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Short Communication

The Development of an Anti-corrosion Wrapping Tape and its Corrosion Protection Effect Evaluation on Mild Steel in Marine Splash Zone

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An anti-corrosion tape was developed and its corrosion protection effect on mild steel in marine splash zone was evaluated. The insulating effect of the tape and the inhibitors in the inner tape play a major role for the splash zone corrosion protection. Field and laboratory tests results proved that the tape is effective in the splash zone corrosion protection of mild steel, having the advantages of easy implementation.

Keywords: Mild steel, corrosion; splash zone, wrapping tape

1. INTRODUCTION

Corrosion of steel facilities in marine environment is very serious. Marine corrosion environments are usually divided into atmospheric, splash, tidal, sea water and sea mud zones [1]. Among the corrosion behaviours of mild steel in these five zones, the corrosion in the splash zone is the most serious [2]. Melchers et al. studied the corrosion mechanism via new field studies [3]. The severe corrosion is due to the factors affecting the corrosion conditions in splash zone: wet-dry alternation, seawater condensation, high oxygen concentration etc. Existing corrosion protection methods in splashed zone are composite Zn-Al alloy/organic coating [4], Ni-Cu alloy coating [5, 6] and heavy-duty coating [7, 8] etc. These methods are effective but the coating procedures are complex. For the purpose of finding a simple method for the protection of mild steel in marine splash zone, a new wrapping tape was develop ed. The protection effect of the tape was evaluated in this paper.

2. EXPERIMENTAL

2.1 Materials and sample preparation

Mild steel was used as test material. Steel rods of ϕ30mm×1000mm were used for field tests. The sample for electrochemical tests was a short rod of ϕ10mm sealed by epoxy resin except the working section of 0.785 cm^2. All the steel samples were grinded to 600# with emery paper before experiments.

2.2 Preparation of the Anti-corrosion Wrapping Tape and field tests

A corrosion inhibitor $N[CH_2CH_2\text{-}O\text{-}PO(OH)_2]_3$ (inhibitor A) with high value of inhibition efficiency was synthesized first. Then, an anti-corrosion paste was prepared by adding $N[CH_2CH_2\text{-}O\text{-}PO(OH)_2]_3$, ZnH_2PO_4 (inhibitor B) and other additives in a resin. The wrapping tape involves an inner layer and an outer layer. The inner layer is nonwoven fabric that infiltrated in the anti-corrosion paste. The outer layer is nonwoven fabric that infiltrated in resin hardener. The purpose of this design is to provide a corrosion protective cover with a soft inner layer and hard outer layer. Experiences show that the soft inner layer can have a better contact with the steel surface than hardened coating. The anti-corrosion effect of the protection layer of the wrapping tape is attributed to the insulating effect of the layer and the inhibiting effect of the inhibitors in the inner layer.

Before wrapping, the grinded steel rods were prepared by wiping the surface with a clean cloth first, followed by wiping with a clean cloth dipped in ethanol and then drying. The procedure was repeated several times to ensure that the steel sample having a clean surface.

The first stage wrapping was to wrap the surface of the steel rods by twisting the inner anti-corrosion strips around the rods. Two layers of inner anti-corrosion strips were applied. Then, an outer layer was applied to form a hard layer.

The protected rods and unprotected rods were tested at splash zone in a field corrosion experimental station (Qingdao, China). The corrosion of the rods was assessed by measurement of their diameter change and by examination of their appearances before and after field tests. Standard de-scaling solution [9] was used to remove the rust from the rods

Conventional weight loss methods were not used because of the large size of the steel sample rods. The corrosion was evaluated by measuring the diameter change of the rods. When measuring, the rod was divided into several segments; each segment was 10 cm apart. Nodes were marked one by one on the rod from the top to the bottom. At every node, the diameter of the rode was measured four times with a vernier caliper at 90 degree interval to obtain four numerical diameter values. The mean value of the diameter was reported.

2.3 Evaluation of inhibitors in the inner wrapping tape by electrochemical tests

Polarization curve measurements were performed on unprotected electrochemical samples in natural seawater at room temperature with and without inhibitors. The potentials are reported versus saturated calomel electrode.

3. RESULTS AND DISCUSSION

3.1 Corrosion rate measurements by field tests

After one and two year's field tests, steel rods were collected from the field test station. After removing wrapping materials from the surface of the protected steel rods, de-scaling of the rusted bare surfaced rods and cleaning, the diameter of the rods was measured.

The corrosion rate *W* (mm/a) of the coupons was calculated using the following formula,

$$W = \frac{d_2 - d_1}{2t}$$

where d_1 is the mean value of the pre-exposure diameter, and d_2 the mean value of the diameter after field exposure tests, t is the duration of the exposure. The calculated corrosion rates are presented in Table 1.

Table 1. Corrosion rate of steel rods by field tests, mm/a.

	Un-protected	protected
One year's exposure	0.2920	0.0025
Two year's exposure	0.3066	0.0011

According to Table 1, the corrosion rate of the steel rod protected by wrapping tap is 99.14% lower than that of un-protected rod. Practically, the protected steel rod does not show any corrosion.

3.2 Appearance of the steel rods before and after field exposure

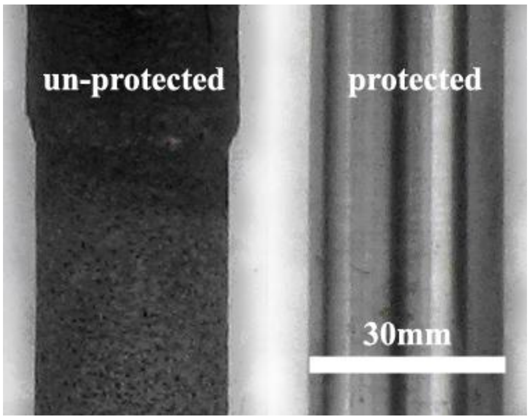

Figure 1. Morphology of unprotected and protected samples after exposure testes at splash zone, showing the severe corrosion and the effect of wrapping tape on corrosion protection.

The effectiveness of the corrosion protection by wrapping tap was also evaluated by the appearance of the steel rods before and after field exposure, which is shown in Figure 1. The de-scaled steel rod without protection showed rough surfaces, while the rod protected by wrapping tape showed shinny surfaces practically without corrosion.

3.3 Comparison of polarization curves of samples in seawater with and without inhibitors

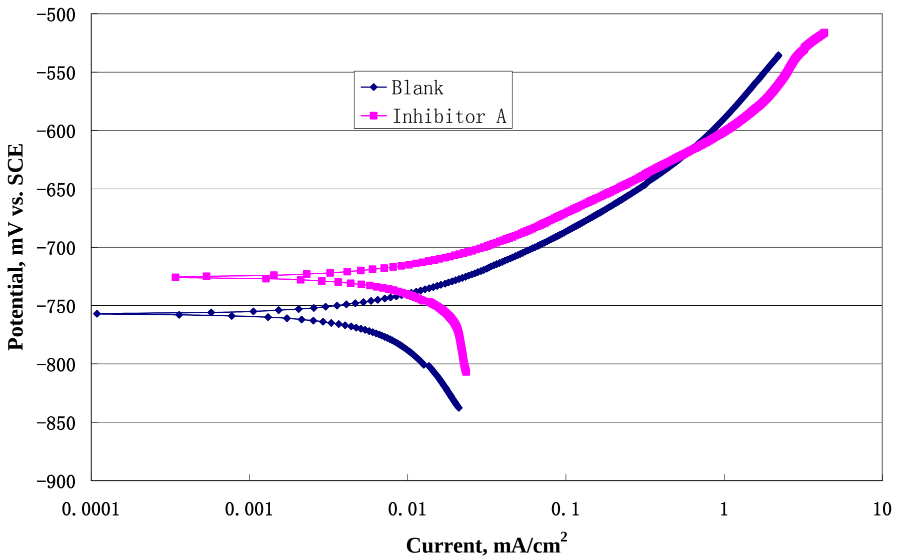

Figure 2. Comparison of polarization curves of samples in seawater (blank) and seawater with inhibitor A: N［CH_2CH_2-O-PO（OH）$_2$］$_3$, 0.18g/L

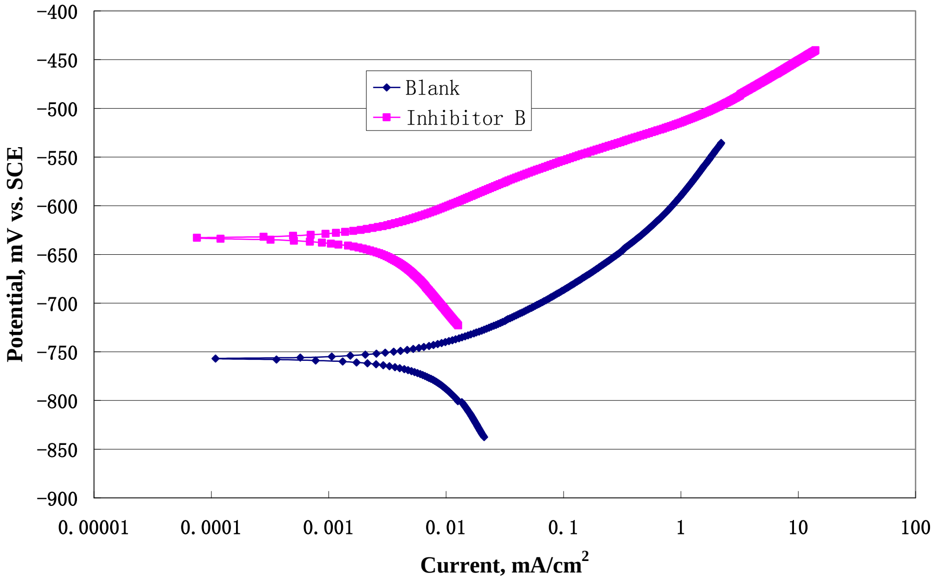

Figure 3. Comparison of polarization curves of samples in seawater (blank) and seawater with inhibitor B: ZnH_2PO_4, 0.18g/L

Figure 2 and 3 show the comparison of polarization curves of samples in seawater (blank) and seawater with inhibitor N［CH_2CH_2-O-PO（OH）$_2$］$_3$ and ZnH_2PO_4 respectively. The calculated electrochemical parameters from these polarization curves are shown in Table 2.

Table 2. Calculated electrochemical parameters of carbon steel in seawater, seawater containing 0.18g/L N［CH_2CH_2-O-PO（OH）$_2$］$_3$, and seawater containing 0.18g/L ZnH_2PO_4 at room temperature

	Blank	N［CH_2CH_2-O-PO（OH）$_2$］$_3$	ZnH_2PO_4
E_{corr}, mV vs. SCE	-758	-725	-633
I_{corr}, mA/cm^2	0.01	0.009	0.0016
β_a, mV/dec	75	60	48
β_c, mV/dec	181	148	131

According to the concept of action coefficient of inhibitors on anodic and cathodic reactions f_a and f_c [10]:

$$\ln(f_a)_{E'_{corr}} = \ln\left(\frac{I'_{corr}}{I_{corr}}\right) - \frac{E'_{corr} - E_{corr}}{\beta_a} \qquad (1)$$

$$\ln(f_c)_{E'_{corr}} = \ln\left(\frac{I'_{corr}}{I_{corr}}\right) + \frac{E'_{corr} - E_{corr}}{\beta_c} \qquad (2)$$

Where I_{corr}, E_{corr}, β_a and β_c are corrosion current density, free corrosion potential, anodic and cathodic reaction Tafel slops of carbon steel in seawater (blank) respectively. I'_{corr} and E'_{corr} are corrosion current density and free corrosion potential of carbon steel in seawater with inhibitor respectively. If the coefficient is lower than 1, then the inhibitor will inhibit the corresponding reaction. The calculated coefficients of the two inhibitors are shown in Table 3. The results show that N［CH_2CH_2-O-PO（OH）$_2$］$_3$ is anodic type inhibitor and ZnH_2PO_4 is mixed type inhibitor.

Table 3. Calculated value of f_a and f_c for N［CH_2CH_2-O-PO（OH）$_2$］$_3$, and ZnH_2PO_4 in seawater

	N［CH_2CH_2-O-PO（OH）$_2$］$_3$	ZnH_2PO_4
f_a	0.58	0.03
f_c	1.08	0.32

ZnH_2PO_4 is mixed type inhibitor, the part $H_2PO_4^-$ in the molecule is anodic type inhibitor. Under the effect of dissolved oxygen in seawater, $H_2PO_4^-$ can react with the anodic corrosion product

Fe^{2+} to form insoluble $FePO_4 \cdot 2H_2O$ and γ—Fe_2O_3 sticking to the surface of steel surface. The formed membrane is firmly combined with the steel matrix, having a good chemical stability, inhibiting the anodic reaction [11].

The Zn^{2+} in ZnH_2PO_4 is cathodic type corrosion inhibitor, possibly forming unstable $Zn(OH)_2$ precipitation membrane.

N［CH_2CH_2-O-PO（OH）$_2$］$_3$ is a kind of anode type corrosion inhibitor. Its hybridized atoms N and O contain one pair and two pairs of lone pair electrons respectively. They are all electron donors and can be used as ligand of chelate coordination bond and they can react with the anode reaction product Fe^{2+} or iron atom of the substrate to form five element chelate with good chemical stability of. The chelate is deposited on the surface of the steel, preventing the contact of corrosion media with steel surface and the release of iron ion into solution, thus inhibit the anodic reaction. In addition, N［CH_2CH_2-O-PO（OH）$_2$］$_3$ has many branched chains with shielding effect. When the surface film is damaged, it has the ability of restoration [12].

When seawater penetrates into the inner layer of the wrapping tape, the inhibitors play the corrosion inhibition role through the above mechanism. The field experiment verified that the corrosion protection of splash zone can be obtained through the wrapping tape procedure.

4. CONCLUSION

The developed wrapping tape is effective for mild steel corrosion protection in splash zone. The wrapping tape has the effect of insulating corrosive media's contact with the surface of steel. When seawater penetrates into the inner layer of the wrapping tape, the inhibitors in the inner layer release from the layer and play the corrosion inhibition role preventing the corrosion of steel at splash zone.

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References

1. K. Zen, *Corros. Sci.*, 47(2005) 2353.
2. R. Jeffrey, R. E. Melchers, *Corros. Sci*,. 51 (2009) 2291.
3. R. Melchers, R. Jeffrey, *Corros. Sci.*, 47(2005) 1678.
4. B. R. Hou, J. Zhang, J. Z. Duan, Y. Li, J. L. Zhang, *Corros. Eng. Sci. Techn.*, 38(2003)157.
5. Institute of chemical machinery, Ministry of Chemical Industry, *Manual of Corrosion and Protection*. Chemical Industry Press, Beijing, China (1991)
6. G. Wildsmith, "Copper Alloys for sea water systems and splash zone protection". Paper to Norges Ingeniørorganisasjon, Conference on Corrosion Control, April 1985

7. Y. Harada, S. Miyata, M. Yoshida, K. Takeda, S. Nishizawa, *Corrosion and Corrosion Control in Saltwater Environments* in D. A. Shifler, P. M. Natishan, T. Tsuru, S. Ito, *Electrochemical Society Series*, 99(2000)119
8. Qingning Li, *China Offshore Platform*, 26(2011)52
9. ISO 9226-1992 Corrosion of metals and alloys; corrosivity of atmospheres; determination of corrosion rate of standard specimens for the evaluation of corrosivity
10. Cao Chu'nan, Yang Qiangang, Lu Min and Lin Haichao, *Journal of Chinese Society for Corrosion and Protection*, 12(1992)109
11. Jiang Fuhua, Zhangping, Zhong Zhaoquan, *Corrosion and Protection*, 15(1994)182
12. Zeng Hualiang, Yang Jiachang，*Electrolysis and chemical conversion film*, Light Industry Press, Beijing, 1987