

Drastic Effect of Acetic Acid on Mild Steel and its Prevention by Vapour Phase Process

Shailendra kumar dwivedi Deptt. Of chemistry, Naraina College of Engg and technology, Ratanpur, Panki, Kanpur 208020

Abstract It is the effect acetic acid on mild steel panels Exposed in open atmosphere. It will corroded. The corrosion product is depends on the humidity and environmental gases. It is observed that at 80%RH to 90%RH rust formation is maximum during entire exposure time .Some nitrobenzene such as m-dinitrobenzene acted as good VCI. it gave 80% to 90% protection in almost all RH and at entire exposure time. Anthraquinone is also acted as good VCI .Its performance was better at very high and very low humidity ,that is at 100%RH and at 40% to 20%RH. In These situation, the protection afforded by Anthraquinone is higher than m-dinitrobenzene it is slightly lower at 60%RH to 80% RH.

Key words: Anthraquinone , m-dinitrobenzene, vapour phase process, Relative Humidity, Protection.

Introduction

Corrosion Problem is well-known problem in worldwide. It is mainly electrochemical process promoted by different type processes differential aeration such as accumulation of dirt, sand, scale and other contamination because this part of metal is poorly oxygenated, hence anodic where corrosion taking place., the area becomes lesser accessible to air and more corrosion leading to the formation of deep cavity or localized pitting in the metal. Sometime partial, cover of metal by block of wood and piece of glass these are working as screen part of metal from oxygen access. As a consequence, differential aeration and corrosion occurs It can be some time prevented by passivation by which a metal or alloys show high corrosion resistance due to formation of high protective, very thin film (about 0.0004 mm thick) and quite invisible surface film but it can take place in different environment .Passivation tend to maintain protective film on the surface as Ti, Cr, Al and Cr containing stainless steel alloys exhibits outstanding corrosion resistant in presence of oxygen. This is due to the formation of thin film on their surface the rate of corrosion is less when the area of cathode is smaller, when cathodic area is smaller, the demands for electrons will be less and this result is the decrease rate of dissolution of metal at anodic regions.

The concept of total corrosion control should be introduced in which corrosion control is more a daily activity at all stages of production than merely an afterthought. Good corrosion control. An inhibitor is a chemical substances that ,When added in small concentration to an environment, effectively decreases the corrosion rate there are several classes of inhibitors conveniently designated passivators¹ organic inhibitors², including slashing compounds and pickling inhibitors, and vapour phase inhibitors³ The practice of corrosion inhibitors are greatly influenced by new regulations that have been developed because of toxicity in environment effect resulting from industrial effluents. There is trends to replace some widely used inhibitor such as chromates, in application where toxicity, environmental damage, and pollution caused by these chemicals are important consideration [1-3]. The extent chemical reduction on initial contact of passivators with metal, according to this view point, must be at least chemically equivalent to the amount of passive film formed as result of such reduction. From the passive film on iron this is in the order of 0.01 c/cm² of apparent surface. The total equivalent of chemically reduced chromate is found to be of

this order and it is probably also same for the other passivators acting on iron. The amount of chromate reduced in the passivation process is arrived at from measurements [4-6]. In the type of vapour phase process various type of material are widely used such as polyaniline [7-9], Polypyrrole [10] and poly acetylene [11]. Heavy effort have been deployed to find suitable corrosion inhibitor for organic origin in various corrosive media [12-15]. In acid media, nitrogen based materials and their derivatives, sulphur containing compounds, aldehyde, thioaldehydes, acetylenic compounds and various alkaloids

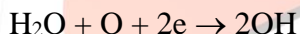
Mechanism of Corrosion Corrosion is the deterioration of a material as a result of reaction with its environment, especially with oxygen. Although the term is usually applied to metals, all materials, including ceramics, plastics, rubber, and wood, deteriorates at the surface to some extent when they are exposed to certain combinations of liquids and /or gases. Common examples of metal corrosion are the rusting of iron, the tarnishing of silver, the dissolution of metals in acid solutions and the growth of patina on copper. Most research into the causes and prevention of corrosion involves metals, since the corrosion of metals occurs much faster under atmospheric conditions than does the corrosion of nonmetals. The cost of replacing equipment destroyed by corrosion in the United States alone is in the billion-dollar range annually. Corrosion is usually an electrochemical process in which the corroding metal behaves like a small electrochemical cell. Since the corrosion of iron by dissolved oxygen is, from an economic standpoint, the most important redox reaction occurring in the atmosphere, it will be used here to illustrate the electrochemical nature of the process. A sheet of iron exposed to a water solution containing dissolved oxygen is the site of oxidation and reduction half-reactions, which occur at different locations on the surface. At anodic areas, iron is oxidized according to the reaction.

Anodic



At the same time, oxygen molecules in the solution are reduced at the cathodic areas. Reaction

Cathodic



The two processes produce an insoluble iron hydroxide in the first step of the corrosion process: Generally, this iron hydroxide is further oxidized in a second step to produce $\text{Fe}(\text{OH})_3$, the flaky, reddish brown substance that is known as rust. Unfortunately, this new compound is permeable to oxygen and water, so it does not form a protective coating on the iron surface and the corrosion process continues. All metals exhibit a tendency to be oxidized, some more easily than others. A tabulation of the relative strength of this tendency is called the electromotive series of metals. Knowledge of a metal's location in the series is an important piece of information to have in making decisions about its potential usefulness for structural and other application

2. Material and Methods

2. Metal Studied

Mild steel panels of the size 7.5 cm × 1.25 cm (cut from single sheet) of pickled cold rolled closed annealed (18 SWG) were used in all experiments. The composition of the mild steel sheet was iron 99.74%, carbon 0.07%, silicon 0.07%, sulphur 0.044%, phosphorus 0.049%, manganese 0.023%. All panels were carefully polished with successive grades of emery paper for removing all surface

defects. The final surface was brought to standard finish by polishing with 000 grade emery paper. All cuts, edges, corners and suspension holes were rounded off and smoothened.

After surface preparation panels were degreased with sulphur free toluene. This was followed by treatment with methyl alcohol to remove sweat residue and finger prints. The specimens were dried and then transferred to a vacuum desiccators in which they were allowed to remain for a period of 24 hours.

Corrosion experiments:

After surface preparation panels were weighed (weighing was done with the help of single pan weighing machine). For the identification of panels all the panels were numbered and suspension holes were made.

Weighed metal panels, were exposed to synthetic atmosphere of different humidity or corrosive vapours. The samples were with drawn after a specified time and the extent of corrosion was determined by weight gain or weight loss method. The de rusting was done by using appropriate de rusting solutions. The de rusting solution used was conc. HCl containing 5% stannous chloride and 2% Antimony trioxide at room temperature. After removal of corrosion product, the metal panels were washed with distilled water followed by immersion in absolute alcohol or acetone, drying with hot air, cooling in desiccators and weighing. The weight losses of specimens due to corrosion were determined by subtracting the weights of de rusted panels from their original weights.

The specimens were suspended in sealed desiccators (one liter capacity) by glass hooks with the help of glass rod fixed tightly on the inner walls of the desiccators. Care was taken to put grease on the lid properly so that once closed, the system was fully sealed.

In order to make sure that the un corroded metal was not removed from the panels by the de rusting solutions, blank was run in each case to check the amount of metal removed in the process of de rusting. It was found that metal removed from the blank did not exceed 0.1% of the total corrosion value.

It has been reported by Evans if the rust consists of $\text{Fe}(\text{OH})_2$ and no other compounds, the loss in weight should be 1.69 of that of the gain in weight. Since in our study, other compounds were likely to be formed the weight increments might not give the true picture, as in many cases where the corrosion product were not of adherent type or where leaching of the corrosion product could have been possible, the weight increments were not suitable as a method for assessment of the corrosion rate. The corrosion has been measure in mg/dm^2 of the surface area.

Preparation of synthetic humid atmosphere:

The humid atmosphere of known RH was produced by using sulphuric acid of appropriate density, AR quality sulphuric acid was used for the purpose and the required dilution was done by distilled water. The concentration of acid for different RH was as follows:

For 20%RH H_2SO_4 31.39 % by volume

For 40%RH H_2SO_4 25.90 % by volume

For 60%RH H_2SO_4 20.80 % by volume

For 80%RH H_2SO_4 14.55 % by volume

For 100%RH H_2SO_4 0.0 % by volume (Distilled water)

The amounts of dilute acid taken were 30cc in the desiccators of 1000 cc capacity. The sealed desiccators containing the solution were kept at room temperature for three days before the panels were introduced in them.

Preparation of other corrosive environments:

The acetic acid environment was created by taking 1cc of acetic acid of desired concentration soaked in cotton and hanging it inside the desiccators with the help of glass hooks. The environment of wood exhalations was created by hanging wet wood piece of size 1 inch \square 1 inch

□ 2 inches with the help of cotton threads inside the desiccators for 7 days. Woods pieces were kept immersed in distilled water for 24 hours at room temperature before hanging.

Volatile corrosion inhibitor:

Few volatile corrosion inhibitors reported by Rajagopalan as very good inhibitors were tested at different RH. Those found excellent were used to prevent corrosion by vapours emitted by woods. They were also incorporated in ordinary brown paper to prepare VCI paper.

0.5 gm of VCI was taken in a glass plate and was kept inside the desiccators (IL) at required humidity with and without wood. The weight losses of the panels in the absence of VCI (W_u) and in the presence of VCI (W_i) were determined for different time durations. The inhibitor efficiency (I) was calculated by the following equation.

$$I = \frac{W_u - W_i}{W_u} \times 100$$

Majority of the state and Industrial standards, for evaluation of the performance of vapor corrosion inhibitors, used the Federal Standard No. 101C, Method 4031, (Corrosion inhibiting ability of VCI vapours). This test is applied for testing of the VCI films, papers and powders and is included in Japanese Industrial Standards JISZ 1519, JISZ 1535 JISK 2246. According to this test the VCI material is placed inside a Jar that serves as a test chamber. The Jar contains water glycerin solution of different strength, which produces different relative humidity. There is also a metal specimen inside the Jar. This specimen does not contact the VCI material. For non-VCI material this condition will cause corrosion. If the material contains an adequate amount of VCI, metal surface remains protected. According to German Military Standard TL 8135, Corrosion protection provided by the VCI material is graded by visual inspection of the metal specimen. Keeping in mind the above standard, we planned our experiment mild steel due to Anthracene for different RH

Table-1. Protection of mild steel due to Anthracene for different time durations at different RH.

s. no	Time (days)	100% RH		80%RH		60%RH	
		Wt loss(mg/dm ²)	Protection %	Wt loss(mg/dm ²)	Protection %	Wt loss(mg/dm ²)	Protection %
1	15	0.0	100	209	100	1.7	85
2	30	0.0	100	4.3	85	8.0	77
3	45	7.0	77	8.0	69	3.0	79
4	60	8.0	79	10.4	58	10.0	79

Table-2. Protection of mild steel due to Naphthalene for different time durations at different RH.

s. no	Time (days)	100% RH		80%RH		60%RH	
		Wt loss(mg/dm ²)	Protection %	Wt loss(mg/dm ²)	Protection %	Wt loss(mg/dm ²)	Protection %
1	15	1.7	88	0.0	100	5.0	55
2	30	6.0	72	4.1	85	5.5	57
3	45	11.9	60	11.9	69	8.0	71
4	60	16.0	58	19.7	58	11.0	65

Table-3. Protection of mild steel due to meta dinitrobenzene for different time durations at different RH.

s. no	Time (days)	100% RH		80%RH		60%RH	
		Wt loss(mg/dm ²)	Protection %	Wt loss(mg/dm ²)	Protection %	Wt loss(mg/dm ²)	Protection %
1	30	7.3	77	2.4	95	5.0	85
2	60	9.7	78	14.4	74	12.5	67
3	90	19.5	65	28.0	62	30.0	71
4	120	24.4	64	30.0	79	40.0	65

Table-4. Protection of mild steel due to Anthraquinone for different time durations at different RH.

s. no	Time (days)	100% RH		80%RH		60%RH	
		Wt loss(mg/dm ²)	Protection %	Wt loss(mg/dm ²)	Protection %	Wt loss(mg/dm ²)	Protection %
1	30	21.1	96	7.0	97	8.0	55
2	60	26.5	96	15.2	96	12.5	57
3	90	29.5	97	18.2	97	20.0	71
4	120	55.5	99	25.7	99	41.0	65

3. Results and Discussion

3.1. Anthracene

Table.1, depict the protective performance of Anthracene for mild steel corrosion at different RH (100% RH to 60% RH) for time durations of 15 days to 60 days. Results show that at 100% RH inhibitor completely protected mild steel corrosion up to 30 days. There was no rust spot on the panels. The inhibitor efficiency reduced to 77% and 79% during 45 days and 60 days respectively. The weight loss obtained was 7.0 mg/dm² during 45 days and 18.0 mg/dm² during 60 days. At 80% RH percentage protection obtained was 83% and 84% during 15 days and 30 days respectively which reduced to 79% and 78% during 45 days and 60 days respectively. The weight loss obtained ranged between 2.9 mg/dm² to 10.4 mg/dm² during 15 days to 60 days. At 60% RH, the percentage protection ranged from 85% to 79% and weight loss ranged between 1.7 mg/dm² to 10.0 mg/dm² during the exposure time 15 days to 60 days.

3.2. Naphthalene

Table.2, depicts the protective performance of Naphthalene for mild steel corrosion at different RH (100%RH to 60% RH) for time durations of 15 days to 60 days. Results show that the inhibitor efficiency obtained at 80% RH was better than that at 100% RH. Weight loss obtained during 15 days to 30 days was also less at 80% RH than that at 100% RH, although the weight loss in uninhibited system was greater as 80%RH than that at 100% RH. In shorter durations, during a period of 30 days, the protective performance was 85% and above at 80% RH, 72% and above at 100% RH and approx 55% at 60% RH. The inhibitor efficiency obtained was not so good during longer exposure time i.e. 45 days to 60 days. It was between 58% to 70% at all humidities. protection was 78% in 15 days and 61% at 60 days. The weight loss obtained increased from 2.4 mg/dm² at 15 days to 12.0 mg/dm² at 60 days.

3.3. Meta Dinitrobenzene T

Table.3, depicts that protective performance of m-dinitrobenzene for mild steel corrosion at different RH (100% RH to 60% RH) for time durations of 30 days to 120 days. Results show that m-dinitrobenzene appears to be a very good volatile corrosion inhibitor for mild steel at 100% RH. In shorter durations (up to 30 days) it afforded complete protection and panels were completely rust free. In 60 days the percentage protection obtained was 85% and the weight loss was 5.0 mg/dm². When mild steel was exposed for 60 days, the percentage protection decrease to 67% and weigh loss increased to 12.5 mg/dm². At 80% RH, the inhibitor efficiency was less than that at 100% RH. Percentage protection obtained during 30 days was 95% and during 60 days it was 77%. The weight loss increased from 7.0 mg/dm² to 15.2 mg/dm² during a period of 30days to 60 days. At 60% RH, the inhibitor efficiency was 55% during 30 days, which gradually reduced with increased exposure time and was 57% during 60 days Thus it shows that under aggressive conditions inhibitor efficiency of m-dinitrobenzene was between 75% to 100%.

3.4 Anthraquinone

Table.4, depict the protective performance of Anthraquinone for mild steel corrosion at different RH (100% RH to 60% RH) for time durations of 30 days to 120 days. Results show that m-dinitrobenzene appears to be a very good volatile corrosion inhibitor for mild steel at 100% RH. In shorter durations (up to 30 days) it afforded complete protection and panels were completely rust free. In 60 days the percentage protection obtained was 95% . When mild steel was exposed for 60 days, the percentage protection decrease to 86% and weigh loss increased to 52 mg/dm². At 80% RH, the inhibitor efficiency was less than that at 100% RH. Percentage protection obtained during 30 days was 87% and during 60 days it was 77%. The weight loss i from 90days to 120 days percentage protection is 71% to 65%. ncreased from 15.2 mg/dm² to 11.0 mg/dm² during a period of 90days to120 days. At 60% RH, the inhibitor efficiency was 71% to 65% during 120 days, which gradually reduced with increased exposure time and was 71% during 60 days. Thus it shows that under aggressive conditions inhibitor efficiency of m-dinitrobenzene was between 75% to 100%.

4. Conclusions

VCI derivative shows good inhibition efficiency of corrosion by the formation of physical barrier between metal and corrosive environment by the interaction. The volatile corrosion inhibitor of mild steel carried out by using meta dinitrobenzene, anthraquinone, naphthaline and anthracene of metal and inhibitor molecules these are more effective.

Investigation shows that VCI provides very effective corrosion protection processes for the mild steel materials such as boilers and feeders. VCI can apply in the powder form at the time of manufacturing of mild steel equipments.

It is confirmed that VCI provides protection to the metal located at few centimeterst from the VCI source.

As per to the testing data. VCI is compatible. VCI can also lower the corrosion rate.

All types of the inhibitors can used in combination with process of vapour phase and plasma impulsing.

Acknowledgement

Authors are thankful to the Director, Indian Institute of technology Kanpur, India for providing infrastructure facilities to carry out this work and also thankful to Director NCET Panki Ratanpur Kanpur for providing Lab Facilities.

Reference

- [1] Hatch, G., 1973. *In corrosion inhibitor, edited by Nathan*. Houston, Texas: National association of Corrosion Engineers. pp. 144-145.
- [2] Robinson, J., 1979. *Corrosion inhibitors:Recent Developments,Chemical Technology Review No. 132 Noyes data Corp*. Park Ridge,N. J, pp. 24-31.
- [3] Brunn, A., 1983. *Jr,Mater.Perf.*, vol. 22,
- [4] Uhlig, H. and King, P., 1959. "Closure to "discussion of "the flade potential of iron passivated by various inorganic corrosion inhibitors." *J.Electrochem.Soc.*, vol. 106, pp. 1-7.
- [5] Power, R. and Hackrman, N., 1953. "Surface reactions of steel in dilute $Cr_51 O_4$ – Solutions: Applications to passivity." *J. Electrochem. Soc.*, vol. 100, pp. 314-319.
- [6] Cohen, M., Beck, A., and Electrochem, Z., 1958. "The passivity of iron in chromate solution, i. Structure and ... Film." *Zietschrift Elektrochemie*, vol. 62, pp. 696-699.
- [7] Shepsis, L. V., Pendrow, P. D., Mahalingam, R., and Osman, M. A., 2001. "Modeling and experimental comparison of pulsed plasma deposition of aniline." *Thin Solid Films*, vol. 385, pp. 11-21.
- [8] Gong, X., Dai, I., Mau, A. W. H., and Griesser, H. J., 1998. "Plasma-polymerized polyaniline films: synthesis and characterization." *J. Polym. Sci., Part A, Polym. Chem*, vol. 36, p. 633.
- [9] Olayo, M. G., Enriquez, M. A., Cruz, G. J., Morales, J., and Olayo, R., 2006. "Polymerization of halogenated anilenes by plasma" *journal of applied polymer science*: vol 102,pp 4682-4689
- [10] Morales, J., Olayo, M. G., J., C. G., Castillo, O., M. M., and Olayo, R., 2000. "Electronic conductivity of pyrrole and aniline thin films polymerized by plasma." *Journal of Polymer Science, Part B: Polymer Physics*, vol. 38, pp. 3247-3255.
- [11] Goya, K. O., Mahalingam, R., Pendrow, P. D., and Osman, M. A., 2001. "Mass transport characteristics in a pulsed plasma enhanced chemical vapor deposition reactor for thin polymer film deposition." *IEEE*
- [12] M. Bouklah, B. Hammouti, T. Benhadda, and M. Benkadour "Thiophene derivatives as effective inhibitors for the corrosion of steel in 0.5M H_2SO_4 ," *Journal of Applied Electrochemistry*,vol. 35, no. 11, pp. 1095–1101, 2005.
- [13] A. S. Fouda, A. A. Al-Sarawy, and E. E. El-Katori, "Pyrazolonederivatives as corrosion inhibitors for C-steel HCl solution," *Desalination*, vol. 201, pp. 1–13, 2006.
- [14] A. Fiala, A. Chibani, A. Darchen, A. Boulkamh, and K.Djebbar, "Investigations of the inhibition of copper corrosion in nitric acid solutions by ketene dithioacetal derivatives," *Applied Surface Science*, vol. 253, no. 24, pp. 9347–9356, 2007.
- [15] U. R. Evans, *The Corrosion and Oxidation of Metals*, Hodder Arnold, 1976.