

## Tar-Free Epoxy/Amine Curing System for Corrosion Protection of Ballast Tanks

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Preservation of seawater ballast tanks is one of the biggest maintenance burdens. It is well known that coal tar is one of the best materials to protect steel substrates against marine corrosion and is also prevalently widely used in ship tanks so far. However if tar-containing paint is applied, it is harmful to health and especially dark color (black or brown) is only available, which makes uneasy to detect the defects of painting and rust. We have studied and developed a light color, modified amine cured epoxy coating system, which reveals perfect protection performance even though without tar for long-term service period. The coating system is less harmful to health as it does not contain coal tar materials and meets the stringent VOC regulation in view of its low content of organic solvent (SVR>80%).

Experiments have been carried out on three kinds of substrates, shop-primed panels, blast-cleaned panels and pre-rusted panels. All test specimens were compared with commercialized tar containing epoxy coating on equivalently treated steel substrates. We will report the test results in laboratory, general anti-corrosion properties, adhesion properties and cathodic protection data from seawater cycle test and wave tank simulation device. And also the results being reported will include the survey for field applications.

**Keywords** : corrosion, barrier, epoxy, tar, tank.

### 1. Introduction

Marine coatings are the key materials used to obtain the full design service life from ships, structures, and equipment exposed to the marine environment. The marine environment is characterized by constant exposure to salt water, sunlight, and abrasion. The atmosphere has constant moisture that ranges from high salinity seawater (3.5% salts) to nearly distilled water from rain and condensation. The constant spray and splash of water, coupled with the salt concentrating effect of drying, causes materials to degrade much more rapidly than would be the case away from the sea. Surface temperatures range from below freezing to as high as 65 °C for a dark surface on a sunny day. The thermal shock, caused by alternating exposure to hot sun, cold seawater and rain, severely stresses materials used in the marine environment. So, unprotected metals corrode rapidly, lose strength, and become more susceptible to damage from the stresses of wind and waves combined action of sunlight and the penetration of water and salt. The severity of this environment is often not fully appreciated, particularly by people who have only worked in inland locations. Fig. 1 illustrates the general types of

environmental exposures encountered.

Marine coatings are distinguished from other coatings by their intended usage. Most are classified as heavy-duty industrial coatings that have been tested and proven for use in the arduous marine environment. Marine coatings serve two basic functions. First, they help prevent the deterioration of materials caused by exposure to the marine environment. Second, they impart physical and chemical properties to surfaces that cannot be obtained in any other way. Typical uses of marine coatings are as follows:

- \* Protect metallic structures and the elements (hull, equipment, or electronics) from damage due to corrosion
- \* Prevent fouling (the attachment and growth of marine organisms)
- \* Protect cargoes from contamination
- \* Provide safety warnings and information markings
- \* Provide cosmetic and camouflage colors
- \* Roughen walking surfaces to prevent uncontrolled slipping and sliding on wet or moving decks
- \* Provide high dielectric strength coatings required for effective, economical cathodic protection
- \* Reduce fire hazards

The two general types of marine corrosion control coatings

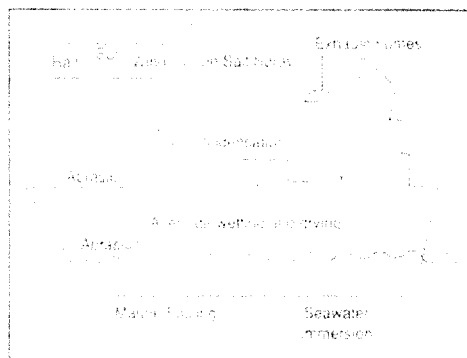


Fig. 1. Marine environment.

are those intended for intermittent exposure to moisture and those designed for continuous immersion service. The intermittent exposure systems are typically used on the exterior portions of structures above the waterline. Continuous exposure systems are used in ballast tanks, wet bilge, fuel/ballast tanks, and on the underwater portions of structures. The primary difference between these systems is the mechanism used to protect the metal. Continuous immersion systems are high dielectric strength insulating layers coupled with cathodic protection systems to prevent corrosion. Intermittent exposure systems rely on the formation of a high dielectric strength insulating layer and/or chemical inhibition to prevent corrosion. These coatings all need to have low permeability to moisture and ions barrier property.<sup>1)</sup>

The most common and most economical method used to slow or stop the corrosion reaction is to break the connection between the metal and the electrolyte by using a coating to form a barrier between the electrolyte and the metal.<sup>2)</sup> Barrier coatings are often formulated to include corrosion inhibitors. However, substituting inert ingredients for the corrosion inhibitors (e.g., substituting iron oxide for red lead) often has no effect on the protective value of the coating. This suggests that the barrier properties of coatings are their most important property for use in the marine environment.

The barrier effect is performed most effectively when the coating film is highly hydrophobic and water-repellent. Coal tar is considered as the best material for the purpose of barrier protection, and widely used with other materials to protect marine corrosion (e.g., epoxy or polyurethane).<sup>3),4)</sup>

Coal tar coatings are made from processed coal tar pitch and dissolved in suitable petroleum solvents. They form a film by evaporation of the solvent and the film can be redissolved again by solvents. Coal tar films provide very good corrosion protection. However the dry film is damaged by direct exposure to sunlight, which causes rapid, severe cracking. Coal tars are normally blended with other

resins to improve on their light stability, to increase their chemical resistance, and to increase the number of colors available. Without expensive processing, most coal tar resins are very dark colored and the only colors that can be made from them are black or silver/black (made by using flake aluminum for pigment).

One of the common blending resins with coal tar is epoxy material. Coal tar epoxy paints are blends of epoxy resins with coal tar. Coal tar epoxy films have high chemical resistance, easily form thick films, and have a high dielectric strength. The high dielectric strength makes them particularly suitable for use near anodes in cathodic protection systems. The high current densities in these areas can damage other types of coatings. Coal tar epoxy coatings are known to exude low molecular weight fractions, which cause recoating problems. Recently the U.S. Navy limits the use of coal tar and coal tar epoxy coatings due to the possibility of low levels of carcinogens in the refined coal tar.<sup>5)</sup>

Epoxy coatings came into general use in the 1960s.<sup>6)</sup> These coatings are used where high wear resistance and resistance to seawater immersion or chemical attack is required, like tanks, freeboard areas, decks, and on the underwater hull. Epoxy coatings for marine applications are typically formed by the chemical reaction of a bisphenol A type epoxy resin with a curing agents (e.g., amines, amine adducts, or polyamide resins). Epoxy coating films are strongly resistant to most chemicals, and make excellent anticorrosion coatings. They are one of the principal materials used to control corrosion in the marine environment.<sup>7)</sup>

We have studied epoxy systems for barrier coatings and developed light colored epoxy coating system having a perfect anti-corrosion property, even though it does not contain tar and so is it less harmful to human.

## 2. Experimental

### 2.1 Formulations

Two types of coating materials were formulated. One was commercialized coal tar epoxy system (which is denoted as CTE), and another was tar free epoxy system (which is denoted as TFE). Table 1 and 2 indicate formulations of two systems.

### 2.2 Preparation of testing panels

Each of the coating material was air-sprayed being 250  $\mu\text{m}$  of dry film thickness on three classes of steel surface treatment. The first class was shot blasted panels to Sa 2½ according to SIS 055900. The second class was shop-primed panels with zinc ethyl silicate shop primer of about

**Table 1. The formulation of CTE system**

Ingredient	Wt%	Vol%
Coal tar pitch	28.6	34.1
Polyamide resin	6.9	9.3
Talc	36.8	18.0
Gelling agent	1.1	1.0
Additives	0.8	1.1
Solvents	13.6	22.2
Epoxy resins	12.2	14.3
Totals	100%	100
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PVC, %	28	
Nonvolatile, %	79	
Volume solids, %	73	
VOC, g/L	250	

**Table 2. The formulation of TFE system**

Ingredient	Wt%	Vol%
Epoxy resins	18.5	23.8
Diluent	4.6	7.1
Talc	36.9	19.7
Titanium dioxide	12.2	4.5
Pigments	1.5	0.9
Additives	3.5	5.5
Solvents	10.0	18.3
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Polyamine	9.3	13.9
Diluent	1.1	1.6
Catalyst	1.3	1.9
Solvents	1.1	2.8
Totals	100%	100%
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PVC, %	32	
Nonvolatile, %	86	
Volume solids, %	81	
VOC, g/L	195	

20 μm after blast-cleaning to Sa 2½. And the third class was pre-rusted panels that were exposed in a salt fog spray chamber for 18 hours-dried 5 hours after blast-cleaning to Sa 2½ and application of vinyl tar on the reverse sides, then this procedure was repeated 4 times.

All panels were cured in a ventilated room at a temperature of 18~25 °C with a relative humidity between 40 and 60%.

The panels were marked B for blasted, Z for zinc rich primed, and R for rusted, respectively.

**2.3 Test methods**

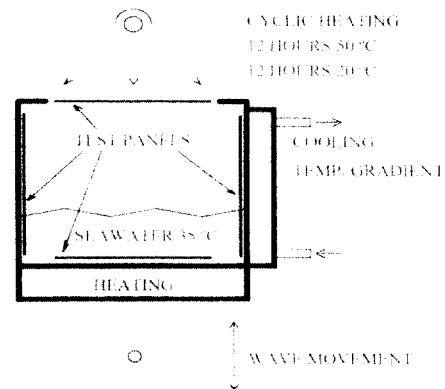
Corrosion tests were carried out in a salt fog spray chamber, ballast wave tank, and condensation chamber. Salt fog spray chamber was Q-Fog cycle corrosion tester manufactured by Q-panel Laboratory Products. The corrosion test was carried out according to ASTM B117.

Ballast wave tank contained natural seawater of 35 °C and room for 4 test panels. The test panels were one deck panel, one side panel with cold wall effect (temperature gradient about 15 °C), one side panel without cold wall effect and one bottom panel with zinc anode. The tank had wave movement to achieve splash of seawater and temperature heating by radiation on the deck panel (12 hours 50 °C / 12 hours room temperature). The test cycle was 2 weeks with the seawater and wave movement and 1 week with seawater below the bottom panel and no wave movement. Fig. 2 represents the block diagram of ballast wave tank.

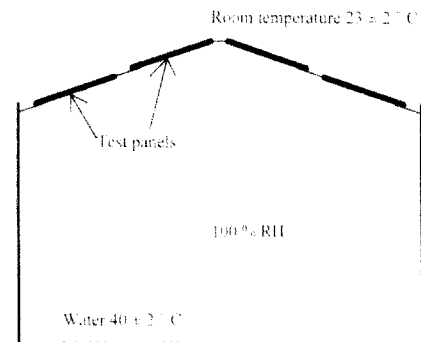
Test panels in condensation chamber were exposed to continuous condensation, which may accelerate moisture penetration and eventually blister formation. A covered plastic chamber had fresh water of 40 °C in the bottom.

The test panels were placed on the top of the chamber at an angle of 15 to the horizontal with the back side to the room temperatures 23±2 °C. Water evaporating from the bottom of the chamber condensed under the panels on the coating to be tested. The block diagram of condensation chamber is represented in Fig. 3.

Pull-off adhesion tests were done before and after corrosion test according to ASTM D4541.



**Fig. 2. Block diagram of ballast wave tank**



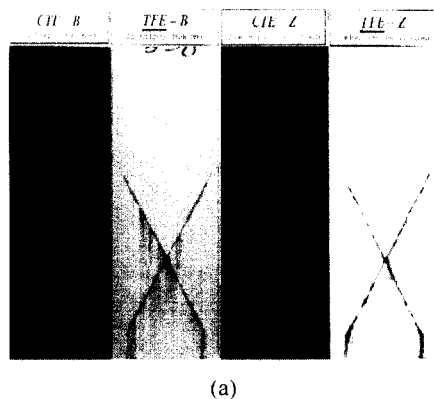
**Fig. 3. Condensation chamber**

### 3. Results and discussion

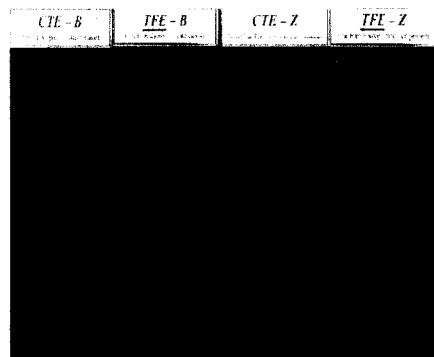
#### 3.1 Salt fog spray and seawater immersion tests

The salt fog spray test was done with 5% NaCl solution at 35 °C according to ASTM B117. The test was prolonged for 3500 hours (about 175 days with instrument operation of 20 hours a day) and at every 500 hours (25 days), the states of test panels were checked out and compared with each other. Fig. 4 represents the results of 1000-hour and 2500-hour test.

Corrosion was not developed in zinc rich primed panels (CTE-Z and TEF-Z) until 500-hour observation but blasted panels (CTE-B and TEF-B) were slightly rusted. After about 800 hours, CTE-Z and TEF-Z started with rust near the scribed area, however the entire test panels, it appeared corrosion to proceed fastest in the period between 2000-hour and 3000-hour exposure. Moreover CTE-B and TEF-B failed at 3500-hour exposure but CTE-Z and TEF-Z stood for corrosion longer than 3500 hours. It was evaluated by checking adhesion power in the region of unscribed area, which values were reduced more than 50% of adhesion power for the case of CTE-B and TEF-B, but there



(a)



(b)

Fig. 4. Results of salt fog spray test of (a) 1000 hours and (b) 2500 hours.

was no loss of adhesion power in CTE-Z and TEF-Z. Fig. 5 shows the result of CTE-Z and TEF-Z after 3500-hour exposure.

When the test panels were immersed in fresh seawater at room temperature for 6 months, corrosion on the scribe underwent nearly negligible compared to panels exposed in salt fog spray chamber and blister or rust was never found in unscribed area. Simple immersion test was not helpful to compare anti-corrosion property of coatings. Fig. 6 shows result of seawater immersion test of 6 months.

The adhesion was from 4.5 to above 8 MPa dependent on substrate treatment without loss.

Tests in ballast wave tank and condensation chamber Tests in the ballast wave tank and condensation chamber were done for another information of nearly close to real corrosion situation. Ballast wave tank was filled to 1/3 of its volume with seawater, which kept a temperature of 35 °C. There were mounted four test panels measuring 20×40×0.3 cm in their size: one on the top, one on the bottom, and two panels on opposite vertical sides. The reverse side of the panels was painted with three coats of vinyl tar. The top panel was heated to 50 °C for 12 hours

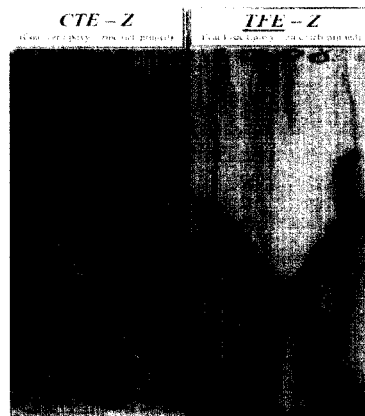


Fig. 5. Result of 3500-hour exposure of Zinc rich primed panels



Fig. 6. Result of 6-month seawater immersion test.

and 20 °C for 12 hours, in order to simulate the temperature change from daytime and nighttime. One of the vertical panels was cooled at the reverse side, giving a temperature gradient of 15~20 °C through the coating. Such gradients had been found to be detrimental to many types of coatings, and this effect would simulate e.g. a cooled bulkhead in a ballast wing tank. The other vertical panel had no heating/cooling and the bottom panel had a fixed sacrificial zinc anode in order to evaluate the effect of cathodic protection.

The test cycle was run for two weeks with seawater and one week empty. When empty, some seawater was left in bottom to achieve a high relative humidity in the tank. In this period, it could simulate an empty tank with no effect from the anode.

On the other hand, corrosion in condensation chamber was done according to ISO 6270. This test is specially designed to evaluate coatings for the protection of steel in environments with high humidity and condensation, giving an information regarding the water permeability of a coating system. The size of test panels was 15 × 15 × 0.3 cm.

The exposure time was 6 months for coatings on zinc rich shop-primed and blast-cleaned panels and 60 days for coatings on pre-rusted panels for all tests. For all test panels, no significant rust was found except the panels on the top of ballast wave tank, which were only the panels applied thermal shock cycle of simulating day and night. It is a very important information giving us what the major effect on corrosion is. Because the coating is organic material, the physical state of coating film is dependent on temperature. That is, at high temperature, it becomes more flexible and increases free volume, so be more permeable for water or any other elements of accelerating corrosion. On the other side, at low temperature, the coating film becomes less permeable, so the corrosion goes relatively slow down. However when the temperature fluctuates high and low repeatedly in such a case as panels on the top of ballast wave tank, the coating film ages faster than that of under steady circumstance (such as other panels in ballast wave tank or condensation chamber) whether temperature gradient is or not. At this point, the aging of coating again accelerates corrosion of steel.

Another important fact is that because tar mostly does not react with epoxy group, thus it just remains in coating film and acts as plasticizer. It changes crosslinking density and gives flexibility more to coating film even though the film reaches full curing,<sup>8),9)</sup> this causes corroded materials (e.g., zinc salts and iron oxides produced by under coat corrosion) to bleed out more easily through the coating film. But there was no bleeding of corrosion on unplasticized

(not containing tar) epoxy coating. Fig. 7 displays very well the phenomena of rusts bleeding through coal tar epoxy coating of the panels on the top of ballast wave tank in comparison with tar free epoxy coating in equivalent environment.

For the other test panels, there was neither significant rust nor blister. Fig. 8 shows the example of the test panels in condensation chamber, which are also same in the degree of rust development as panels except on the top in ballast wave tank. In all cases of test, zinc rich shop-primed panels were less corroded and pre-rusted panels were more corroded than blast-cleaned panels. These results suggest that steady states of environment such as immersion in seawater, contact with seawater vapor or temperature difference of steel substrate do not contribute seriously to under coat corrosion of steel, however the environment of temperature fluctuation would take a major role of corrosion.

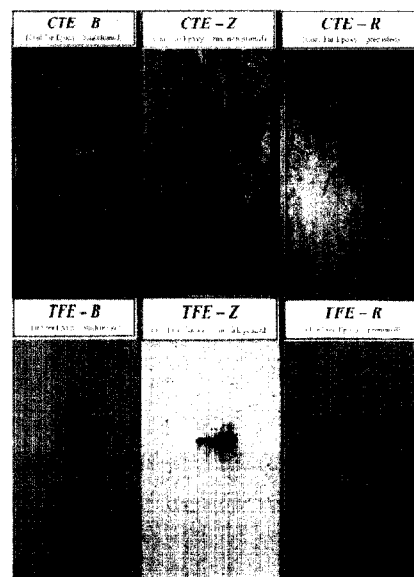


Fig. 7. Test panels on the top of ballast wave tank after exposure

### 3.2 Cathodic protection

Table 3 is data measured from the panels with zinc anode on the bottom of ballast tank and on the top of condensation chamber. The size of zinc anode was 20 mm of diameter and 25 mm of height. It was attached on the center of test panel and was weighed before and after exposure. There was no rust or blister grown in any of test panels, this was for cathodic protection of zinc. The weight loss of zinc anodes attached on blast-cleaned panels was higher than that on zinc rich shop-primed panels. This is a reasonable result because zinc of shop primer also exhibited cathodic protection to reduce consumption of zinc

**Table 3. Results of cathodic protection**

	Coal Tar Epoxy			Tar Free Epoxy		
	CTE - B	CTE - Z	CTE - R	TFE - B	TFE - Z	TFE - R
<i>Zinc anode weight loss(g)</i>						
Ballast wave tank	0.369	0.321	0.074	0.732	0.275	0.141
Condensation chamber	0.134	0.132	0.207	0.183	0.169	0.043
<i>Current demand(mA/m<sup>2</sup>)</i>						
Ballast wave tank	1.0	0.9	2.1	2.0	0.7	1.1
Condensation chamber	1.3	1.3	1.7	1.8	1.6	1.2

anode on zinc rich primed panels, however blast-cleaned panels had only zinc anode to prevent corrosion. In the case of pre-rusted panels it is impossible to compare the values of them with other test panels because they were exposed for shorter time.

The consumption of zinc anode was higher in the test of ballast wave tank than condensation chamber. In the ballast wave tank, test panels were contacted with saline water almost for test period but in the condensation chamber just vapor was contacting the test panels. Ionic components are very important to accelerate corrosion, so test panels exposed in ballast tank spent zinc anode more than those in condensation chamber.

Impedance measurements were typically carried out at the open-circuit potential with 10 mV amplitude of 60 Hz. The current demand for a good protective coating is below 10 mA/m<sup>2</sup> and for bare steel is from 60 to 100 mA/m<sup>2</sup> dependent on temperature and seawater flow velocity.<sup>10)</sup> The results measured were from 1 to 2 mA/m<sup>2</sup> without any trend for treatment of steel substrate, these values are sufficiently low to suppress under film corrosion. As a result, it suggests again that steady states of environment do not play an important role of corrosion.

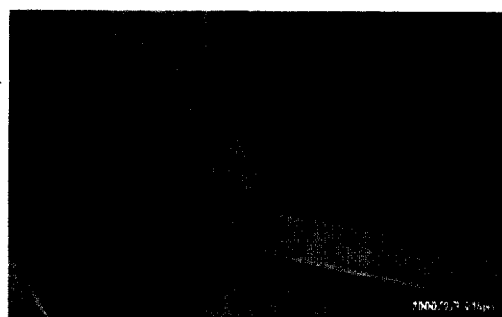
There was no loss of adhesion, it was from 4.5 to above 8 MPa dependent on treatment of steel substrate.

#### Survey for field applications

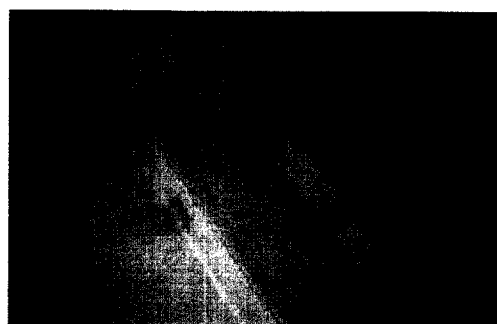
Tar free epoxy coating material, which had been developed and evaluated in laboratory test, has been commercialized and applied to more than 70 ships since 1996. It has been set a high value on its very successful corrosion protection performance, famed as one of the most trustworthy coating materials for water ballast tank of ship. Fig. 9 shows the pictures of actual results after 38-month and 64-month service periods on water ballast tanks.

### 3.4 Conclusions

A tar free epoxy coating material was developed and applied on water ballast tanks in substitution for coal tar



(a)



(b)

**Fig. 9.** Photographs of survey (a) after 38-month and (b) 64-month service periods

epoxy coating material. Its corrosion protection performance under fixed environment proved equivalent with coal tar epoxy coating, however it was superior of anti-corrosion property to coal tar epoxy coating in the condition of especially thermally changing environment. This is due to plasticizing effect of coal tar that remained unreacted in coal tar epoxy coating film. As a result, most contributing factor on aging of coating film and undercoating corrosion is irregular thermal change of steel substrates and epoxy coating material is more suitable for expecting long term protection of water ballast tank than coal tar epoxy coating.

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