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A Study on the Corrosion Inhibition Effect of Hexamethylene Tetramine on Welded API 5L X70 Steel in E10 Fuel Ethanol Environment

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Abstract-
The inhibition effect of hexamethylenetetramine (HT) in E10 environment for the corrosion protection of welded API 5L X70 pipeline steel was examined using immersion tests. Welded samples of API-5L X70 steel of dimension 30 mm x 15 mm were immersed into E-10 fuel ethanol containing hexamethylenetetramine concentration of (0.2, 0.4, 0.6, 0.8) g and the control for a minimum of 4 days and a maximum of 28 days. Analysis was done using mass loss, corrosion rate, inhibitor efficiency and ANOVA test. From the mass loss and corrosion rate analysis, it was observed that 0.2g HT, which was the lowest concentration of inhibitor, proved best for inhibiting corrosion at 24 days.

Key words: Inhibition, corrosion, hexamethylene tetramine, E10

1. Introduction
Metallic corrosion entails corrosion of metallic materials. In practice, metals degrade in atmospheric and aqueous environments. A significant problem usually encountered in our industrialized society is metallic corrosion. Hence, corrosion is a subject that is being extensively studied in recent times [1, 2]. In the early twentieth century, modern corrosion science started out through Evans’ model for local cell and the corrosion potential model shown by Wagner and Traud [1]. In addition, the dual models which describe metallic corrosion to be a collective electrochemical response entailing anodic metal oxidation and cathodic oxidant reduction, have united into the contemporary electrochemical concept of corrosion. Corrosion data is predominant for a number of engineering materials in so much that the greater amount of the data are particularly for full immersion environments. The National Research Council in US [3] has reported that the quantity of environs for corrosion study is limited and this has resulted in incapability to generate an evocative nation-wide record of corrosion data valuable to academia, government and industry. There are a wide range of corrosion environments ranging from complete immersion to non-aqueous environments. Fuel grade ethanol is an illustration of such non-aqueous environs. It requires the capacity to forecast its effect on production materials worldwide due to its forecasted global usage.

Ethanol being an unconventional energy source, is an alcohol prepared by inflaming corn or other comparable biomass material. When ethanol is mixed with unleaded gasoline, there are increases in octane levels, improvements in combustion–assisting the fuel to burn more fully, decreases carbon monoxide emissions, and extends the supply of gasoline. E10 (10 percent
ethanol by volume) was the first ethanol-blended gasoline, as far back as in the 1970s. A study conducted by the API (American Petroleum Institute) revealed that the subject matter of metallic SCC (stress corrosion cracking) in fuel ethanol is an area where cognizance of the subject is rising enthusiastically because of documents existing on expertise as well as investigations in headway [4-10]. Discoveries by API indicate that recognized disasters of ethanol end-user process line goes back to no earlier than the early 1990s. It is therefore necessary to expand the existing body of knowledge regarding inhibition studies in fuel ethanol. The thrust of this work centers on studying the inhibition of welded pipeline steel in E10 fuel ethanol environment.

2. Methodology

2.1 Material Processing

API 5L X70 pipeline steel utilized for the work were sectioned out from a new pipeline steel of diameter, 160 mm in as received conditions. Its chemical composition is presented in Table 1 and its microstructure is shown in Figure 1. From the SEM image in Figure 1, it shows that the API-5L X70 steel has a Ferrite-Pearlite Microstructure.

| Material  | C   | Mn   | Si   | Nb  | Ti   | Cr   | P   | S    | N    |
|-----------|-----|------|------|-----|------|------|-----|------|------|
| API 5L X70| 0.06| 1.55 | 0.18 | 0.055| 0.017| 0.02 | 0.01| 0.002| 0.0071|

Figure 1: SEM micrograph of surface of welded API-5L X70 steel at magnification of (a) 1000X and (b) 4000X
Two strips of metal were welded using Olicon Electrode (E-12) and continuous welding was applied. Each welded specimen was ground to obtain a smooth surface. Drilling of each sample was done at the edge of the sample on the drilling machine using a HSS drill bit (0.5mm) to allow for suspension of the metal in the test environment. The welded steel was cut into the prerequisite sizes 1.5 cm x 1.5 cm and dry-abraded using different grades of abrasive paper (80, 150, 320, 600 and 800 μm). The test environment used for the study was E10 which contains 10% simulated fuel grade ethanol and 90% gasoline.

The simulated fuel grade ethanol was prepared according to ASTM standard D-4806 (2015) for fuel grade ethanol. Reagents used consist of: 99.8% ethanol, acetic acid with purity of 99.8%, distilled water, pure methanol, and pure NaCl with purity >99%. The NaCl was liquefied in water and subsequently poured in ethanol to attain the stated water and NaCl concentrations. HT concentrations of 0.2, 0.4, 0.6 and 0.8 grams were utilised for the inhibitor tests. The control test was conducted in the absence of HT.

### 2.2 Immersion Tests

The corrosion media were poured in conical flasks of 200ml with varied inhibitor concentration (0g, 0.2g, 0.4g, 0.6g and 0.8g). The API-5L X70 steel samples were weighed initially before immersion into the environment. Five samples constituted a test period. The test periods were 4 days, 8 days, 16 days, 20 days, 24 days and 28 days, and each test was duplicated with the purpose of determining the reproducibility of the test. After the samples were exposed to the test environment for each test period, the corrosion products were scraped off mechanically, the specimens were cleaned, allowed to dry and the final weight of the specimens were taken.

Corrosion rate was calculated from the mass loss data (Equation 1). The corrosion rate was also used in calculating the inhibitor efficiency for the different days (Equation 2).

\[
CR = \frac{KW}{DAF} \quad (1)
\]

Where \( CR \) is the corrosion rate (mm/yr),

- \( K \) is a constant (534),
- \( W \) is the mass loss in milligrams (mg),
- \( A \) is the area to the nearest sq. inches (0.6975in\(^2\)),
- \( T \) is the time of exposure in hours to the nearest 0.01h and
- \( D \) is the density of the material (8.03) in g/cm\(^3\)

\[
\text{Inhibitor Efficiency} \% = \frac{CR_{\text{uninhibited}} - CR_{\text{inhibited}}}{CR_{\text{inhibited}}} \times 100 \quad (2)
\]
3. **Result and discussions**

3.1 **Effect of exposure time on corrosion rate and inhibitor efficiency**

The variation between corrosion rate and exposure time is shown in Figure 2. The graphical representation shows that lowest corrosion rates were obtained from the inhibitor tests. There was large disparity between the control curve and the inhibitor curves. Furthermore, a similar trend of increase in corrosion rate within the first 10 days and a gradual decrease afterwards is displayed by all the tested conditions. A passivating action of the oxide films formed on the samples at the beginning of the experiment is an explanation for the decrease in corrosion rate [7]. The sudden increase in corrosion rate on the 24th day could be explained as a transpassive reaction where pitting takes place and corrosion degradation increases.

![Figure 2: Variation of corrosion rate with exposure time for welded API 5L X70 in E10. Error bars show 5% of standard error.](image)

Figure 3 shows the disparity of inhibitor efficiency with exposure time. It can be deduced from the Figure that 0.2g of inhibitor concentration proved most effective to inhibit corrosion at 24 days while 0.4g of inhibitor concentration was the least effective at 12 days of exposure. This indicates that the inhibitor is most effective at lower concentrations.
3.1 Effect of inhibitor concentration on corrosion rate

The disparity of corrosion rate with HT concentration for the entire test duration (28 days) is shown in Figure 4. Generally highest corrosion rates were seen in the control tests (absence of inhibitor) which infers that protection was achieved with the HT inhibitor. Best protection was achieved with 0.8 g HT at 24 days. The protection efficacy of HT can be clarified by the absorption of the amine molecules on the surface of the steel [11].
The distinct and joint effects of varying exposure time and inhibitor concentration on corrosion rate of welded API 5L X70 steel was calculated using two-factor ANOVA (Analysis of Variance) test. From the results presented in Table 2, it can be resolved at 90 percent confidence level, that both exposure time and HT concentration significantly affects the corrosion rate of welded API 5L X70 steel.

Table 2: Analysis of Variance Test Results

| Source of Variation | SS    | Df | MS    | F     | Significance |
|---------------------|-------|----|-------|-------|--------------|
| Exposure Time       | 17.63 | 6  | 2.94  | 20.99 | 2.04         |
| Concentration of HT | 6.42  | 4  | 1.61  | 11.46 | 2.19         |
| Residual            | 3.36  | 24 | 0.14  |       |              |
| Total               | 27.40 | 34 |       |       |              |

4. Conclusion
The use of hexamethylene tetramine to inhibit corrosion of welded API-5L X70 pipeline steel in E-10 environment has been investigated. From the study, it can be postulated that corrosion of the welded steel in E10 is best reduced with lower HT concentration. ANOVA test results also showed that HT concentration and exposure time significantly affected corrosion rate.

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