As a preliminary conclusion we can say that two different factors are responsible for changes in the oxidation potential. The electronic nature of the substituents affects mainly the first oxidation potential. The second oxidation potential is much less sensitive to variation of the electronic nature of the substituent. Furthermore a steric effect is operative. The steric interaction between the *meso-* and β-substituents affects the first and the second oxidation potential significantly. The rate constant of the first electron transfer is mainly controlled by the electronic nature of the substituent and not by steric interaction between the substituents.

**Acknowledgements**: Thanks are due to the JNICT-INIDA program and to DAAD, to IBM-Deutschland GmbH, to Siemens AG and to the Fonds der Chemischen Industrie for funding this work.

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# Mechanism of Corrosion Inhibition of Ni and Ni-Mo-Fe Alloy in Dilute Nitric Acid by some Azole Compounds

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## Abstract

Inhibition of corrosion of nickel and nickel base (Ni-Mo-Fe) alloy in 4 percent nitric acid has been studied in the presence of some azole compounds, using electrochemical polarization technique, at various concentrations of inhibitors and at different temperatures (25, 35, 45°C). All the inhibitors investigated were able to suppress both the anodic and cathodic processes appreciably for both the systems. However, in each case the inhibition afforded by these molecules towards the corrosion of nickel in nitric acid is always greater than those for nickel base alloy-nitric acid system. Among these inhibitors, 2-mercaptobenzothiazole was found to be the most effective inhibitor for both the systems. These inhibitor molecules, though structurally similar do not follow the same mechanism of inhibition. Either of the two mechanisms, viz., adsorption or surface complex formation or sometimes both of these have been found valid for individual inhibitors.

## Introduction

Pure nickel is rarely used as a structural metal, but nickel plated metals and nickel base alloys are frequently used in certain manufacturing processes involving nitric acid as one of the reactants or products. Although, the mechanism of corrosion and inhibition of nickel and its alloys has been extensively studied in a variety of media (1-5), the studies pertaining to corrosion behaviour of nickel and nickel base alloys in nitric acid and their inhibition in presence of organic molecules are rare.

At a concentration less than 0.5 percent, aqueous solutions of nitric acid are highly corrosive towards nickel and nickel base alloys. The electrochemical behaviour of both, the metal and the alloy in 4 percent nitric acid, are similar except that the passivity exhibited by the alloy is not very distinct. Ni-Mo-Fe alloy dissolves much faster than pure Ni in dilute nitric acid. No attempt has been made to control the corrosion rate of these materials in nitric acid by any means. Inhibitors can be used conveniently for the present systems. A number of organic compounds have been found to inhibit corrosion of Ni and alloys in other environments. Thus, it is interesting to investigate into the probable applicability of some such compounds for the present systems, as well.

In this paper, the influence of some azole compounds on the corrosion behaviour of nickel and Ni-Mo-Fe alloy in 4% nitric acid solution at temperatures 25, 35 and 45°C have been reported and an attempt has been made to elucidate the mechanism of inhibition.

## Experimental

Nickel (100%) and Ni-Mo-Fe (61.41-26.37-7.21%) sheets were used for the preparation of test electrodes. The size of the electrode was 1x1 cm with a 4 cm long tag, partially coated with paraffin wax. The sheets were mechanically polished with different grades (0/0 to 4/0) of emery paper to achieve a mirror like surface. Platinum foil of size 2x2 cm and a Luggin type saturated calomel electrode were used as counter and reference electrodes respectively. BDH Analar grade, nitric acid was used for the preparation of the test solutions. The inhibitors used were of AR grade (E. Merck).

The polarization experiments were carried out using a Wenking potentioscan (Model POS 73) with 4 percent nitric acid solution at 25, 35 and 45°C. The concentration of nitric acid chosen for the present study refers to that concentration in which the corrosion rate is maximum. The temperature was thermostatically controlled within the limit ±0.2°C. The concentrations of inhibitors taken for determination of the inhibition efficiencies were 50, 100, 150, 200 and 250 ppm. Initially, the open circuit potential was recorded after it attained a constant value. The specimen was then cathodically polarised at a fixed interval upto -350 mV with respect to the measured open circuit potential. The polarisation currents were noted after the specimens were stabilised for about 1 min at each potential. The specimen was then kept under open circuit condition for 30-60 min until a steady open circuit potential was again obtained and there after the anodic polarisation experiment was performed. The experiments were repeated three times and the mean value of current density was plotted against applied potential.

## Results and Discussion

Potentiostatic polarization experiments were performed to determine the corrosion behaviour of nickel and its alloy in presence of different concentrations of azole compounds at temperatures 25, 35 and 45°C. Figs. 1 and 2 represent the anodic polarization behaviour of nickel and Ni-Mo-Fe alloy in 4% nitric acid containing 50, 100, 150, 200 and 250 ppm of 2-mercaptobenzothiazole respectively. It is observed that in case of nickel, the active-passive nature of the curve is not affected by the presence of the inhibitor at its different concentrations. However, a transition in the behaviour of the curve from almost active to a curve which resembles active-passive behaviour on the addition of the

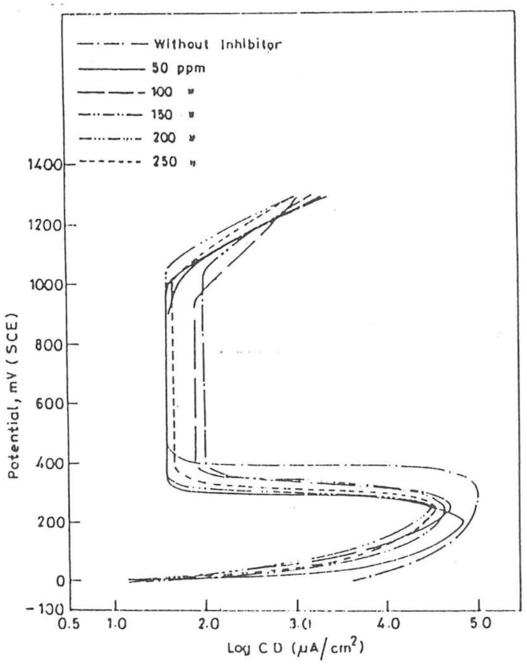

FIG. 1 ANODIC POLARIZATION CURVES OF NICKEL WITH DIFFERENT CONCENTRATIONS OF 2-MERCAPTOBENZOTHIAZOLE AT TEMPERATURE 25°C

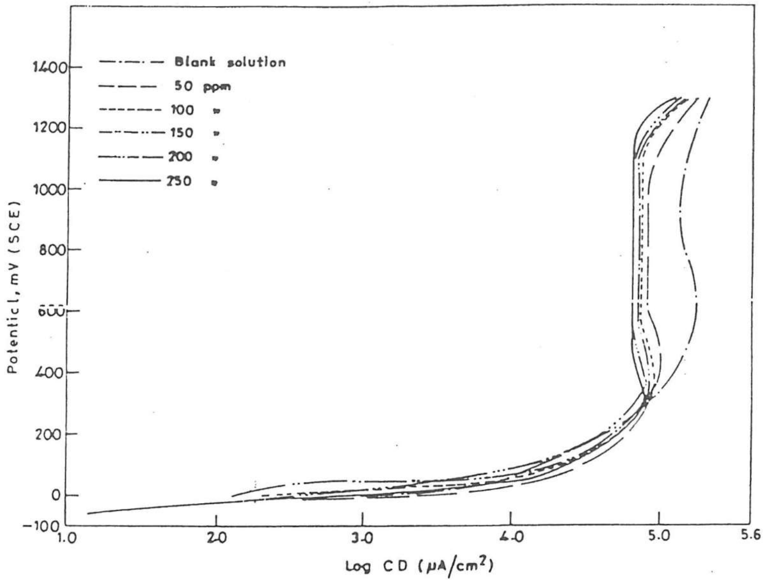

FIG. 2 ANODIC POLARIZATION CURVES OF Ni-Mo-Fe ALLOY IN PRESENCE OF DIFFERENT CONCENTRATIONS OF 2- MERCAPTOBENZOTHIAZOLE AT TEMPERATURE 35°C

inhibitor to nitric acid is observed for Ni-Mo-Fe/nitric acid system. The curves in the absence of the inhibitor show a slight tendency for passivation with large passivation current ($i_p$). With the addition and subsequent increase in the concentration of the inhibitor the active-passive behaviour becomes distinct and the $i_c$ values become smaller as the curves are shifted towards lower current density region. The magnitude of the shift in current density for both the systems were found to be a function of the concentration of the inhibitor.

The nature of the anodic polarisation curves (apc) observed for other inhibitors shows a similar trend of variation with increasing inhibitor concentration and hence to avoid duplication these are not being shown. It is clear from the above observation that the additive molecules retard the corrosion process, by affecting the anodic reaction. The anodic parameters like E, $i_c$, $i_c/i_{co}$ and passive potential range for all the inhibitors at their different concentrations and the three temperatures are summarized in Tables 1-3 and 4-6 for nickel and Ni-Mo-Fe alloy at 25, 35 and 45°C respectively. It is clear from the data in the table that i and $i_c/i_{co}$ values decreases with increase in concentration of inhibitors and the passive potential range increases.

**Table 1** : Corrosion parameters from anodic polarization curves of nickel in different concentrations of inhibitors at 25°C.

| Inhibitors and concentrations (ppm) | $E_{pp}$ (mV) | $i_c$ (mA/cm$^2$) | $i_c/i_{co}$ | $E_b$ (MV) | Percentage efficiency |
|---|---|---|---|---|---|
| Blank solution | 300 | 100 | - | 900 | - |
| 2-Mercaptobenzothiazole | | | | | |
| 50 | 200 | 90.0 | 0.90 | 1000 | 80.95 |
| 100 | 250 | 54.0 | 0.54 | 900 | 84.92 |
| 150 | 230 | 46.0 | 0.46 | 1050 | 90.47 |
| 200 | 210 | 34.0 | 0.34 | 1050 | 93.52 |
| 250 | 230 | 40.0 | 0.40 | 1000 | 92.50 |
| Benzotriazole | | | | | |
| 50 | 240 | 38.0 | 0.38 | 1000 | 76.19 |
| 100 | 240 | 28.0 | 0.28 | 950 | 84.92 |
| 150 | 220 | 25.0 | 0.25 | 950 | 87.30 |
| 200 | 210 | 23.0 | 0.23 | 1000 | 90.65 |
| 250 | 200 | 26.0 | 0.26 | 1000 | 91.26 |
| Sulphathiazole | | | | | |
| 50 | 250 | 48.0 | 0.48 | 950 | 63.35 |
| 100 | 250 | 45.0 | 0.45 | 1000 | 68.25 |
| 150 | 220 | 43.0 | 0.43 | 950 | 73.01 |
| 200 | 200 | 39.0 | 0.39 | 1000 | 80.95 |
| 250 | 200 | 35.0 | 0.35 | 1000 | 82.53 |
| Benzimidazole | | | | | |
| 50 | 220 | 35.0 | 0.35 | 950 | 60.32 |
| 100 | 200 | 31.0 | 0.31 | 900 | 65.07 |
| 150 | 150 | 28.0 | 0.28 | 900 | 68.25 |
| 200 | 150 | 26.0 | 0.26 | 1000 | 71.42 |
| 250 | 150 | 23.0 | 0.23 | 1000 | 76.19 |
| Tinidazole | | | | | |
| 50 | 200 | 40.0 | 0.40 | 900 | 44.44 |
| 100 | 180 | 34.0 | 0.34 | 900 | 55.55 |
| 150 | 150 | 24.0 | 0.24 | 950 | 63.35 |
| 200 | 150 | 22.0 | 0.22 | 1000 | 68.25 |
| 250 | 190 | 20.0 | 0.20 | 1000 | 74.71 |

**Table 2:** Corrosion parameters from anodic polarization curves of nickel in different concentrations of inhibitors at 35°C.

| Inhibitors and concentrations (ppm) | $E_{pp}$ (mV) | $i_c$ (mA/cm$^2$) | $i_c/i_{co}$ | $E_b$ (mV) | Percentage efficiency |
|---|---|---|---|---|---|
| Blank solution | 350 | 169.82 | - | 750 | - |
| 2-Mercaptobenzothiazole | | | | | |
| 50 | 250 | 125.0 | 0.74 | 900 | 81.25 |
| 100 | 220 | 120.0 | 0.70 | 1000 | 86.25 |
| 150 | 210 | 100.0 | 0.59 | 1150 | 88.75 |
| 200 | 200 | 85.0 | 0.50 | 1150 | 95.23 |
| 250 | 200 | 95.0 | 0.55 | 1100 | 93.12 |
| Benzotriazole | | | | | |
| 50 | 250 | 64.0 | 0.38 | 950 | 88.75 |
| 100 | 230 | 58.0 | 0.34 | 950 | 91.25 |
| 150 | 250 | 54.0 | 0.29 | 1000 | 92.12 |
| 200 | 200 | 46.0 | 0.26 | 1000 | 93.37 |
| 250 | 200 | 55.0 | 0.32 | 1000 | 88.12 |
| Sulphathiazole | | | | | |
| 50 | 300 | 81.0 | 0.50 | 1000 | 68.75 |
| 100 | 300 | 80.0 | 0.47 | 1050 | 71.87 |
| 150 | 270 | 71.0 | 0.42 | 1100 | 78.12 |
| 200 | 250 | 65.0 | 0.38 | 1100 | 81.25 |
| 250 | 250 | 63.0 | 0.37 | 1100 | 85.62 |
| Benzimidazole | | | | | |
| 50 | 250 | 115.0 | 0.67 | 900 | 68.75 |
| 100 | 250 | 110.0 | 0.65 | 900 | 71.87 |
| 150 | 230 | 98.0 | 0.58 | 850 | 75.00 |
| 200 | 200 | 94.0 | 0.55 | 900 | 80.00 |
| 250 | 200 | 90.0 | 0.54 | 900 | 83.75 |
| Timidazole | | | | | |
| 50 | 220 | 121.0 | 0.71 | 950 | 68.75 |
| 100 | 220 | 100.0 | 0.59 | 950 | 74.00 |
| 150 | 200 | 84.0 | 0.49 | 1000 | 77.00 |
| 200 | 200 | 80.0 | 0.47 | 1000 | 84.37 |
| 250 | 200 | 78.0 | 0.46 | 950 | 85.50 |

**Table 3:** Corrosion parameters from anodic polarization curves of nickel in different concentrations of inhibitors at 45°C.

| Inhibitors and concentrations (ppm) | $E_{pp}$ (mV) | $i_c$ (mA/cm$^2$) | $i_c/i_{co}$ | $E_b$ (mV) | Percentage efficiency |
|---|---|---|---|---|---|
| Blank solution | 400 | 580 | - | 750 | - |
| 2-Mercaptobenzothiazole | | | | | |
| 50 | 300 | 110.0 | 0.19 | 800 | 85.00 |
| 100 | 300 | 88.0 | 0.15 | 800 | 87.50 |
| 150 | 280 | 60.0 | 0.10 | 850 | 91.00 |
| 200 | 250 | 55.0 | 0.094 | 850 | 97.50 |
| 250 | 300 | 65.0 | 0.11 | 850 | 95.00 |
| Benzotriazole | | | | | |
| 50 | 300 | 122.0 | 0.21 | 800 | 91.50 |
| 100 | 250 | 100.0 | 0.17 | 850 | 93.50 |
| 150 | 220 | 84.0 | 0.14 | 900 | 95.00 |
| 200 | 150 | 54.0 | 0.09 | 900 | 95.00 |
| 250 | 200 | 68.0 | 0.12 | 950 | 92.00 |
| Sulphathiazole | | | | | |
| 50 | 300 | 120.0 | 0.21 | 950 | 71.50 |
| 100 | 300 | 112.0 | 0.19 | 950 | 75.00 |
| 150 | 280 | 98.0 | 0.17 | 1000 | 81.00 |
| 200 | 250 | 94.0 | 0.16 | 1000 | 85.50 |
| 250 | 250 | 90.0 | 0.15 | 1000 | 90.00 |
| Benzimidazole | | | | | |
| 50 | 300 | 130.0 | 0.22 | 950 | 70.00 |
| 100 | 250 | 122.0 | 0.21 | 900 | 75.00 |
| 150 | 230 | 115.0 | 0.20 | 950 | 77.50 |
| 200 | 200 | 105.0 | 0.18 | 950 | 82.50 |
| 250 | 220 | 100.0 | 0.17 | 950 | 86.00 |
| Tinidazole | | | | | |
| 50 | 300 | 175.0 | 0.30 | 850 | 71.00 |
| 100 | 300 | 166.0 | 0.29 | 850 | 76.00 |
| 150 | 280 | 150.0 | 0.26 | 900 | 80.50 |
| 200 | 250 | 140.0 | 0.24 | 900 | 82.00 |
| 250 | 250 | 120.0 | 0.20 | 900 | 85.00 |

**Table 4:** Corrosion parameters from anodic polarization curves of Ni-Mo-Fe alloys in different concentrations of inhibitors at 25°C.

| Inhibitors and concentrations (ppm) | $E_{pp}$ (mV) | $i_c$ (mA/cm$^2$) | $i_c/i_{co}$ | Passive potential range(mV) | Percentage efficiency |
|---|---|---|---|---|---|
| Blank solution | 650 | 141.25 | - | 700-850 | - |
| 2-Mercaptobenzothiazole | | | | | |
| 50 | 400 | 82.23 | 0.776 | 500-1050 | 45.41 |
| 100 | 350 | 75.62 | 0.713 | 500-1050 | 55.58 |
| 150 | 325 | 70.15 | 0.662 | 550-1050 | 68.38 |
| 200 | 325 | 67.00 | 0.632 | 550-1100 | 79.81 |
| 250 | 350 | 72.28 | 0.682 | 550-1100 | 77.77 |
| Benzotriazole | | | | | |
| 50 | 400 | 86.70 | 0.818 | 600-1050 | 41.80 |
| 100 | 375 | 80.23 | 0.075 | 550-1050 | 52.38 |
| 150 | 350 | 78.50 | 0.740 | 550-1100 | 62.14 |
| 200 | 350 | 72.28 | 0.682 | 550-1100 | 76.78 |
| 250 | 325 | 77.00 | 0.726 | 500-1050 | 71.45 |
| Sulphathiazole | | | | | |
| 50 | 400 | 92.00 | 0.868 | 500-1000 | 35.48 |
| 100 | 400 | 88.75 | 0.837 | 500-1000 | 48.60 |
| 150 | 375 | 84.08 | 0,793 | 550-1050 | 61.12 |
| 200 | 350 | 80.72 | 0.761 | 550-1050 | 71.20 |
| 250 | 350 | 78.75 | 0.743 | 550-1050 | 74.42 |
| Benzimidazole | | | | | |
| 50 | 450 | 94.00 | 0.887 | 550-1000 | 33.46 |
| 100 | 425 | 90.25 | 0.851 | 550-1000 | 46.64 |
| 150 | 400 | 85.75 | 0.809 | 500-1000 | 60.08 |
| 200 | 400 | 83.45 | 0.787 | 500-1050 | 68.38 |
| 250 | 400 | 82.65 | 0.774 | 500-1050 | 72.64 |
| Tinidazole | | | | | |
| 50 | 550 | 100.00 | 0.940 | 550-950 | 27.28 |
| 100 | 525 | 95.00 | 0.896 | 550-1000 | 36.80 |
| 150 | 500 | 92.00 | 0.868 | 550-1000 | 43.21 |
| 200 | 500 | 90.00 | 0.849 | 550-1000 | 58.51 |
| 250 | 525 | 88.00 | 0.830 | 500-1000 | 64.90 |

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**Table 5:** Corrosion parameters from anodic polarization curves of Ni-Mo-Fe alloys in different concentrations of inhibitors at 35°C

| Inhibitors and concentrations (ppm) | $E_{pp}$ (mV) | $i_c$ (mA/cm$^2$) | $i_c/i_{co}$ | Passive potential range(mV) | Percentage efficiency |
|---|---|---|---|---|---|
| Blank solution | 700 | 180.0 | - | - | - |
| 2-Mercaptobenzothiazole | | | | | |
| 50 | 400 | 98.0 | 0.583 | 600-1000 | 55.33 |
| 100 | 350 | 92.0 | 0.547 | 550-1100 | 74.88 |
| 150 | 350 | 87.0 | 0.518 | 550-1150 | 80.04 |
| 200 | 300 | 80.0 | 0.476 | 500-1150 | 84.15 |
| 250 | 350 | 83.0 | 0.494 | 550-1100 | 82.20 |
| Benzotriazole | | | | | |
| 50 | 500 | 110.0 | 0.655 | 700-1000 | 49.88 |
| 100 | 475 | 100.0 | 0.595 | 700-1000 | 68.37 |
| 150 | 450 | 90.0 | 0.536 | 650-1050 | 74.88 |
| 200 | 450 | 82.0 | 0.488 | 650-1100 | 82.20 |
| 250 | 480 | 850 | 0.506 | 650-1050 | 80.20 |
| Sulphathiazole | | | | | |
| 50 | 550 | 115.20 | 0.686 | 650-1000 | 44.72 |
| 100 | 500 | 107.0 | 0.637 | 650-1050 | 62.00 |
| 150 | 500 | 92.0 | 0.548 | 600-1000 | 68.75 |
| 200 | 450 | 84.0 | 0.500 | 600-1100 | 76.00 |
| 250 | 400 | 80.0 | 0.476 | 600-1100 | 81.78 |
| Benzimidazole | | | | | |
| 50 | 500 | 125.21 | 0.745 | 650-1000 | 43.77 |
| 100 | 480 | 110.0 | 0.655 | 600-1000 | 60.19 |
| 150 | 450 | 95.0 | 0.565 | 650-1050 | 68.37 |
| 200 | 400 | 85.0 | 0.506 | 600-1100 | 74.88 |
| 250 | 350 | 80.0 | 0.476 | 600-1100 | 80.04 |
| Tinidazole | | | | | |
| 50 | 450 | 135.23 | 0.805 | 650-1000 | 36.91 |
| 100 | 400 | 126.00 | 0.750 | 550-1050 | 49.88 |
| 150 | 400 | 105.00 | 0.625 | 550-1050 | 60.19 |
| 200 | 350 | 95.0 | 0.505 | 550-1100 | 71.81 |
| 250 | 350 | 90.0 | 0.536 | 500-1000 | 77.61 |

Table 6 : Corrosion parameters from anodic polarisation curves of Ni-Mo-Fe alloys in different concentrations of inhibitors at 45°C.

| Inhibitors and concentrations (ppm) | $E_{pp}$ (mV) | $i_c$ (mA/cm$^2$) | $i_c/i_{co}$ | Positive potential range(mV) | Percentage efficiency |
|---|---|---|---|---|---|
| Blank solution | 950 | 200.0 | - | - | - |
| 2-Mercaptobenzothiazole | | | | | |
| 50 | 400 | 121.25 | 0.652 | 550-1000 | 74.88 |
| 100 | 360 | 110.6 | 0.591 | 550-1050 | 79.19 |
| 150 | 350 | 104.0 | 0.559 | 500-1050 | 84.29 |
| 200 | 325 | 90.0 | 0.484 | 500-1100 | 88.67 |
| 250 | 335 | 96.0 | 0.516 | 550-1100 | 87.74 |
| Benzotriazole | | | | | |
| 50 | 400 | 130.0 | 0.699 | 600-1000 | 72.30 |
| 100 | 375 | 125.0 | 0.672 | 500-1050 | 76.71 |
| 150 | 375 | 110.0 | 0.591 | 550-1050 | 83.00 |
| 200 | 350 | 93.0 | 0.500 | 550-1100 | 87.74 |
| 250 | 375 | 98.0 | 0.527 | 600-1050 | 86.74 |
| Sulphathiazole | | | | | |
| 50 | 420 | 135.0 | 0.726 | 600-1050 | 71.04 |
| 100 | 400 | 128.0 | 0.688 | 600-1050 | 74.15 |
| 150 | 400 | 115.0 | 0.618 | 600-1100 | 79.14 |
| 200 | 380 | 98.0 | 0.527 | 550-1100 | 83.60 |
| 250 | 375 | 95.0 | 0.511 | 530-1150 | 85.49 |
| Benzimidazole | | | | | |
| 50 | 400 | 140.0 | 0.752 | 600-1000 | 69.75 |
| 100 | 400 | 130.0 | 0.699 | 600-1000 | 72.83 |
| 150 | 425 | 115.0 | 0.618 | 600-1100 | 74.82 |
| 200 | 380 | 101.0 | 0.543 | 550-1100 | 81.07 |
| 250 | 380 | 96.0 | 0.516 | 550-1100 | 84.15 |
| Tinidazole | | | | | |
| 50 | 450 | 150.0 | 0.806 | 650-1000 | 67.89 |
| 100 | 400 | 140.0 | 0.752 | 650-1000 | 71.81 |
| 150 | 350 | 132.0 | 0.709 | 600-1000 | 74.82 |
| 200 | 350 | 125.0 | 0.672 | 550-1050 | 76.45 |
| 250 | 350 | 120.0 | 0.645 | 500-1050 | 80.75 |

*The curves in Figs. 3 and 4 illustrates anodic*

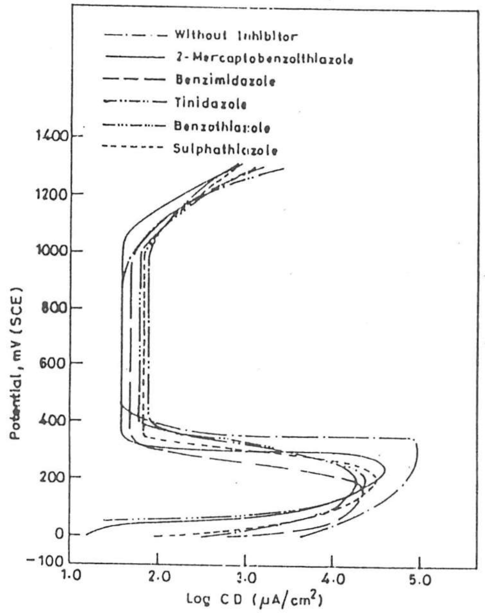


FIG. 3 ANODIC POLARIZATION CURVES OF NICKEL WITH 250 ppm OF ADDITIVES AT TEMPERATURE 25°C

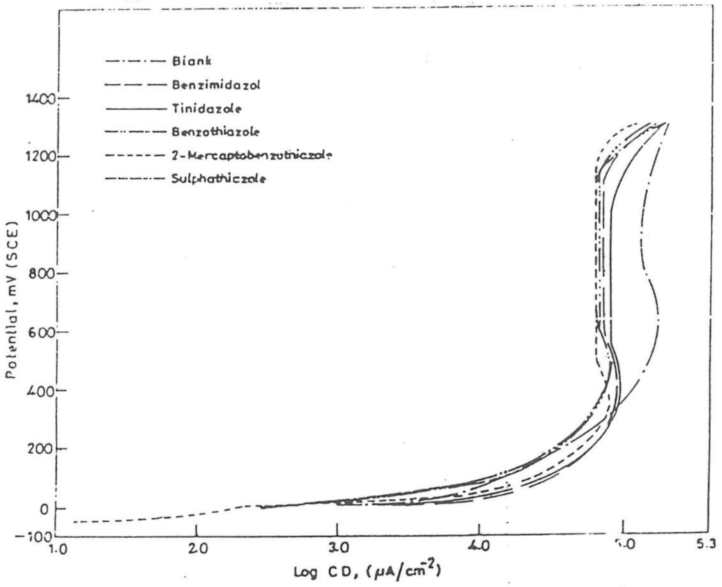


FIG. 4. ANODIC POLARIZATION CURVES OF Ni-Mo-Fe ALLOY IN PRESENCE OF DIFFERENT AZOLES COMPOUND

*polarization behaviour in the presence of all the additives studied at their 250 ppm concentration for nickel and Ni-Mo-Fe alloy respectively. It is observed that 2-mercaptobenzothiazole shows maximum and tinidazole shows minimum shift in anodic polarization curves for Ni-Mo-Fe alloy and the observed trend is : 2-Mercaptobenzothiazole > Benzotriazole > Sulphathiazole > Benzimidazole > Tinidazole, whereas in case of nickel, tinidazole shows maximum and 2-mercaptobenzothiazole shows minimum shift in apc's and observed trend is : Tinidazole > Sulphathiazole > Benzimidazole > Benzotriazole > 2-mercaptobenzothiazole. Further, the values of* $i_c/i_{co}$ *in case of Ni-Mo-Fe alloy follow the same trend as that observed for the shift in apc's, but not for pure nickel. This indicates that though each of them is quite effective in blocking the anodic sites for the process of corrosion, the extent to which they retard the anodic process depends upon the composition of corroding materials.*

*Figs. 5 and 6 represent the cathodic polarisation*

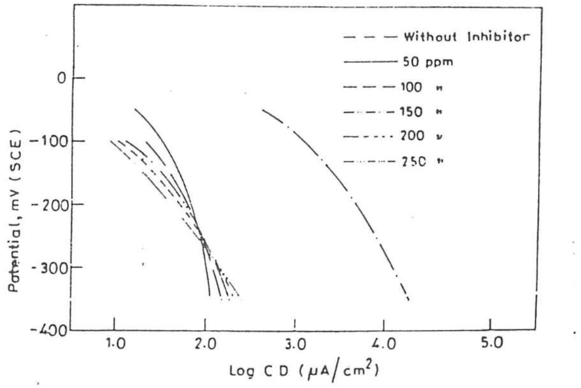


FIG. 5 . CATHODIC POLARIZATION CURVES OF NICKEL IN PRESENCE OF DIFFERENT CONCENTRATIONS OF 2-MERCAPTOBENZOTHIAZOLE AT 25°C

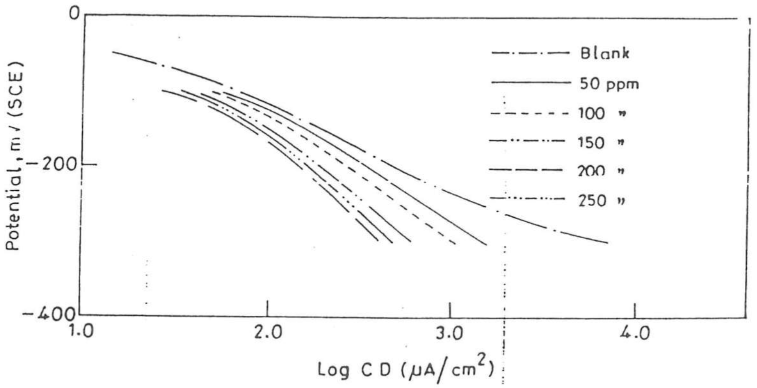


FIG. 6 CATHODIC POLARIZATION CURVES OF Ni - Mo-Fe ALLOY IN PRESENCE OF DIFFERENT CONCENTRATION OF 2-MERCAPTOBENZOTHIAZOLE AT TEMPERATURE 25°C

*curves (cpc) in the presence of different concentrations of 2-mercaptobenzothiazole for nickel and Ni-Mo-Fe alloy respectively. It is observed from the figures that almost similar curves are found both in the presence and the absence of the inhibitor. On the addition of the inhibitor the curve is bodily shifted downwards indicating retardation in cathodic process. With increase in concentration of the inhibitor larger shift in cpc's is observed showing the improved effectiveness of the inhibitor at higher concentration. The trends observed for other azoles at all concentrations and temperatures were similar. Also, at a fixed concentration all the inhibitors show downward shift which is maximum in the presence of 2-mercaptobenzothiazole and minimum with tinidazole.*

*The data of the present investigation have been analysed in terms of the potential dependent adsorption of inhibitors on the corroding surface. The two-dimensional* adsorbate layer can affect the basic corrosion reactions in different ways (6) and may be discussed by determining the inhibition efficiency as follows:

$$IE = I - I_{inh}/I \qquad (i)$$

where I and $I_{inh}$ represent the corrosion current densities of the electrode reaction in the absence and presence of inhibitors, respectively. Corrosion current density was determined by Tafel Extrapolation method (7). The plots of % IE of all the inhibitors at a concentration of 250 ppm are shown in Figs. 7 and 8 for Ni/nitric acid and Ni-Mo-Fe/nitric acid systems respectively. The effectivenesws of the inhibitors, as indicated by the % IE follows the same trend for both the systems viz., 2-mercaptobenzothiazole > Benzotriazole > Sulphathiazole > Benzimidazole > Tinidazole.

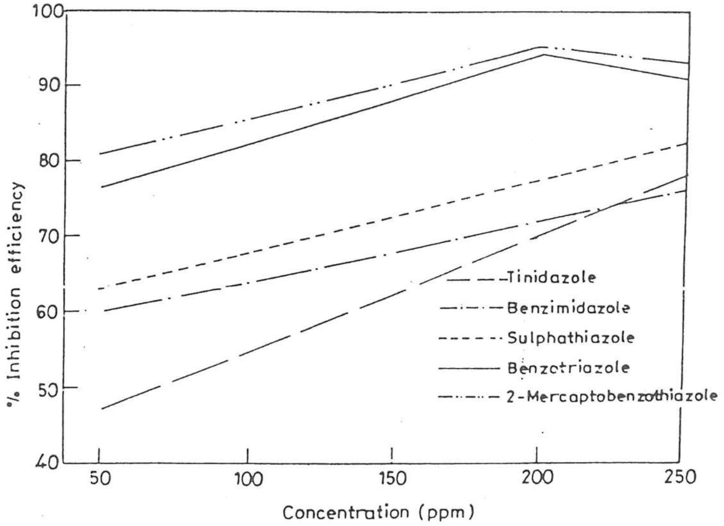


FIG. 7 INHIBITION EFFICIENCY OF INHIBITORS IN NICKEL SOLUTION

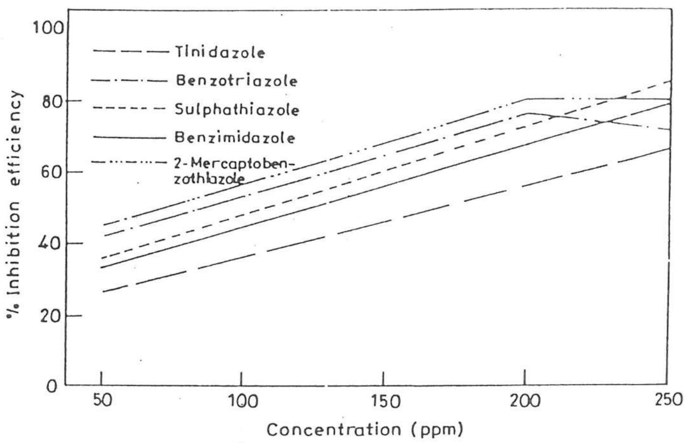


FIG. 8 INHIBITION EFFICIENCY OF AZOLES COMPOUND FOR Ni-Mo-Fe ALLOY

It was found that 2-mercaptobenzothiazole is the most potential and tinidazole is the least effective inhibitor for both the systems suggesting that the same mechanism of inhibition is followed in both cases. On comparing the observed IE for the two systems, it is observed that all the inhibitors are more effective for Ni/nitric acid system at each concentration.

The plots of % IE vs concentration (ppm) are shown in Figs. 9 and 10 for nickel and Ni-Mo-Fe alloy respectively at

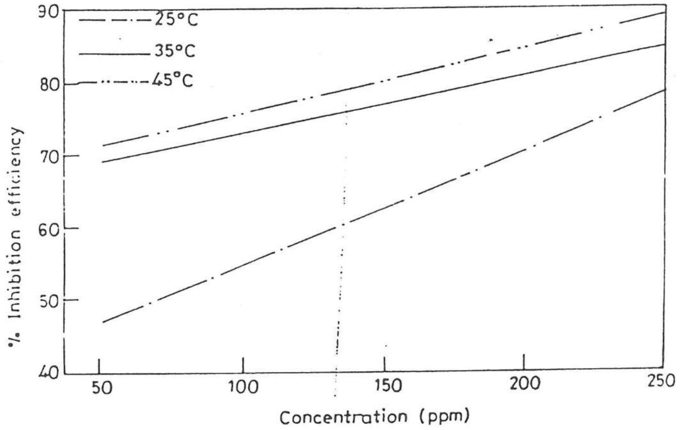


FIG. 9 INHIBITION EFFICIENCY OF TINIDAZOLE IN NICKEL SOLUTION

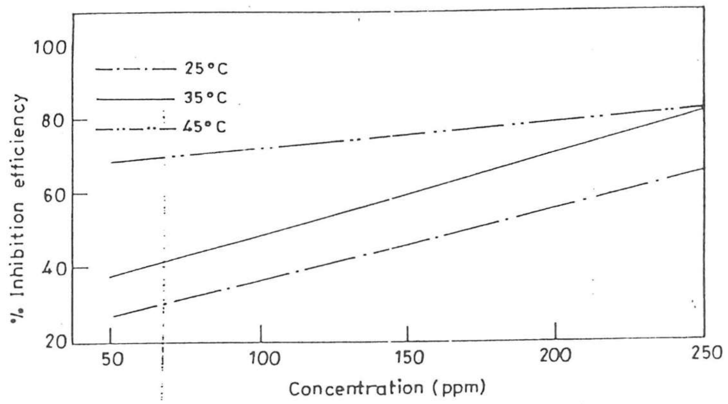
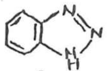


FIG. 10 INHIBITION EFFICIENCY OF 2-MERCAPTOBENZOTHIAZOLE FOR Ni-Mo-Fe ALLOY AT DIFFERENT TEMPERATURE

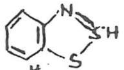
*temperatures 25, 35, 45°C for 2-mercaptobenzothiazole. A linear relation was observed between the % IE and concentration at all three temperatures. It is evident from the figure that with increase in temperature and the concentration of the inhibitor, there is an improvement in the protective power. This is true for other inhibitors, as well. The increase in IE with rise in temperature may be due to the higher activation energy available for the adsorption at elevated temperatures (8).*

*The effectiveness of these inhibitors may be explained on the basis of the extent of adsorption of these inhibitors and/or their relative capacity to form surface complexes with nickel. A significant role of adsorption during the inhibition process may be always presumed. In such a case the inhibitor efficiency would depend upon the number of active centres such as N, S and O atoms and delocalised electron density. For molecules having equal number of active centres the inhibition efficiency is believed to depend upon the surface area of adsorbed inhibitor molecules. From the structure of the inhibitor molecules -*

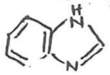
*(i) Benzotriazole*



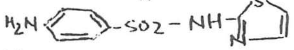
*(ii) 2-mercaptobenzothiazole*



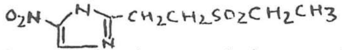
*(iii) Benzimidazole*



*(iv) Sulphathiazole*



*(v) Tinidazole*



*it appears that inhibitors (iv) and (v) should act as better inhibitors than others. However, the data on inhibition efficiency obtained from the present investigation indicate that inhibitor (ii) i.e., 2-mercaptobenzothiazole is the best inhibitor. It may be inferred from this that adsorption alone does not determine the effectiveness of all the inhibitors investigated.*

*The lack of correlation between the structures of inhibitor molecules and the IEs afforded by them may be explained on the basis of the formation of surface complexes due to the interaction between the inhibitor molecule and the metal ion on the metal side of Helmholtz layer. It has been reported earlier (9,10,11,12) that the formation of surface complexes do occur in the case of inhibitor (I) and inhibitor (II). 2-mercaptobenzothiazole forms polymeric complexes (13) with nickel and it may be assumed that the formation of such a complex leads to retardation in the* corrosion rate. The nature of the complex being polymeric, it is expected to behave as an excellent inhibitor due to larger surface coverage. Inhibition efficiencies of the order of 90-95 percent confirm their potentiality. On the other hand, benzotriazole gives a monomeric complex, providing comparatively smaller surface area of the metal to be covered and hence its inhibition efficiency is not that large.

The percentage inhibition efficiencies observed in the case of sulphathiazole and tinidazole may be mainly due to their adsorption, as such, on the corroding surface. The formation of surface complexes in these cases is not favourable as apparent from their structures neither there is any evidence in literature. The difference between IEs may be attributed to their relative surface area and number of active sites in these molecule. Sulphathiazole having larger surface area with N and S atoms and phenyl ring as active centres should act as a better inhibitor than tinidazole, as is the actual case. However, benzimidazole, exhibiting percentage IE in between inhibitor [iv] and [v], may be considered to retard the corrosion process, both through adsorption as well as surface complex formation. The involvement of ring nitrogen only may be considered to form a comparatively weaker complex with metal ions. Thus, from above discussion it may be concluded that not only structure and their simple adsorption phenomenon affect the IE but the

nature of complex formed and their stability, also affects the inhibition process. Assuming that the percentage area covered by inhibitor either due to adsorption or surface complex formation is directly related to the retardation in corrosion rate, the compound should obey the Langmuir adsorption isotherm equation (14)

$$\log \theta/(1-\theta) = \mathrm{LOG}\ A + \mathrm{LOG}\ C - Q/(2.303\ RT) \qquad (ii)$$

where, $\theta$ is the surface coverage due to the adsorbed inhibitor molecules and $1-\theta$ is the bare surface. A being a temperature independent constant, C the concentration of inhibitor (ppm) and Q is the heat of adsorption.

Figs. 11 and 12 show the Langmuir adsorption curves for the studied azoles in 4% nitric acid for nickel and

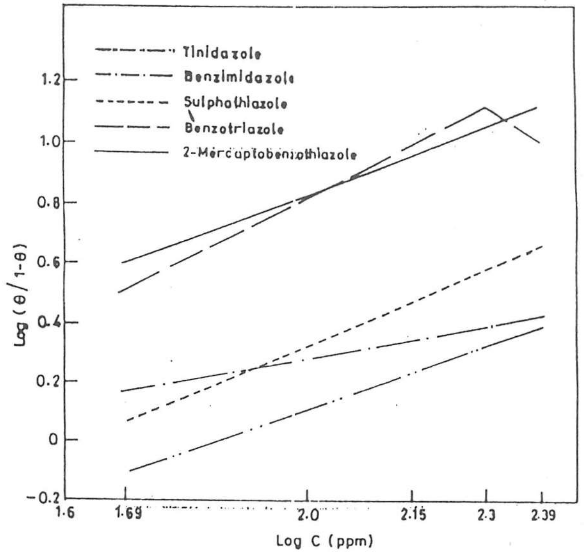


FIG. 11. LANGMUIR PLOTS OF DIFFERENT AZOLES AT TEMPERATURE 25°C

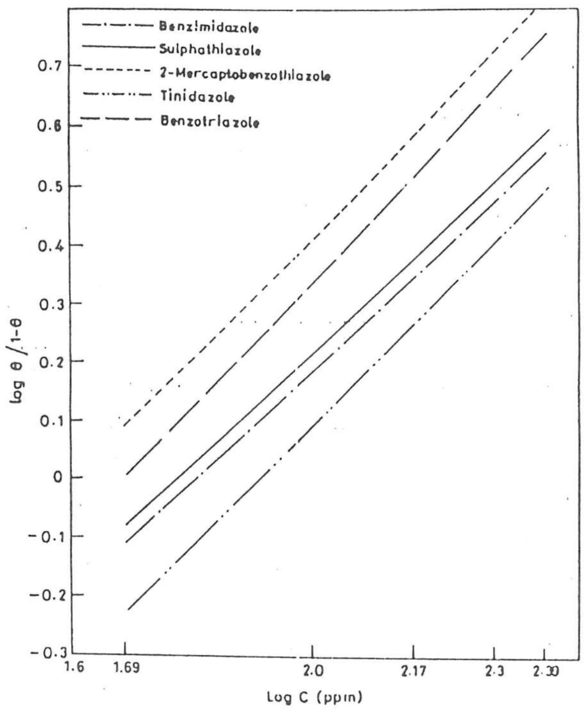


FIG. 12 LANGMUIR ADSORPTION ISOTHERM OF Ni-Mo-Fe ALLOY IN PRESENCE OF DIFFERENT AZOLES AT 35°C

*Ni-Mo-Fe respectively (similar curves were obtained at all investigated temperatures). The plots are linear and their gradients are very close to unity (0.91-0.93) for nickel and (0.93-0.86) for Ni-Mo-Fe alloy. The deviation becomes larger with increase in temperature. The gradient at 25°C is 1 and decreases with increase in temperature from 1 to 0.75. This deviation is an indication of enhancement in the interaction between adsorbed species and the metal surface.*

*The heat of adsorption was calculated from the plots of log vs. 1/T as shown in Figs. 13 and 14. The values of heat of adsorption becomes more negative with increase in concentration of the additive. In the selected range of*

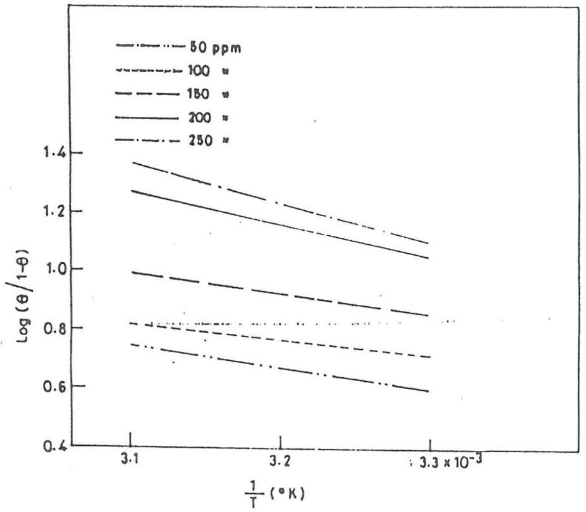


FIG. 13. CALCULATION OF HEAT OF ADSORPTION

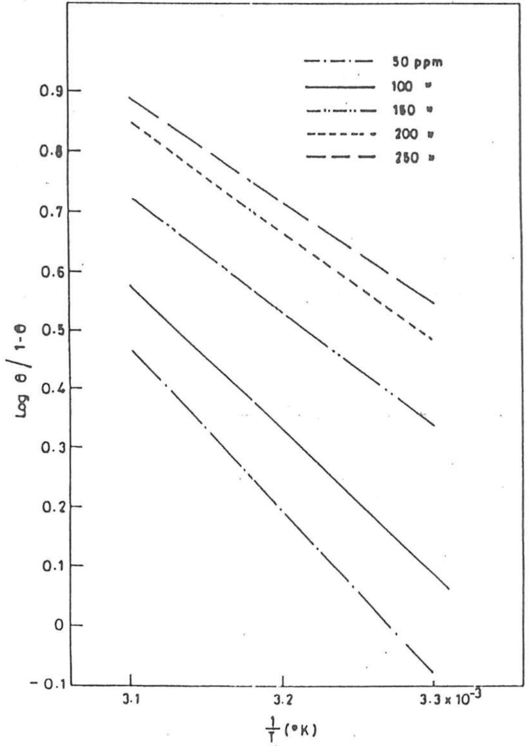


FIG. 14. CALCULATIONS OF HEAT OF ADSORPTION

*concentration of the inhibitors the values of heat of adsorption lies between -7.83 and -13.8 Kcal for Ni-Mo-Fe alloy and between -3.63 and -6.9 Kcal for nickel/nitric acid system. This indicates that the inhibitor is more strongly adsorbed on the surface of the alloy than on nickel.*

*Figs. 15a,b and 16c,d show optical micrographs for nickel and Ni-Mo-Fe alloy respectively, taken after their*

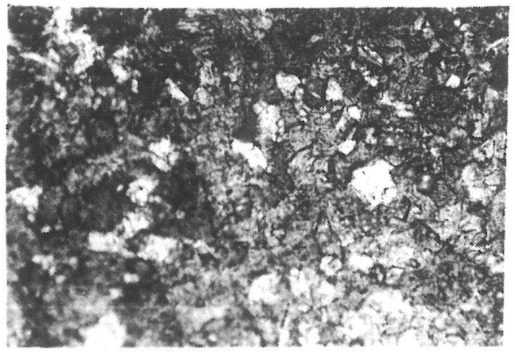


*Fig.15a. Nickel 4% $HNO_3$ solution (640X).*

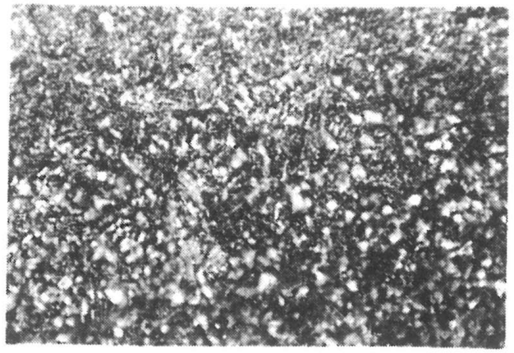


*Fig.15b. Nickel in presence of 2-mercaptobenzothiazole (640X).*

*Fig.15c. Ni-Mo-Fe alloy in 4% $HNO_3$ solution (640X).*

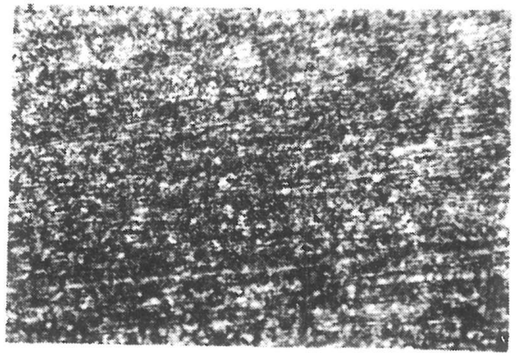


*Fig.15d. Ni-Mo-Fe alloy in presence of 2-mercaptobenzothiazole (640X).*

polarisation studies upto +200 mV in 4 percent nitric acid solution in absence and presence of 200 ppm of 2-mercaptobenzothiazole at 25°C. On comparing these micrographs, it is evident that in the presence of 2-mercaptobenzothiazole, the surface of test materials have improved remarkably. However, in the absence of chemical analysis it is difficult to predict the nature of the film.

## Conclusion

1. All the inhibitors tested are found to be very effective for both the systems.
2. All the inhibitors are more effective for Nickel/nitric acid system than Ni-Mo-Fe alloy/nitric acid.
3. 2-mercaptobenzothiazole was found to be most effective for both the systems.

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