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COATINGS FOR MARINE ENVIRONMENTS

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In India the cost of corrosion prevention in marine industries may be of the order of Rs.100 crores. The different areas of service are: (1) Immersed in seawater (2) Splash waterline (3) Super structure area near seawater. Painting is the principal means of protection; other methods such as cathodic protection, are used only in conjunction with paint coatings. Hence it is necessary to provide long term maintenance-free protection and to minimise the time out of service when maintenance of ship is essentially required.

In this article the mechanism of corrosion prevention by paints, pretreatment, paint system, method of application of paint for different types of structures and equipments used in marine environments are described. A comprehensive protective system consisting of primer + under coat + finishing paint + antifouling paints is included. Application of the organic coatings and details of type of fouling and the use of different types of antifouling compounds used in the paint formulation are given. The protective schemes for dock and harbour installation, offshore structure, super structures and deck areas are discussed. The causes of paint failure and the specification, requirements of paints are described.

Key Words: Organic coating, corrosion prevention, marine environment

INTRODUCTION

The electrochemical mechanism of corrosion of steel in seawater has a great bearing on the properties required of a protective paint system for ships' hulls and structures in marine environments. Painting is the principal means of protection, other methods such as cathodic protection being used only in conjunction with paint coatings. On the underwater areas of ships' hulls, special paints are used to prevent attachment and growth of marine plants and animals. The formulation of these paints, called antifouling compositions, is a specialised aspect of marine paints technology. The different areas of service are: (1) immersed in seawater (2) splash water line (3) super structure area near sea water. It was estimated in 1971, that the cost of corrosion and its prevention in U.K. marine industries was 280 million pounds a year and that the use of existing knowledge could save 55 million pounds. In India, the cost of corrosion prevention in marine industries may be of the order of Rs.100 crores. Hence it is necessary to provide long term maintenance-free protection and to minimise the out of service time when maintenance of ship is eventually required. The use of sophisticated protective coating system is fully justified under these circumstances. Paints for freight containers for ships and high performance coatings, chemical resistant coatings to meet performance requirements for marine, chemical plants, offshore installations are being imported. It is estimated that requirement of offshore paints by the ONGC for the period 1984-1990 would be 3 lakh litres costing nearly 10 crores of rupees.

CORROSION PREVENTION BY PAINTS

The corrosion of steel in sea water can be prevented by suppressing the electrochemical reaction and this is theoretically possible by (a) suppressing the anodic reaction (b) suppressing the cathodic reaction (c) interposing such high electrical resistance between the metal and the seawater so as to prevent the flow of corrosion current. In general, highly cross linked films have the highest ionic resistance. An obvious practical consideration is that the resistance of paint film increases with its thickness.

Paint systems

The specification must suggest a complete coating system from individual primers, anticorrosive midcoats, tie coats and antifouling top coats. Each component is selected to perform a specific function to be compatible within the total system. The marine environment contains such destructive forces as salt water, constant washing, sunlight and fouling. These are complicated by high condensing humidity, chemical pollution in ports, extreme variations in services, temperatures and severe mechanical abuse within the extremely hostile environment. Marine coating systems are required to protect vessels, offshore structures and docks, terminals, and storage facilities. The paint should provide (a) high electrical resistance between metal and seawater and (b) withstand alkaline condition.

Types of structures in marine environment

Vessel must be subdivided into: Commercial, Government, Pleasure
Area: Exterior, interior, decks, bottom
Substrate: Steel, aluminium, fibre glass, wood
Service/size: Cargo vessels, tanker, tug barge, work boat, motor launch, hydrofoil
Offshore structures: Drilling platform, Navigational aid
Dock facilities: Tanks, piling
Terminals and storage: Pumping equipment require interior facilities and exterior coatings

Marine painting has by necessity, been approached under this most adverse condition of climate and time, hence even a most general estimate of expected service life is unreliable. The following may be considered:

(1) Selection of proper materials with specification
(2) Rigid adequate surface preparation

(3) Employing satisfactory application technique
(4) Insisting of sufficient time schedules to implement the programme.

Surface preparation and application

Commonly used methods of surface preparation are:

(a) Blast cleaning
(b) Pickling
(c) Flame cleaning
(d) Hand cleaning with power driven tools

The following Swedish pictorial standards are used:

SA3	White metal
SA2 1/2	Near white metal (95% clean)
SA2	2/3 of white metal
SA1	Brush off blast (removal of loose rust)

Application

Avoid early morning and late afternoon dampness and all cold weather painting and allow sufficient time for drying coating, applied by spraying.

Coating system

(1) Primer coating for metal
(2) Articorrosive coatings
Shop blast primer + epoxy resin zinc rich
(3) Antifouling coatings

Shop plate primers — Cure quickly, not toxic, not interface with flame cutting.

1. Wash primer or pretreatment primer or metal conditioning primers (7.5 - 10μ thickness)

Advantages of wash primer are:

(1) Possible use over damp, newly blasted surface
(2) Ease of handling application
(3) Excellent adhesive bond with minimum air cure time
(4) Economy
(5) Ideal touch capability

2. Primers based on specific vehicles

Marine primers include formulations based on specific materials such as vinyl, chlorinated rubber, epoxy, epoxy - coal tar. Most of these materials are used as resin basis for successful high performance anticorrosive and antifouling coatings.

3. Zinc rich primer

A single coat provides galvanic protection of steel in atmospheric exposure but a top coat is generally required for long exposure and more severe service such as immersion or exposure to strong acid or alkaline conditions. Zinc rich primers are used extensively as shop primers and as weld primers in new work, and they enjoy wide service in repair yard. They are of two major types according to vehicle, organic epoxy and inorganic (e. g. silicate).

Subsequent top coats vinyl, epoxy are applied to inorganic zinc silicate primer, the adhesive bond being mostly mechanical and polar. Organic zinc rich primer can tolerate poor surface preparation. Both types can be easily applied to 25-75μ. Organic zinc rich primers are softened by top coat.

Inorganic zinc rich paint is more fire resistant than organic. Organic zinc rich paints are well suited for spot repair but they are not suitable for immersion service.

	Post cured type - Required acid curing
Zinc silicate	Self cured type - based on hydrolysed ethyl silicate
	Water type - based on water soluble silicates

All the inorganic types have excellent abrasion resistance, hardness and toughness, but not flexibility. Other vehicles, like lithium silicate, phosphates, silicate ester, zinc, lead silicates, red lead, lead peroxide, chromates and sulphides are added to extend pot life.

Organic zinc rich

The principal binder today is vinyl, epoxy, epoxy - polyamide, chlorinated rubber. But primer based on styrene polyester, acrylics, urethanes, silicates are also used.

Vinyl zinc rich primer with top coat of vinyl chloride is well suited for fresh water immersion.

Organic zinc rich have longer service life than inorganic because of less conduction.

Methyl isobutyl ketone: Xylene (70 : 30)

Methyl ethyl ketone : Xylene: cellosolve acetate (45:45:10)

The corrosivity of seawater is affected by interaction of many chemical, physical and biological factors. They are given in Table I.

TABLE-I : Factors in seawater environment

Chemical	Physical	Biological
Dissolved gases O_2, CO_2	Velocity, air bubbles, suspended silt	Biofouling, hard shell type. Type without hard shell Mobile/semi-mobile type
Chemical equilibrium Salinity pH	Temperature	Plant life Oxygen generation CO_2 consumption
Carbonate Solubility CO_2 generation	Pressure	Animal life O_2 consumption

The paint failures are generally due to one or more of the following causes:

(1) The choice of unsuitable interior paint system
(2) Inadequate surface preparation
(3) Painting under adverse ambient conditions
(4) Insufficient dry film thickness
(5) Failure due to insufficient time for surface preparation and paint application.

Types of paints used in various structures in different environments are given in Table II.

TABLE-II: Paints used in various structures

Area of shops	Type of paint system		
	1st choice	2nd choice	3rd choice
1. Under water	Epoxide	Oleoresinous	Chlorinated rubber
2. Boot topping	Chlorinated rubber	Epoxide	Oleoresinuos
3. Top side	Epoxide	Oleoresinous	Chlorinated rubber and vinyl paints
4. Super structure	Oleoresinous	Polyurethane	-do-
5. Weather deck	Epoxide	Oleoresinous	-do-

Paint should conform to minimum specifications:

(1) Freedom from undue settlement, thickening or gas evolution on storage
(2) Freedom from skinning
(3) Ease of application by brush or spray or roller
(4) Minimum drying time for repainting
(5) Freedom from unreasonable health or safety hazards.

The coatings used in underwater paint system and the minimum thickness required are given below:

Type of paint	Minimum DFT (μ)
1. Bitumen or pitch pigmented with aluminium powder	175 - 225
2. Oleoresinous	175 - 225
3. Epoxide resin	200 - 250
4. Coar tar epoxide resin	250 - 375
5. Vinyl resin	150 - 200
6. Chlorinated rubber	175 - 225

High performance protective paint systems

The long periods in service with short maintenance periods are necessary for economical operation and for this high performance coating systems are required. These are based on the newer types of non-saponifiable resins such as epoxies, vinyls and chlorinated rubber which resist the alkaline conditions associated with cathodic protection and are in general applied at a dry film thickness of 100 μ per coat. The coatings depend mainly on their high film thickness for their protective properties and provide resistance inhibition, chemical inhibitive properties being of secondary importance. Typical systems have a total dry film thickness of 300 - 400 u and are obtained by air-less spray in 3 or 4 coats.

INSPECTION

Painting must be inspected regularly to ensure that specification regarding:

(i) Surface preparation (ii) Wet and dry film thickness (iii) Mixing of two pack materials (iv) Application of two pack materials within the stated pot life (v) Drying time, over coating intervals and (vi) Quality of workmanship are met.

Techniques have been developed for underwater cleaning of ship bottoms using rotary nylon or wire brushes; in some ports this is used regularly to remove light fouling and to revise the surface of an antifouling composition without dry docking the vessel.

APPLICATION METHODS AND HAZARDS

The area of the outer hull of a 3 lakh tonnes tanker exceeds 30000 m^2. High build paint coatings can be satisfactorily applied at 100-125 μ per coat by brush. An airless spray gun however is capable, under practical conditions of applying about 50 - 80 l/hr, which corresponds to a rate of 150 - 400 m^2/hr, when applying typical high build paint. Here, marine paints are formulated and manufactured so as to be suitable for airless spraying i. e. they must be capable of application to vehicle surfaces at the wet film thickness (200 - 250 μ) without sagging or running. Airless praying is the most widely used method for applying marine paints.

ANTIFOULING COMPOSITIONS

Types of fouling

'Fouling' is the term applied to the growths, either animal (shell fish) or vegetable (weed) which can infest a ship's bottom. Fouling takes place mainly when the ship is at rest, and its presence can seriously reduce the speed of a vessel or result in increased fuel consumption to maintain the scheduled speed.

Degree of fouling

The degree of fouling depends on several factors: (a) Season of year—around the British Isles, fouling takes place from April to September; in tropical waters, all the year round (b) temperature of water (c) geographical location (d) the amount of light reaching surface.

Types of toxics (poisons) used

Copper compounds have been the most widely used toxics since the time when copper sheathing was used to protect wooden vessels. Red cuprous oxide (Cu_2O) is the common form, but white copper thiocyanate and electrolytic copper powder are also used.

Yellow mercuric oxide was formerly used to augment the cuprous oxide and to extend its toxicity to a wider range of plant forms. The improved performance, however, does not justify the very high cost of mercury compounds, and their use in antifouling compositions has been discontinued.

A large number of organic toxics have been examined in antifouling compositions, and the organo-tin compounds have been found to be very effective, particularly the tributyl and triphenyl-tin compounds.

A more recent development has been copolymerization of organo-tin compounds with polymers so that the tin becomes part of the organic film. For example, interesting antifouling properties are shown by copolymers of tributyl-tin methacrylate with acrylic and styrene polymers.

With organo-tin compounds, the critical leaching rate of tin is considerably lower; published figures suggest that tin is nearly ten times as effective as copper.

TYPES OF COMPOSITION

Soluble matrix

These are based on a solution of rosin and oleoresinous medium. They function by slow dissolution of the acidic rosin in the slightly alkaline seawater (pH 8.0 - 8.2) so that fresh poison is being exposed continuously. The dissolution rate can be controlled by inclusion of water-insoluble substances. Materials employed in the medium include rosin, linseed/tung/modified phenolic varnish, pitch, Stockholm tar, waxes etc. The service life of this type of composition is influenced by the film thickness, and by the application of multiple coats and at least two years, life is possible.

Insoluble matrix

In this type of composition, the toxic is leached out slowly while the binder remains in tact and unaffected by the sea water. The concentration of toxin is sufficiently high to give particle to particle contact, so that as each particle is dissolved by the sea water, another is exposed. Concentrations of toxin are of the order of 0.8 to 1.0 kg of cuprous oxide per litre of mixed cuprous oxide and copper powder. Types of binder employed include chlorinated rubber and vinyl resins.

DRY HOLDS

In addition to protection of the steel, abrasion resistance is required, together with maximum light reflectance. A typical painting scheme consists of red oxide/zinc chromate primer on a tung oil/phenolic medium followed by an aluminium paint on the same type of medium. Harder films are provided by epoxy esters, but when very high abrasion resistance is required, two pack epoxies are used.

OIL TANKS

These may contain cargos of mineral, animal or vegetable oils and may often hold sea water as ballast. Two pack epoxies are employed for refined products, but for crude oils, when slight discoloration is not important, the cheaper epoxy/coal tar pitch coatings are used.

DOCK AND HARBOUR INSTALLATIONS

The surfaces to be protected fall into three classes: (i) those above the waterline such as warehouses, cranes, and pier superstructures (ii) surfaces intermittently immersed in water, such as pier and jetty supports and the seaward side of dock-gates and (iii) surfaces permanently immersed such as the dock side of lock gates and the bottoms of navigation buoys and lightships. The type of coating used in different classes is given in Table III.

TABLE-III: Paint coatings for marine structures

Area	Prime service requirements	Typical coatings
1. Bottom (vessels) mud line to splash zone (off shore structures) piling (Docks)	Resistance to abrasion, impact, salt water, pitting, fouling, cathodic protection, smoothness (vessel)	1. Wash primer - Bituminous hot or cold plastic or coal tar 2. Vinyl primer, rosin vinyl 3. Epoxy, inorganic zinc or organic zinc rich primer, epoxy coal tar or epoxy polyamide
2. Boot top (vessels) splash zone (legs substructure, first platform in in offshore structure)	Flexibility, resistance to abrasion, impact, thermal shock, salt water plus spray, oxygen, UV light, under-cutting, smoothness, cathodic protection	1. Inorganic zinc primer, epoxy polyamide, epoxy coal tar or tie coat plus vinyl alkyd 2. Organic zinc rich primer, high build epoxy or tie coat plus vinyl alkyd
3. Free board (vessels) sides plus racks (barges deep load line to top of gunnel (work boats) tug motor vessels)	Resistance to abrasion, thermal shock, undercutting, salt spray, gloss and colour retention	1. Epoxy or epoxy coal tar primer, high build epoxy or epoxy coal tar 2. Organic zinc rich primer, high build epoxy or vinyl tie coat plus vinyl alkyd

Area	Prime service requirements	Typical coatings
		3. Vinyl primer, vinyl plus vinyl alkyd top coat 4. Inorganic zinc primers, high build epoxy or vinyl, epoxy-polyamide modified vinyl, top coat plus vinyl plus alkyd 5. Modified alkyd primer, various top coats
4. Super structures (masts, stacks, fitting for all vessels, derricks, towers, exposed machinery for off-shore structures)	Resistance to under-cutting, edge cor-rosion, salt spray, gloss and colour retention	1. Wash primer, vinyl, vinyl alkyd plus coat 2. organic or inor-ganic zinc primer tie coat plus alkyd, tie coat plus vinyl alkyd, high build epoxy or vinyl,epoxy polyamide, or vinyl plus modified acrylic top coat, modified vinyl plus oil based top coat 3. For aluminium: epoxy primer high build epoxy.
5. Heat exchangers, hot stock exterior	Resistance to temp. of 540°C, corrosion, salt spray, gloss, colour retention	1. Inorganic zinc silicone 2. Stainless steel pigmented epoxy resin.
6. Dry cargo space Dry stores	Resistance to impact, abrasion, corrosion	1. Wash primer, alkyd top coat 2. Epoxy or vinyl primer, high build epoxy, vinyl top coat 3. Organic zinc primer, high build epoxy top coat
		4. Inorganic zinc primer, tie coat plus alkyd, tie coat plus vinyl alkyd, chlori-nated rubber top coat
7. Tankers (cargo and Ballast)	Resistance to salt water	1. Inorganic or organic zinc primer + high build epoxy 2. Epoxy coal tar 3. Polyester glass (ballast only)
8. Tanks (fire peak and mud)	Resistance to general corrosion	1. Epoxy coar tar 2. Organic zinc or epoxy primer, high build epoxy
9. Tanks (Potable water)	Resistance to general corrosion, inert, in fresh cracks.	1. Wash primer, vinyl 2. Inorganic zinc alone, or as primer for epoxy coal tar or epoxy polyamide
10. Deep tanks (Chemicals, edible oil)	Resistance to general corrosion	Generally high build epoxy but cargo dependent
11. Tanks (sweet plus sour crude oil)k	-do-	1. Organic zinc primer, epoxy coal tar, high A1 epoxy coal tar or high build epoxy 2. Wash primer, Modified phenolic
12. Tank (solvent)	Resistance to general corrosion, specific cargo	Inorganic zinc
13. Tank (clean, fuel petroleum aviation gas)	Resistance to general corrosion	1. Organic zinc 2. Epoxy primer, build epoxy

OFFSHORE STRUCTURES

These are complicated steel structures used by the oil companies (known as rigs) or by the gas industry for the extraction and collection of natural gas (known as gas platforms). Both types of structures are situated in the open sea and are therefore exposed to an extremely aggressive environment. They are designed for a life of 20 to 25 years and so require the most efficient form of protection available.

Totally submerged sections are given heavy protection at the fabrication stage. Several systems are employed, one of the most favoured consisting of blast cleaning to first-quality bright metal or SA3. This is followed by zinc silicate primer and epoxy/coar tar pitch. If sacrificial anodes are used, the high-build type of epoxy/coal tar pitch is employed.

SUPERSTRUCTURE AND DECK AREAS

Efficient blast-cleaning to SA3 is followed by either zinc silicate or two pack epoxy primer. Several types of finishing coats are available. The zinc silicate primer can be over-coated with either two-pack epoxy, chlorinated rubber or vinyl finishes.

CONCLUSION

A brief description about the corrosion and mechanism of protection by paint is given. The surface preparation and the paint system for (a) ships (b) dock and harbour installations and (c) off-shore structure, are described.

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