Corrosive effect of Farmic and Acetic acid on Ferrous metal andPrevention by VCIs

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Abstract Corrosive Effect of Formic and Acetic acid on Ferrous have been observed from very long time .Most of electronic and electrical assemblies are packed in wooden boxes. It get failure on coming time due rust formation in ferrous materials because most of wood emitted vapors' of acid (Acetic and Formic acids) which accelerate the rust formation in different time duration at different RH, varies from 20% to 100%.Woods are generally made up of polysaccharides e.g hemicelluloses, xylan etc acetyl group attached to hemicelluloses which on hydrolysis gives acetic acid these vapors derived from acetyl group. Wood are mainly used in packaging materials. On degradation ,they gives acetic acid and carbonic acid vapors which corrode iron and other material which packed inside the box.(meduka indica) common name mahua wood exhalation has been studied for their corrosive behavior of mild steel.Corrosion rate of iron increased with in crease in the concentration of acetic acid.

Key words hemicelluloses, wood exhalation, degradation, meduka indica, ferrous.

Introduction

It has been generally established that the free acid vapors are derived from mild and progressive hydrolysis of acetyl group attached to hemicelluloses group in wood. The acetyl content of wood hemicelluloses is differs from species to species as also from timber to timber with in species. [1,2] Orthro –acetylated, polysaccharides were obtained from green wood of both sweet chest nut and wych alm.Extraction with water at 98^{0}C gives a mixure of polysaccharides containing xylose,galactose,glucose and uronic acid.Analysis show that only xylane in green sweet nut and green wych alm is orthro acetylated.Extraction of orthro acylated xylane showed that sweet chest nut losses 74.2% and wych alm losses43.4% acetyl groups, respectively.The lost acetyl group from wood is converted in acetic acid which causes severe corrosion[3]. Corrosion is also generally augmented by the presence of organic acid vapours[4]

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 inhibitors 3 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 replaced some widely used inhibitor such as chromates, in application where toxicity, environmental damage, and pollution caused by these chemicals are important consideration [5-6]. 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 of0.01 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 [7-9]. In the type of vapour phase process various type of material are widely used such as polyaniline [10-12], Polypyrrole [13] and poly acetylene [14).Heavy effort have been deployed to find suitable corrosion inhibitor for organic origin in various corrosive media [15-18]. 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. 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. Reaction Anodic $Fe \rightarrow Fe^{++} + 2e$

$Fe \rightarrow Fe^{+++} + 3e$

At the same time, oxygen molecules in the solution are reduced at the cathodic areas. Reaction Cathodic $H_2O + O + 2e \rightarrow 2OH$

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 Fe (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 Fe (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/dm2 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 □ 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 (Wu) and in the presence of VCI (Wi) 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 no.1 Corrosion of ferrous metal for different time duration at differentRH.

s.no	Time (indays)	100%RH wt loss(mg/dm^2)	80%RH wt loss(mg/dm^2)	60%RH wt loss(mg/dm^2)	40%RH wt loss(mg/dm^2)	20%RH wt loss(mg/dm^2)
1	15	14.0	28.0	11.0	7.0	4.0
2	30	22.0	27.0	13.0	8.0	7.0
3	45	30.0	38.0	28.0	14.0	10.0
4	60	38.0	48.0	31.0	19.0	12.0

Table no.2

Corrosive effect of vapours emitted by different Packaging wood on ferrous metal at 80% RH.

s.so	Time in months	Wt loss in mg/dm^2						
		without wood	Mango wood	Jamun wood	Eucalyptus wood	Mahua wood	Kathal wood	Chir wood
1	1	22	45	35	30	97	36	48
2	2	37	74	51	48	148	56	64
3	4	45	107	92	97	189	75	85
4	6	66	122	151	110	231	146	115

Table no.3 Corrosive effect of vapours emitted by different packaging woods on ferrous matals at 100%RH.

S.No.	**Time in months**	**Wt loss in mg/dm^2**						
		without wood	Mango wood	Jamun wood	Eucalyptus wood	Mahua wood	Kathal wood	Chir wood
1	1	18	25	24	20	27	32	22
2	2	24	32	28	34	48	45	30
3	4	32	47	44	50	64	56	37
4	6	44	50	62	48	75	68	48

Table No.4

Protective effect of metadinitrobenzene on corrosion due to vapours emitted by mahua wood at different RH

S.No.	Time in months	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	1	9.7	63	2.4	97	1.8	99
2	2	11.0	77	2.8	98	2.2	99
3	4	18.0	71	3.6	98	4.6	96
4	6	30.0	60	5.2	98	4.5	96

Table. no.5

Corrosion of ferrous metal in the presence of 0.1% acetic acid vapours at different RH for different time duration.

S.No.	**Time in (days)**	**Wt loss (mg/dm^2)**				
		20%RH	**40%RH**	**60%RH**	**80%RH**	**100%RH**
1	10	2.4	7.3	417.2	2603	Panel heavily rusted and broken
2	20	4.8	19.7	500.2	2899	
3	30	6.9	24.8	854.0	3595	
4	40	7.3	84.2	1002.8	4816	

Result and discussion

Table .1depicted that corrosion of ferrous metal at different relative humidity(100%RH to20%RH) for different time duration result showed that corrosion of ferrous metal increased with exposure time (15 days to 60days). The corrosion rate was maximum

at 80% RH during entire exposure time. It was minimum at 20%RH.The corrosion rate at 100% RH slightly less than that of 80%RH.The corrosion rate at 60%RH was less than that of100%RH and corrosion rate at 40%RH is less than that at 60%RH
Table No.2 show the corrosive effect of vapors emitted by different packaging woods e.g. mahua wood *(meduka indica*) on ferrous metals at 80%RH for duration of one month to six month. Corrosion of ferrous metal in the absence of wood i.e. in the presence of 80% relative humidity only is shown.Result showed that all the woods accelerated ferrous metal corrosion during entire exposure time. Vapors emitted by mahua wood(*meduka indica*) was highly corrosive.It accelerate corrosion rate approximately four time during entire exposure time (one month to six month)
Table No.3 Show the corrosive effect ofvapours emitted by different packaging woods at 100%RH for the time duration of one month to six month .Corrosion of ferrous metal in absence of wood at 100%RH is also shown .Result show that all the wood accelerate corrosion at100% RH also. However the rate of increase of corrosion was less in this case. Mahua accelerate corrosion two times in given time duration

In our sdudied related to performance of volatile corrosion inhibitor,it was found that metadinitrobenzene and anthraquinone are highly efficient corrosion inhibitor at100%RH,80%RH and 60%RH.Their performance at 40%RH to20%RH was not studied at these RH metal loss was very low
Table No.4 This table depicted protective effect metadinitrobenzene on ferrous metal corrosion due vapours emitted by mahua wood at 60%RH to 100%RH, during a period of one month to six month.Result show that metadinitrobenzene is very good volatile corrosion inhibitor for corrosion of ferrous metal due to vapours emitted by mahua wood at 80%RH.In this condition it afforded 98% protection.In the presence of inhibitor wt loss obtained was very low.It was 2.4 mg/dm^2 during one month which increased to 5.2 mg/dm^{2}during six month.At 100%RH the wt loss was obtained was higher and percentage protection was lower the wt loss during one month was 9.7 mg/dm^2 which increased to 30 mg/dm^2 during six months.The percentage protection ranges between 60% to77% during two month and 66% during six months.
Table No.5 Dipicted the corrosion of ferrous metal due to 0.1% of acetic acid vapours at different RH(20%RH to100%RH) for time duration of 10 days to 40 days.Result show that there is practically no corrosion at 20%RH.The wt loss obtained during 10 days were 2.4 mg/dm^2 which increased to 7.3 mg/dm^2 in 40 days. At 40% RH the wt loss was slightly higher than that at20%RH.It was 7.3 mg/dm^2 during 10 days which increased 84.2 mg/dm^{2}during 40 days. Finaly at 100%RH in days panels was highly rusted and broken.the corrosion product was leached out from the panels.

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 Ferrous metal carried out by using meta dinitrobenzene.Most of woods produced vapours which increase the rate of corrosion formation.It is proved by testing in presence of closed chamber (dessicators) mainly mango wood and Mahua woods are acid emitting woods which increases rate of corrosion formation at 80%RH to 100%RH.The rate of corrosion formation also increases due presence of vapours of acetic acid in 0.1% inside the test chamber
Investigation shows that volatile corrosion inhibitors provides very effective corrosion protection processes for the Ferrous metals such as boilers, feeders and industrial pipe lines. Volatile corrosion inhibitors can apply in the powder form at the time of manufacturing of iron equipments.
It is confirmed that VCIs provides protection to the metal located at few centimeters from the VCI source.
All types of the inhibitors can used in combination with process of vapour phase process.

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