ANTI-CORROSIVE PERFORMANCE OF WASH PRIMER BASED ON MANGROVE TANNIN

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ABSTRACT

Aqueous acetone extract from bark of *Rhizophora appiculata* or locally known as bakau minyak was tested for anti-corrosive properties by incorporating the powdered extract in wash primer formulation. The anti-corrosive behaviour of steel panels treated with water-based formulations was assessed employing salt spray accelerated test (ASTM B 117) in comparison with the standard chromated wash primer. The results indicated that the wash primer formulated solely with tannin as an anti-corrosive agent showed significant anti-corrosive properties in reducing the corrosion of steel. However, the fully tannin-based wash primer showed an inferior performance compared to the standard chromated primer. On the other hand the superior performance of tannin-based wash primer had been achieved by a mixture of tannin with zinc phosphate in the ratio of 1: 3. The anti-corrosive properties of the mangrove bark extracts seem to be related to the tannin which are capable of chelating with Fe^{3+} giving a highly stable, and insoluble ferric-tannate complexes. The tannin in the wash primer may act as Fe^{3+} scavengers that converts the ferric ions into ferric-tannate which inhibited the diffusion of dissolved oxygen to underlying steel.

BACKGROUND

Common steels are protected from corrosion principally by painting schemes in such applications as manufacturing, structure protection and automobile fabrication. Paint life depends on various factors such as the metallic substrate, the selected painting scheme and the paint-substrate inter-phase. In automobile and manufacturing industries, where plain steel generally is painted, a wash primer coat is typically used to increase the adherence and to improve the anticorrosive quality of painting films. These primers, known as reaction primers are formulated basically with phosphoric acid (H_3PO_4) and zinc chromate ($ZnCrO_4$) in alcohol medium, where polyvinyl butyral participates as a ligand of the reaction product [1].

Chromate based pigments have been used for many years as anticorrosive pigments in wash primers and other alkyd and epoxy primers. In recent years, chromium, and especially chromates (hexavelant chromium), have been found harmful. Chromates have been found to cause irritation of the respiratory tract, produce ulcerations and perforations of the nasal septum, and produce lung cancer in workers employed in chromium manufacturing plants in West Germany and the United States [2].

There have been several investigations into alternative anticorrosive pigments, such as zinc phosphates, barium metaborate and alkoxy titanates and ziconates, in alkyd resin systems [3,4,]. A Chromate-free wash primer based on a polyvinyl butral resin containing a combination of phosphate and borate anticorrosives pigments,coloring pigments, alcohol solvents, and an organofunctional silane has also been developed [2].

Due to its toxicity, chromates constitute a hazard and need to be replaced by more environmentally acceptable corrosion inhibitors. In this sense a system containing tannins, a class of natural, non-toxic, biodegradable organic compounds has been proposed [2,5]. The tannins were found to react with a ferric cation to yield ferric-tannate, producing a film that inhibits further oxidation.

In this study, wash primers based on mangrove tannins have been formulated and the anticorrosive properties have been investigated, leading to the development of chromate free wash primer having properties superior to the chromated wash primers.

EXPERIMENTAL

The extraction of tannin from mangrove barks (*Rhizophora appiculata)* was carried out by total immersion of finely ground barks (150 mesh) in 70% aqueous acetone for 72 hours at room temperature. The solution was filtered using the Buchner apparatus and the acetone was removed under reduced pressure at ≤ 30 °C. The filtrate was then defatted with hexane and brown solids of tannins were obtained after freeze-drying the aqueous solution. The freezed-dried tannin yielding 15-20% of the dry barks was used for the wash primer formulation without further purification.

Wash primers of a two component system were prepared as shown in Table 1. Part A (Formula 1-6) and Part B were mixed in 4 : 1 ratio. A simple formulation of Formula 7 consisting of 20% (w/w)

tannin solution acidified to pH 2 with phosphoric acid and containing 0.25% isopropanol was prepared and referred as a tannin rust converter. The Canadian General Standard Board Specification of 1-GP-121wash primer formulation [5] as shown in Table 2, was prepared and used as a standard.

Mild-steel panels approximately 7.0 cm x 13.0 cm and 2.5 mm thick which had been mechanically wire-brushed and abraded with aluminium oxide paper down to visual brightness and free of any residual rust were used as exposure panels. The panels labeled B1 – B6 (corresponding to formula 1-6) were coated with wash primer at a dry film thickness of 10-15 μm. The panels that were coated with CGSB-1-GP-121 formulation were labeled as K, while panels labeled H were panels which were coated with a formulation using zinc phosphate instead of zinc tetroxy chromate in the CGSB-1-GP-121 formula. Panels labeled F7 were coated with tannins rust converter of formula 7, and a steel panel without any coating was included as a control. All panels were scratched with an X (5 cm in length) except the F7 and the control panels. The panels were subjected to the salt spray accelerated tests (ASTM B 117) for 24 hours, after which they were removed from the chamber for evaluation of general and scribe corrosion as described in Table 3[2]. The evaluations were conducted at 24 hour intervals for the next 144 hours (6 days).

Table 1: Wash primer formulation

Part A	Formula 1	Formula 2	Formula 3	Formula 4	Formula 5	Formula 6	Weight (g)
Resin 10% *PVBR (w/w)	✓	✓	✓	✓	✓	✓	64.5
Solvent	✓	✓	✓	✓	✓	✓	28.5
Tannin pigment	✓					✓	3.60
Zinc chromate pigment		✓					
Zinc phosphate pigment			✓		✓		
Fe_2O_3 pigment				✓			
Fe_2O_3 (s)	✓	✓	✓	✓			1.00
Tannin					✓	✓	
Pyrogenic Silica	✓	✓	✓	✓	✓	✓	0.40
Talc	✓	✓	✓	✓	✓	✓	2.00
Total							100.00
Part B							% (w/w)
85% (w/w) H_3PO_4	✓	✓	✓	✓	✓	✓	18.0
H_2O	✓	✓	✓	✓	✓	✓	16.0
Iso-propanol	✓	✓	✓	✓	✓	✓	66.0
Total							100.0

*PVBR – polyvinyl butyral resin

Table 2: Canadian General Standard Board Specification 1-GP-121 formulation.

Part A	Weight (g)
Polyvinyl butyral resin	30.50
Zinc tetroxy chromate	29.40
Magnesium silicate	4.40
Lamp black	0.33
n-butanol	68.00
Ethanol (denatured)	207.00
Total	339.60
Part B	
85% (w/w) H_3PO_4	15.30
H_2O	13.60
Ethanol (denatured)	57.10
Total	86.00

Table 3: Qualitative Description of Performance Rating.

Rating	General Description	Scribe Corrosion
6	No rust staining	No rust in score
5	Minor rust staining	Minor rust in score
4	Light rust staining	Light rust in score and up to 1mm from score
3	Rust staining over 20% of surface	Rusting in score and up to 2mm from score
2	Rust staining over 50% of surface	Rusting in score and up to 5mm from score
1	Heavy rust over entire surface	Heavy rust in score and up to 5mm from score

RESULTS AND DISCUSSION

After 24 hours of exposure, all panels showed a minimum amount of rust being formed at the scratched area while the rest of the surface remained clean except for the control panels that almost rusted throughout the surface. A fair amount of rust formed on the F7 panel (rust converter) which indicated that the rust converter exhibited a corrosion protection when compared to the control panel. After 48 hours of exposure, the F7 panel was mostly covered with rust indicating that the tannin rust converter failed to retard further corrosion.

Figure 1 shows some photographs of high rated performances of formulated wash primers, while the results of the salt spray tests for panels B1 –B6, H and K after 144 hours are presented in Figure 2. The results indicated that wash primers of Formula 3, 5 and 6 containing zinc phosphate, zinc phosphate in combination with tannins and tannins respectively have great potentials as anti corrosives. Using tannin alone (B6) did not greatly improve the corrosion resistance as compared to the use of zinc phosphate (B5). However the use of tannins in combination with zinc phosphate in the ratio of 1: 3 exhibited an inhibitive property superior to that of the chromated wash primers(B2 & K). This result is in agreement with the fact that tannin, when combined with phosphoric acid yielded a product more acidic than the phosphoric acid itself. The acid constant of the product obtained by the reaction between tannin and phosphoric acid was found to be equal to 4.0×10^{-2} while the first acid constant for phosphoric acid is 7.0×10^{-3}. This association compound enhanced the adhesive strength of tannin in steel [5].

Natural tannins are polyphenols of vegetal origin and the proximity of hydroxyl groups on the aromatic rings makes them able to chelate iron ions. A rapid reaction was found to occur between rusty iron and natural tannins. The transformation of rusty iron into the blue-black coating layer has been attributed to the complexation of the polyphenolics moiety of the tannin to the iron oxides and oxyhydroxides [7]. Although other complexation products undoubtedly formed, the ferric tannate complex has been cited as the major product. Ferric tannate of dark blue colour are highly insoluble and acts as a barrier layer on the metal surface [8].

The following corrosion inhibiting mechanism which was proposed when a reaction primer formulated with pine tannins at pH 3.2 was used, further affirms the results obtained :

$$Fe + 3H^+ + \tfrac{3}{4}.O_2 = Fe^{3+} + 3/2\ H_2O \quad (1)$$

$$Fe + 2H^+ + \tfrac{1}{2}O_2 = Fe^{2+} + H_2O \quad (2)$$

$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ = Fe^{3+} + \tfrac{1}{2}H_2O \quad (3)$$

$$\text{Tannin-OH} + Fe^{3+} = (\text{Tannin-O-}\ Fe^{3+})^{2+} + H^+ \quad (4)$$

$$\text{Tannin-2OH} + Fe^{3+} = (\text{Tannin-2O-}\ Fe^{3+})^{+} + 2H^+ \quad (5)$$

$$\text{Tannin-2OH} + (\text{Tannin-2O-}\ Fe^{3+})^{+} = (\text{Tannin-4O-}\ Fe^{3+})^{-} + 2H^+ \quad (6)$$

The iron tannates formed contained corrosion inhibitor characteristics. Tannate formation acidified the reaction environment, making its reaction with clean or oxidized metallic substrate selfcatalyzed[9].

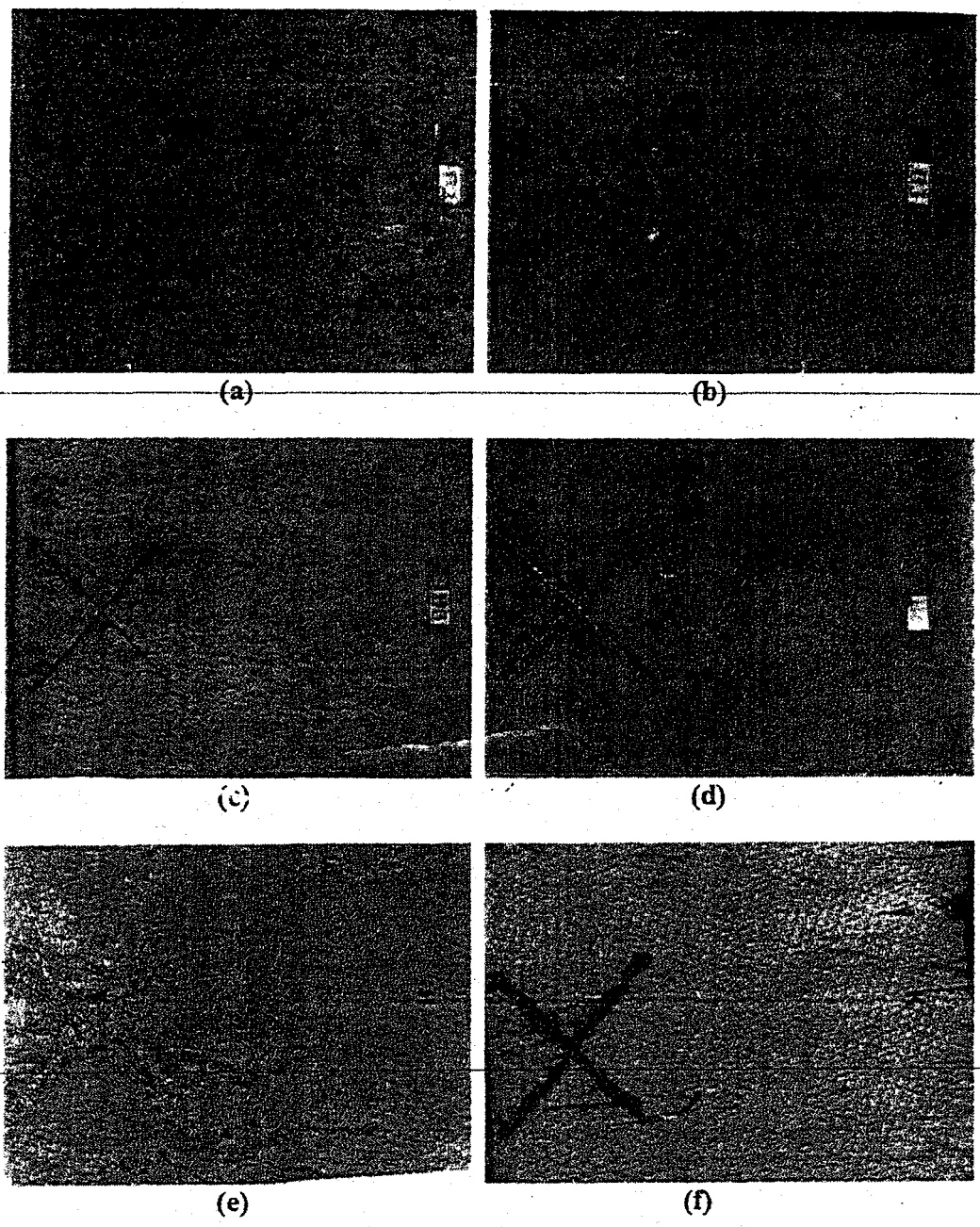

Figure 1 : Photographs of (a) B2; (b) B3; (c) B5; (d) B6; (e) H and (f) K after 144 hours salt spray exposure tests.

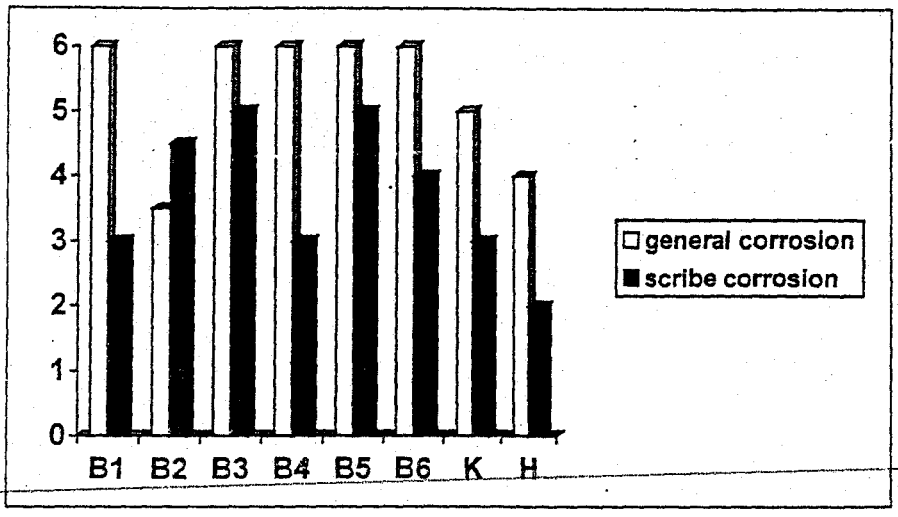

Figure 2 : Rating of general and scribe corrosion performance on steel panels after 144 hr exposure of various primers.

CONCLUSION

1. Mangrove tannins had shown a considerable anticorrosive property as a rust converter and wash primer. The tannins based rust converter was not able to achieve a good corrosion protection in aggressive environments for long periods of exposure. It could only be used for temporary corrosion protection.
2. Wash primers based on tannins alone, exhibited a remarkable anticorrosive property. However it's inhibitive performance was inferior with respect to the phosphate and chromate containing wash primers.
3. Wash primers based on the combination of tannins and zinc phosphates in the 1:3 ratio, showing superiority over the chromated and standard chromated wash primers, provided the best alternative to formulating a chromate free wash primer.
4. The anticorrosive property of mangrove tannins indicated that it could be developed for future use in the various corrosion protection areas.

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ACKNOWLEDGEMENT

The authors wish to thank Universiti Sains Malaysia for the financial support through the IRPA short term grant : 305/PKIMIA/622187.