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The New Anticorrosive Coating Systems For Ship Hulls

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The paper describes the research works of new anticorrosive coatings systems for ship hull. The protective coating systems include two anticorrosive primers: fast drying water-based inorganic silicate zinc coating and a special organic zinc-rich coating which is mainly contained zinc flakes, as well as tie coat and top coat. The coating systems have passed a series of tests, including the common performance testing in Lab, accelerated testing, the simulate exposure test in sea water and ship tests. The testing results indicate that the performances of the protective coating systems are superior to that of actual applying on ships now.

Keywords *: anticorrosive coatings, performance test, ship hulls, epoxy zinc primer*

1. Introduction

The coating on ship hull, especially above water line , will be easily failed soon, as the sea water eroding, the sun light exposure as well as impact and abrasive mechanical factors. The maintenance interval is very short. Generally it should be applied several times a year. The research workers are more concerning with the work with long-term live of anticorrosive coating systems.

2. The Screening Of Formulas And Performance Tests

In order to improve the anticorrosive performances of ship coating systems it should be pay more attention with the selection of primers and compatibility of total coating system. The main research works include two parts: the high performance anticorrosive primer and total coating systems.

2.1 The high performance anticorrosive primer

Concerning with the ship construction and maintenance works two kinds of primers are selected, fast drying water-based inorganic silicate zinc primer and a special epoxy primer which is mainly contains zinc flakes. It can be applied with both primers while the surface treatment and field conditions are suitable for application, such as the new ship building and the steel surfaces can be cleaned with sandblasting. While it is more difficult for surface treatment and application the special epoxy zinc-rich primer can be more suitable for ship painting work.

2.1.1 The water based high modular and self curing inorganic zinc-rich primer

The first step is made a special high modular silicate gel, then formulate a fast drying and self curing inorganic silicate zinc coating. According to the standards both in home and abroad a series of performance tests had been carried on. The main test methods and results is listed in Table 1.

2.1.2 A special epoxy zinc primer

The epoxy zinc-rich primer is the one of the most common primers in ship industry in China at present. In order to applied enough electrical protection the percentage of zinc dust in the dry film should be very high. The high zinc content is easily settled and caking. The mixed coating should be continuously agitate during application to ensure zinc particles can be dispersed evenly.

The another type of zinc dust is a laminated zinc pigment. The zinc flakes within the film could not only play the role of sacrificial anode, but also show certain barrier property as zinc flakes arrange in parallel with the surface of coat. That will improve the ability of corrosion resistance of coating and application easily. Because of the lamella nature of zinc pigments the settling of coating in storage might be considerably reduced.[1,2,3)]

According to the formula design of epoxy zinc-rich primer and the properties of raw materials the Table 2 lists the test methods and conditions for formula screening.

Table 1. Performance test methods and results for water based inorganic zinc coating

Item	Test method	Test conditions	Results
1	Storage stability	Two components, after 1 year storage at the room temperature, shall be mixed in 4 hours	Two components can be easily mixed into a smooth, uniform mixture by hand.
2	Dry time	The cured panel shall be subjected a running water test in accordance with GB 1729-79.	surface dry ≤30min, hard dry:2h and the cured coat film can be subjected a running water test.
3	Pot life	The mixed coating shall be sealed and stored at 23±1℃, RH=80±5%, Determine the time between mixing and the loss of adequate brushing and spraying properties.	The mixed coating can be used in 6h.
4	Flexibility	The cured film shall be bent 180 degrees over a 16 mm mandrel in accordance with GB/T 6742-86.	No cracking or disb.nding from substrate.
5	Adhesion	Both adhesive tape test and direct pull-off test	Adhesive tape test: no lifting and flaking Direct pull-off test: 8.38 MPa
6	Abrasive resistance	Determining the loss of film as weight 1000g, rotor 1000 circles in accordance with GB/T 1768-79.	The loss of film :0.057g .
7	Accelerated weathering	Checked after 1000h and 2500h exposure in accordance with GB/T 1865-80.	No blistering, rusting or flaking
8	Humidity resistance	The panels shall be exposure at 47±1℃, RH=96(2%, checked after 3500h in accordance with GB/T 1740.	No blistering, rusting or flaking
9	Salt spray resistance	Checked after 5000h in accordance with GB/T1771.	No blistering, rusting or flaking d after 5000h expose.
10	Cathodic protection	The coated panels with a 40 mm and 65 mm diameter circle bare metal area immersion in synthetic seawater.	The coated panels with aφ 40 mm circle bare metal area can prevent corrosion in 210 days andφ 65 mm in 90 days.

Table 2. Performance test methods for epoxy zinc primers

Item	Test method	Test conditions
1	Salt spray resistance	Checked after 336h in accordance with GB/T1771.
2	Humidity resistance	The panels shall be exposure at 47±1℃, RH=96(2%, checked after 168h in accordance with GB/T 1740.
3	Adhesion	The direct pull-off test in accordance with ASTM D4541
4	Flexibility	The cured film shall be bent 180 degrees over a mandrel in accordance with GB/T 6742-86.
5	salt water immersion	0.5M NaCl solution

2.2 The selection of tie coat

The tie coat is a necessarily part for the anticorrosive coating system. The consideration for selecting tie coat is as follow: a. The binder of tie coating should be the same or compatible with that of the primer and top coat. b. The tie coating contains lamella barrier pigments. c. The tie coating should have excellent properties, such as sea water resistance, impact resistance etc.

Considering the primers are water base silicate zinc or epoxy zinc coatings the epoxy coating containing micaceous iron oxide (MIO)had been chosen. Two kind of epoxy MIO tie coatings had been carried screening tests, including salt resistance and adhesion measurement.

2.3 The performance tests for anticorrosive coating systems

2.3.1 Accelerated testing in Lab

Accelerated testing program includes 100h salt spray chamber exposure alternating with 100h in artificial weathering (Fluorecent UV-Condensation type) as a cycle. Total 1000h conduct 5 cycles. After testing the coating performances are evaluated[4)]

The test results include blister and rusting on the coat after exposing in salt spray chamber; the chalking color loss and cracking after artificial weathering test.

2.3.2 Actual expose tests in marine environment

Among the performance tests for marine anticorrosive coating system actual expose tests in marine environment are the intermediate stage between tests in Lab and actual ship test. Three expose tests are conducted in the research work:

ⓐ The splash zone expose test

The test panels are placed on splash zone in the floating raft (10~30 cm above water line). Test conditions are much severe, since in addition to the direct UV, further UV is reflected off the water surface, and sea water always splashes on the surface of panels and humidity is high

ⓑ Marine atmosphere expose

The test panels are fixed on the flames which are very closely to seaside for long time expose.

ⓒ The simulate object is placed on the natural sea water in test pool.

The size of simulate object is much bigger than ordinal teat panels in Lab. The coating application is more similar with that in ship.

2.3.3 The ship test

The most important test of marine coating systems is the ship test. Two ships, including deck area and ship hull, are applied and tested since 1996.

3. Results and Discussion

3.1 Anticorrosive primers

3.1.1 The self curing inorganic zinc-rich primer

3.1.1.1 A special potassium silicate gel

A special potassium silicate gel is condensated from compounds of potassium silicate, curing agent and other reactive resins with a control conditions.

Through a lot of screening tests of multi factors and multi levels design the formula KW-8 has been selected for using in coating. The screening tests include the stability in 40±2℃, surface dry time in 25±2℃ and relative humidity 50±5%, water spraying resistance after 4h dry, salt water immersion and adhesion.

A fast drying and self curing inorganic silicate zinc coating: E06-99 is been selected from coating formula screening tests. The results are listed in Table 1.

3.1.2 A special epoxy zinc primer

The formulas: TY513 and TY527 have been selected from screening tests. The main properties are listed in Table 5.

In order to evaluate the effect of performance of anticorrosive while the amount of zinc in the formula TY513 and TY527 is less than that of a common zinc rich primer, the comparison test are conducted between TY513 ,TY527 and an epoxy zinc rich primer. The results are showed in Table 4.

It can be included that there are no effect to their performance of rust resistance in TY513 and TY527 while the amount zinc dust reduced one third compare with a common epoxy zinc rich primer. Meanwhile the storage stability and application performance can be improved.

The cross section of coat film of TY513 in SEM showed that the laminar zinc dust in film are oriented with film surface provided a barrier function.

Table 3. Performance tests

test method	Performance	
	TY513	TY527
salt spray resistance	The film show no blistering, rusting or flaking after 336h expose.	
humidity resistance	The film show no blistering, rusting or flaking after 168h expose.	
flexibility	passing 5mm mandrel	
salt water immersion	The film show no blister, rusting or flaking after 90d expose.	

Table 4. The comparison test between three epoxy zinc rich primer

test method	epoxy zinc rich primer		
	TY513	TY527	common formula
immersion in salt water (0.5M NaCl,30d)			
flat area	very small spots	good, no rust	small spots
cross cutting area	white sediment	good, no rust	no rust
salt spray resistance (336h)			
flat area	good	good	
cross cutting area	good	good	
humidity resistance (49℃, RH≥95%, 168h)	good	good	
adhesion(GB5210-85), MPa	4.50	4.21	4.0

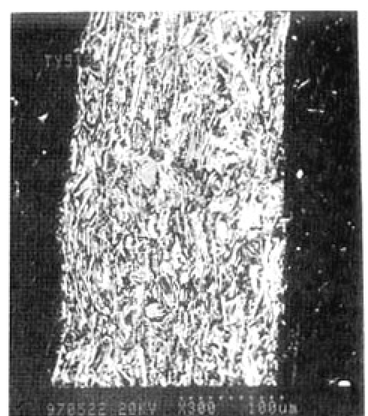

Fig. 1. The SEM analysis of coat film of TY513

3.2 The accelerated corrosion tests of the coating systems

Three coating systems are exposed in salt spray and artificial weathering test. The results are listed in Table 5.

Their corrosion resistance (rusting,blistering and flaking) and weathering properties (color fading, chalking and cracking) of three coating systems are excellent in the flat areas, except slight color fading after 1000h expose time. The anticorrosive properties of coating system, E06/t-coat/EB1 is better than other two in the cross cutting area.

Table 5. The results of accelerated corrosion test 1000h

performances		coating systems		
		TY513/t-coat 2/EB1	TY527/t-coat 2/EB1	E06/t-coat 1/EB1
rusting	flat	no	no	no
	cross cut	slight	slight	very slight
blistering	flat	no	no	no
	cross cut	no	no	no
flaking		no	no	no
color fading		slight	slight	slight
chalking		0 grade	0 grade	0 grade
cracking		0 grade	0 grade	0 grade

3.4 Actual marine exposure test for coating systems

3.4.1 The marine splashing zone exposure

The test results in marine splashing zone after three years are listed in Table 6.

Table 6. The marine splashing zone exposure

coating system	properties
TY513/t-coat 1/EB-1	complete coat, no rust, flaking and blistering
TY527/t-coat 1/EB-1	complete coat, no rust, flaking and blistering
TY513/t-coat 2/EB-1	complete coat, no rust, flaking and blistering
TY527/t-coat 2/EB-1	rust in fixed hole area, others are good
E06-99/t-coat 1/EB-1	complete coat, no rust, flaking and blistering

3.4.3 Actual exposure test of a simulate cylinder specimen

The cylinder specimen is immersed in the sea water pool . The upper half part of cylinder is exposed in marine atmospheric and other half part is immersed in the sea water. The test results are as follow after 2 years expose:

1. The coating system on the upper half part of cylinder shows good appearance, no rust, no flaking and no blistering. A slight rusting appears on the welding spots only.

2. A little marine fouling attached on the lower half part, but coat film is good.

3.5 The ship test for coating systems

3.5.1 The test of No.1 ship

The deck area and partly hull area on 9 and 12 section in ship were conducted coating application test in March, 1999. The testing coating systems show good condition after 1 year. No rusting, blistering and flaking appeare on the test areas. Comparing with other areas which applied with common coatings, it had been applied for three to four times in a year time. It approves that the new anticorrosive coating systems have excellent protection properties.

3.5.2 The test of No.2 ship

The main deck areas are coated the new coating system in three years. The deck areas are subjected very severe marine corrosion environment and adrasion. The testing coating is still showed a good protection.

4. Conclusion

1. The new marine coating systems are reached the following technical properties:

① Adhesion: ≥3MPa

② Accelerated expose test: 100h salt spray +100h accelerated weathering cycling, the coating system show no flaking, slight chalking and color fading after 1000h.

③ Sea water dynamic test: coating system show no flaking and no rusting after 100h testing.

④ The corrosion resistance property of new marine coating system is better than that of actual using in ship now.

2. The water based inorganic zinc coating E06-99 possess an excellent corrosion resistance, curing fast, good in abrasion and heat resistance.

3. The special epoxy zinc primer TY513 is better than common epoxy zinc rich primer in the property of corrosion resistance. Their application and storage stability can be improved much than that of a common epoxy zinc rich primer.

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Effects of Current Wave Forms and Current Densities on the Electroplated Cu Interconnection in Damascene Plating

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Effects of three different types of current waveforms and current densities on damascene copper line filling capability were investigated. The electroplating solution developed for printed circuit board (PCB) was used for Damasçene plating. Three different types of current wave forms i.e. direct current (DC), Pulsed current, and periodic (PR) current methods were chosen for electroplating with the variation of current densities. The cross-section profiles of deposited wafers were analyzed by Field Emission Scanning Electron Microscope (FE-SEM). Trenches were successfully superfilled without void for Cu lines with 0.4 and 0.8㎛ width according to each current waveform. Each current waveform was optimized with the proper current density values. The critical causes for the center and the sidewall void formations were investigated. Copper plating profiles due to DC current waveform showed center void in the final stage of plating because the copper deposition on the trench top corner was faster than those inside of trench. On the contrary, Pulsed or PR current methods tend to result in center voids due to the faster deposition on the sidewall. Sidewall void formation could be attributed to the localized corrosion of copper seed layers due to long immersion of the wafer in the electrolyte at zero current state before plating.

Keywords : Copper, Superfilling, Damascene plating, Current wave form, Current density

1. Introduction

Ever since the development of the integrated circuit about 40years ago, the most pervasively used materials for the fabrication of the wiring structure have been Al as the conductor. As interconnect continue to scale down, the relatively high resistivity of Al became the major problems. The problems are RC delay time and low resistance of elecrtromigration and stressmigration.[1-2) Therefore new material is required as the substitute for Al.

Cu provides desirable high conductivity, 1.67Ωcm, compared with 3.0(cm of Al. For that reason Cu has advantage of the short RC delay time over Al.[1,5) Since the allowed current density of Cu can be more improved due to the higher conductivity and electromigration resistance than Al, the interconnect scale can be reduced. Different from to the conventional Al interconnection by subtractive metal etching of a planer Al film, Cu interconnect is introduced by trenches etched in the dielectric that are subsequently filled with metal.[3) This process is called Damascene process. It is getting difficult to fill trench as the trench width becomes smaller and the aspect ratio bigger. Therefore various deposition methods have been evaluated for copper including PVD, CVD, electroless plating and electroplating. PVD method tends to form center void because of poor step coverage while CVD method may form seam because of conformal deposition. However, in case that Cu electroplating onto the inside trenches can occur preferentially at the bottom, void free deposition can be obtained. This special phenomenon is called superfilling, also known as bottom-up.[1) Filling in trench by electroplating method depends on various parameters such as agitation, additives, current waveforms and current densities.[4) For the damascene process, the trench geometry results in a lower flux of the inhibitor to the bottom of the feature than to the external surface. Consequently, the metal deposition kinetics proceeds more rapidly at the bottom of the trench than at sidewall of the trench, which results in superfilling. Current density and types of wave forms has an effect on the microstructure of Cu film.[4) DC (direct current), Pulse (pulse