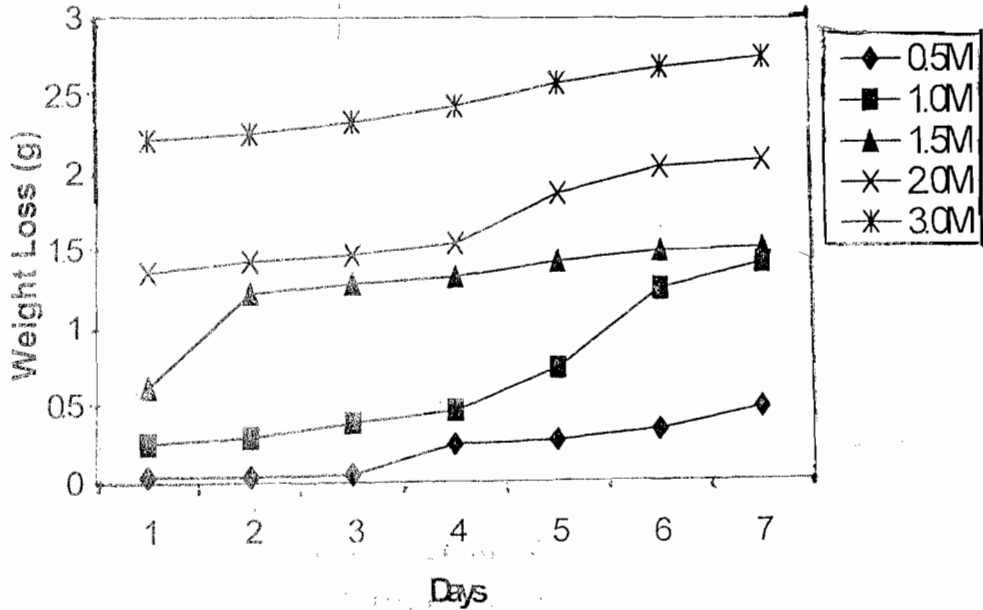


Figure 3: The corrosion of α -brass in HNO_3 solutions of varying molarity at 29°C .

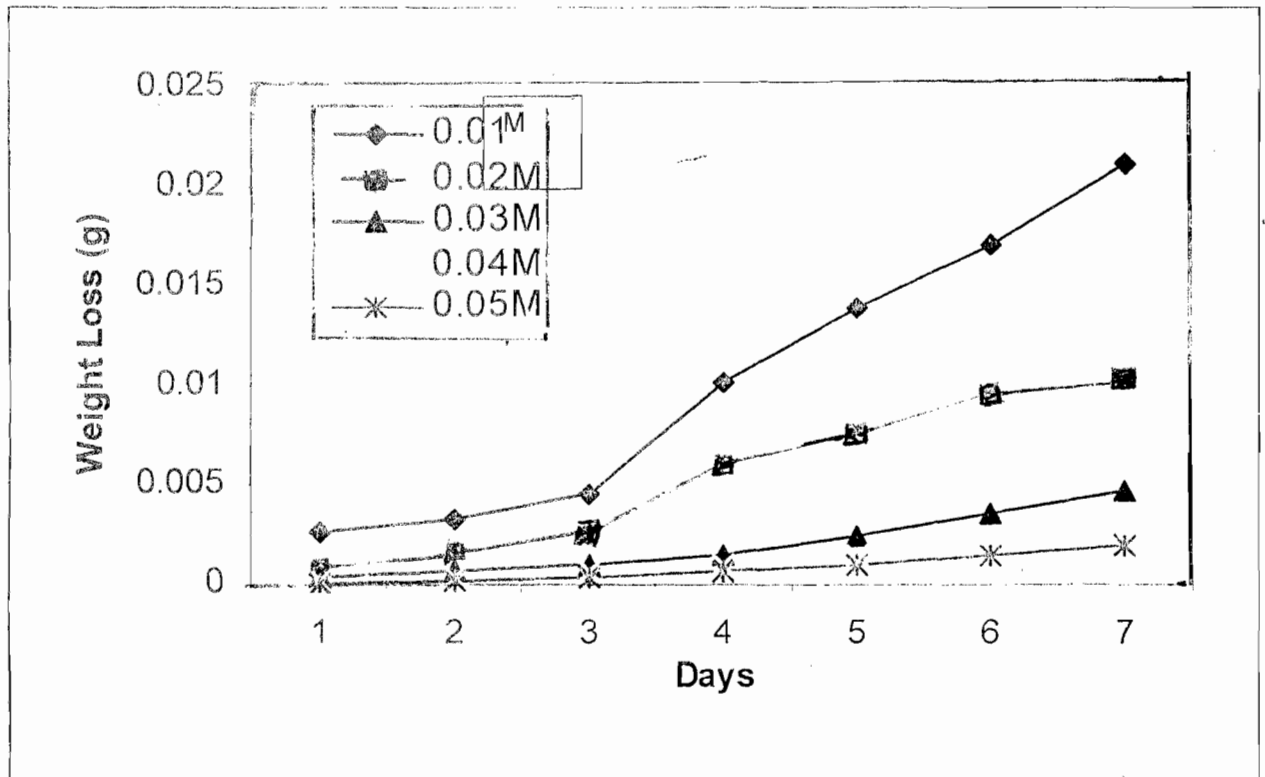


Figure 4: The inhibition of α -brass by HPMP in 3.0M HNO_3 at 29°C .

Weight loss method was used to carry out the tests at ambient temperature (29°C), 40°C , 50°C and 60°C with and without the inhibitor. All the tests without the inhibitor served as the control. The conditions of the experiments for each of the three acids were the same.

Thirty-five of the cleaned coupons were

taken from the dessicator and weighed to determine their initial weights. They were then all immersed in 20ml of the five different concentrations of the three acids, by means of plastic thread fastened through the holes, in a 30ml test tube for a period ranging from 1 day to 7 days. At the end of each day, five corrosive

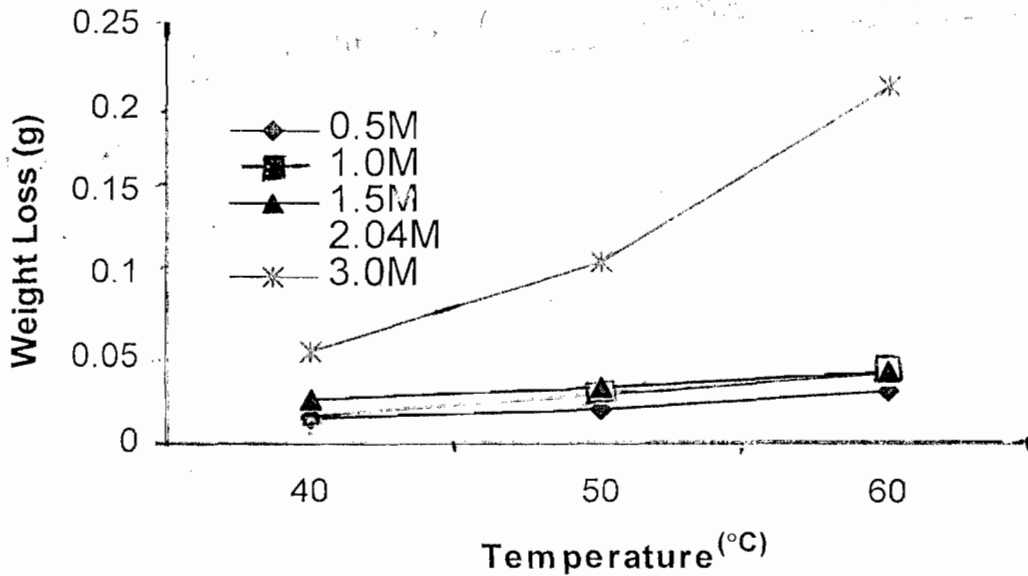


Figure 5: The corrosion of the α -brass in HCl solutions at 40°C, 50°C and 60°C.

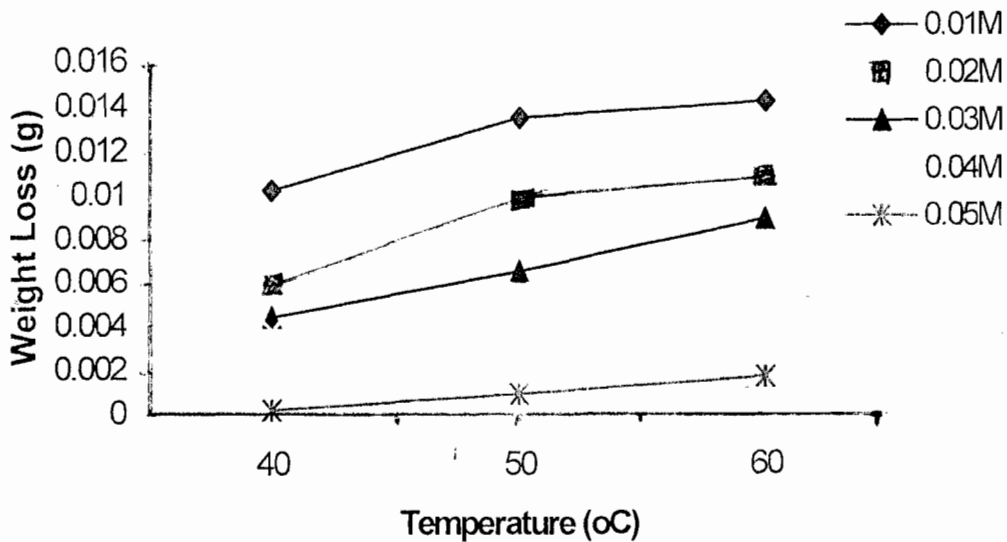


Fig. 6: The inhibition of α -brass by HPMP solutions in 3.0M HCl at the given temperatures

coupons corresponding to each of the five different concentrations were taken out, washed with 20% NaOH, rinsed with distilled water and allowed to dry in the dessicator. The coupons were, after drying to constant weight, weighed to determine the weight loss. This was repeated on daily basis for 7 days.

In the corrosion study of the alpha brass coupons with the additives at 29°C, the HPMP solutions prepared with the three acids were used instead of the pure acids. The experiments without the additive at 40°C, 50°C and 60°C were carried out with the aid of a temperature regulated water bath and monitored at intervals of 1 hr for a period of 7 hours. Mathematical calculations of corrosion inhibition efficiencies (C.I.E.) and rate

constants (K) from the experimental results were also carried out.

RESULTS AND DISCUSSION

Figure 1 shows the results of corrosion of the brass in HCl solutions without the inhibitor at 29°C for seven days. It can be seen that the greatest weight loss of about 0.1454g was obtained with 3.0M HCl on the seventh day, while the least weight loss of about 0.005g was obtained with 0.5M HCl on the first day.

On the other hand, Figure 2 shows the inhibition of the α -brass by HPMP in 3.0M HCl solution at 29°C. It can be seen that on the seventh day, the

highest weight loss of 0.0265g was obtained with 0.01M HPMP and the least weight loss of 0.0073g with 0.05M HPMP, showing a drastic decrease in weight loss when compared with the results of the control experiment.

The weight loss decreased with increase in HPMP (additive) concentration.

Figure 3 shows the result of corrosion of the alpha brass in HNO_3 solutions at 29°C . Weight losses of 0.0121g and 0.496g were recorded with 0.5M HNO_3 on the first day and the seventh day respectively.

For 3.0M of HNO_3 , weight losses of 2.22g and 2.74g were obtained on the first day and on the seventh day respectively. With the inhibitor

however, Figure 4 shows the plots for a concentration of 3.0M HNO_3 , with additives. With 0.01M HPMP weight losses of 0.0026g and 0.0212g were recorded on the first and seventh days. There was zero weight loss on the first day with 0.05M HPMP and only about 0.002g weight loss on the seventh day. It can be seen that the higher the concentration of the HPMP the lesser the weight loss in the corrosive media.

Figure 5 shows the corrosion of the α -brass in HCl solutions at 40°C , 50°C and 60°C on the seventh day. The weight loss is seen to increase with temperature rise. With 3.0 M of HCl for example there was a weight loss of about 0.05g at 40°C and 0.21g at 60°C . But with the HPMP solutions in 3M HCl (Figure 6), for 0.01M HPMP

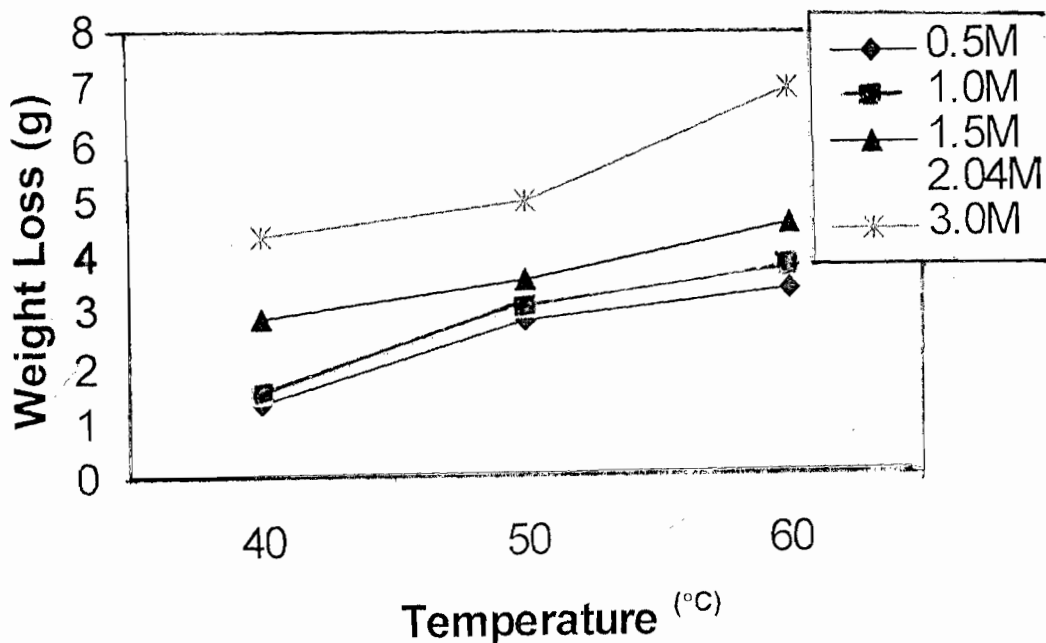


Figure 7: The corrosion of α -brass in HNO_3 solutions at given temperatures without the HPMP.

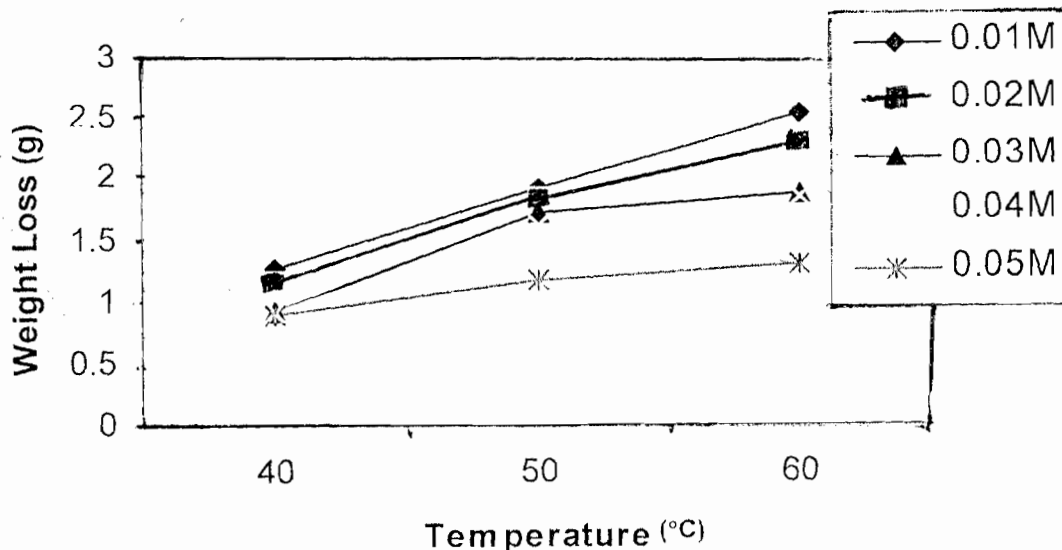


Figure 8: The inhibition of α -brass in 3.0M HNO_3 by HPMP at the given temperatures

the weight loss was 0.01g at 40°C and 0.014g at 60°C. On the other hand, with 0.05M of HPMP at 40°C, the weight loss obtained was 0.0002g and about 0.0017g at 60°C. Even in the presence of inhibitors at all concentrations, the weight loss is still noted to increase with increase in temperature.

Figure 7 shows the corrosion of α -brass in HNO_3 solutions at 40°C, 50°C and 60°C on the seventh day without the inhibitor. The weight losses are quite high at the different temperatures, increasing with HNO_3 concentrations and temperature as opposed to the case with the inhibitor. With 0.5M of HNO_3 , for instance, the weight loss was 1.32g at 40°C and 3.345 at 60°C. At 40°C and 60°C, the weight losses were 4.34g and 6.48g respectively with 3.0M of HNO_3 .

However, with the inhibitor in 3.0M HNO_3 at the same temperatures the weight losses were drastically reduced as depicted by Figure 8. At 40°C for example, the weight loss was 1.269g with 0.01M of HPMP and 2.53g at 60°C. With 0.05M of the inhibitor at 40°C the weight loss was about 0.9g and 1.29g at 60°C.

On the other hand, corrosion of α -brass in HClO_4 solutions at 40°C 50°C and 60°C on the 7th day is shown in Figure 9. From the plot, it can be seen that 0.5M of HClO_4 gave a weight loss of 0.10g at 40°C and about 0.2g at 60°C. 3.0M of HClO_4 at 40°C gave a weight loss of 0.27g and at 60°C it was about 0.37g. But with the introduction of the HPMP under the same conditions the weight losses were reduced as can be seen in Figure 10. For instance from the plot, 0.01M of

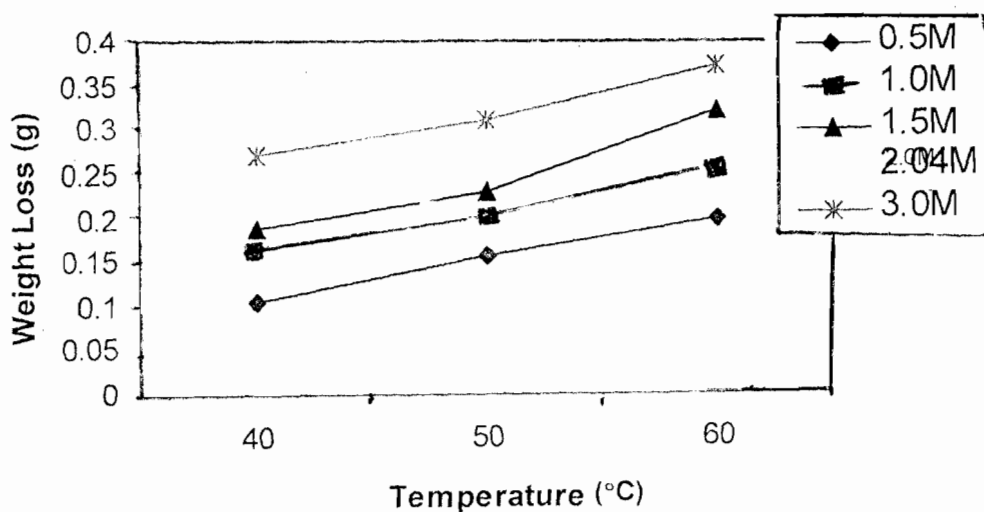


Figure 9: Corrosion of α -brass in HClO_4 solutions at the given temperatures without HPMP on the 7th day.

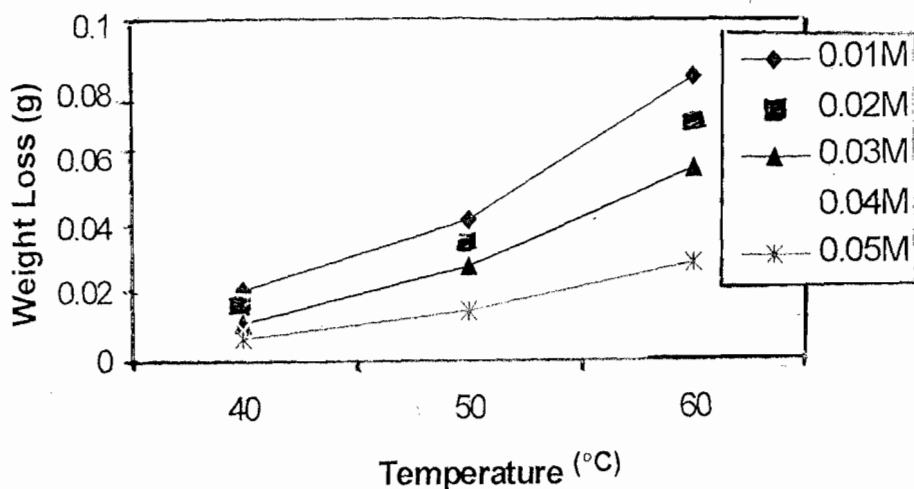


Figure 10: The inhibition of α -brass in HClO_4 by HPMP solutions at the given temperatures

HPMP (the inhibitor) at 40°C the weight loss was only 0.02g while at 60°C it was about 0.08g. With increase in the concentration of the HPMP, the weight losses were further reduced. With 0.05M of HPMP at 40°C, 0.007g weight loss was obtained, while at 60°C it was about 0.029g.

In general therefore, a comparison of the weight loss for the inhibitory and non-inhibitory (uninhibitory) studies of alpha brass in acidic media showed that a marked reduction in weight loss was achieved when the HPMP solutions were used. Weight loss was highest with HPMP in HNO₃ solutions and lowest with HPMP in HCl solutions showing that HNO₃ is the strongest while HCl is the weakest of the three acids used. The presence of the inhibitor minimized the corrosion of alpha brass coupons, however, there was a general increase in weight loss of the alpha brass coupons with increase in temperature. This can be attributed to the fact that the rate of a chemical reaction increases with increasing temperature in most cases. The corrosion inhibition efficiency, (C.I.E.) were calculated using the expression (Abdu.Aal et al, 1994)

$$\text{C.I.E.} = \%E = \frac{W_u - W_i}{W_u}$$

Where W_u = Weight loss of uninhibited medium

W_i = Weight loss of inhibited medium

%E = Percentage efficiency.

Also calculated were their rate constants at the same conditions using the following expression (Dinnappa and Mayanna, 1994).

$$K = \frac{1}{t} \ln \frac{W_i}{W_f}$$

Where W_i = Initial weight of α -brass coupon

W_f = Final weight of α -brass coupon

With HNO₃ acid using the conditions of 0.3M HNO₃ for the uninhibited experiment and 0.03M HPMP for the inhibited experiment at 29°C after the 7th day, it was found out that, C.I.E. = 99.83% and the rate constant (K) = $4.03 \times 10^{-6} (5^{-1})$

CONCLUSION

From the discussions, it can be concluded that HPMP is an effective corrosion inhibitor for alpha brass since it was able to retard the rate of dissolution of alpha brass coupons (i.e. minimize the weight loss) in acidic (corrosive) media in which it was used. The efficiency of the inhibitor (HPMP) is better at higher concentrations of the inhibitor and at low temperatures.

This inhibitor may be profitably applied in the manufacture of industrial coatings especially for corrosion prevention of ship propellers, pipeline valves, bolts, nuts and tanks (those made of brass) in areas where the temperature should not exceed 30°C. However, investigations should be extended to higher temperatures and higher concentrations of the inhibitor (HPMP), to assess its good inhibiting activities.

REFERENCES

- Abdel Aal, M.S., Radwan, S. and Elsaied, A., 1994. Phenothiazines as corrosion inhibition for zinc in NH₄Cl solution National Association of Corrosion Engineers (NACE) Journal on corrosion inhibition. Pp 120-122.
- Davies, D. J. and Oelmann, L.A., 1983. The structure, properties and Heat Treatment of metals. Pitman Press, London.
- Dinnappa, R.K. and Mayanna, S.M., 1994. Dezincification of Brass and its inhibition in acidic chloride and sulphate solutions, NACE Journal on Corrosion inhibition. Pp. 14-19.
- Ebenso, E. E., 1998. Inhibition of aluminium (AA3105) Corrosion in hydrochloric acid by acetamide and thiourea. Nigerian Corrosion Journal (NCJ). pp 29-44.
- Loto, C. A., 1998. The effect of venonia amygdalina (Bitter Leaf) solution extract on the corrosion inhibition of mild steel in 0.5M HCl and H₂SO₄ acids. Nigerian Corrosion Journal (NCJ). Pp. 19-28.
- Shikai, N. and Yufen, L., 1994. A nitric acid pickling inhibitor and preliminary investigations into the inhibition mechanism. NACE Journal on Corrosion inhibition. Pp 48-52.
- Subramanyan, N.C. and Mayomna, S.M. (1994), Halogen-substituted acetic acids as corrosion inhibitors for copper in nitric acid. NACE Journal on corrosion inhibition. Pp 144-148.