COATINGS, MARINE

1. Introduction

The marine environment is highly aggressive. Materials in marine service are constantly exposed to water, corrosive salts, strong sunlight, extremes in temperature, mechanical abuse, and chemical pollution in ports. This climate is very severe on ships, buoys, and navigational aids, offshore structures such as drilling platforms, and facilities near the shore such as piers, locks, and bridges.

Marine coatings are the most important, cost-effective means to preserve steel (qv) and other metals in the marine environment. These coatings impart physical and chemical properties, eg, antifouling, color, and slip resistance, to surfaces that cannot be obtained in any other way. Modern coatings are sophisticated mixtures of polymers and other chemicals, and they require careful control of surface preparation and application conditions. These materials are not as adaptable as earlier coatings to the variety of metals, design features, and surface conditions encountered in marine construction, but they provide long-lasting cost-effective protection when used as part of a corrosion control program (see CORROSION AND CORROSION CONTROL). In 1989 a total of 38×10^6 L of marine coatings were sold in the United States. Shipbuilding consumed 4×10^6 L, construction of pleasure boats required 3×10^6 L and 31×10^6 L were employed for maintenance and repair. The selection and application of marine coatings has become a highly specialized discipline in which governmental regulations are a dominant influence. Many paints (qv) and painting procedures used in the past are no longer permitted or are extremely costly to use.

1.1. Corrosion Control Plan.

A corrosion control plan for each ship or structure, which is designed to control deterioration in the most economical and practical manner and to include all appropriate mechanisms for corrosion control, must be developed before construction begins. For steel in the marine environment, the chief methods available are protective coatings and cathodic protection. Cathodic protection is an electrical method of preventing metal corrosion in a conductive medium by placing a negative charge on the item to be protected. This protection mechanism is specifically designed as part of the total corrosion control system and protects only the submerged portions of steel ships and structures.

Materials most resistant to deterioration are chosen, the strength and available shapes of which have a critical influence upon design. Crevices, areas where water can collect, and sharp edges are to be avoided, and dissimilar metals must be electrically isolated from one another in order to prevent corrosion of the more anodic metal. Sharp edges cause paint to draw thin and should be removed by grinding or sanding. Welds have sharp projections that should be removed by grinding. Weld spatter should be scraped or ground from metal surfaces. Outside corners should be rounded, and inside corners should be filled because they provide a collection site for excess paint that may not fully cure. Crevices and pits should be filled with weld metal or caulking because they collect corrosive agents and accelerate deterioration.

1.2. Protective Coatings.

Each coating in the protective coating system is designed to perform a specific function and to be compatible with the total system. Selection of a coating system is influenced by the chemical nature of the coating and by the conditions the coating is designed to resist. The identity of each material, the number of coats and the dry film thickness of each, the maximum times between blasting and coating and between coats, and the minimum time between application of the last coat and commencement of service need to be defined as do suitable surface preparation techniques, proper methods for the application of paint, and effective quality control procedures. The effectiveness of a coating is directly related to its ability to maintain adhesion to the substrate, its integrity, and its thickness. Areas that cannot be easily or safely repaired, especially those which require drydocking for repair, need to be given the best available coating.

Fouling organisms attach themselves to the underwater portions of ships and have a severe impact on operating costs. They can increase fuel consumption and decrease ship speed by more than 20%. Warships are particularly concerned about the loss of speed and maneuverability caused by fouling. Because fouling is controlled best by use of antifouling paints, it is important that these paints be compatible with the system used for corrosion control and become a part of the total corrosion control strategy.

2. Environmental Concerns

Local environmental regulations have significantly affected the production, transportation, use, and disposal of coatings.

2.1. Volatile Organic Compounds. As coatings dry, solvents are released into the atmosphere, where they undergo chemical reactions in sunlight and produce photochemical smog and other air pollutants (see AIR POLLUTION). As a general rule, the volatile organic compound (VOC) content of marine coatings is restricted to 340 g/L. In the locations where ozone (qv) levels do not conform to the levels established by the Environmental Protection Agency, regulations require an inventory of all coatings and thinners from the time they are purchased until they are used.

The VOC regulations have been the driving force behind the development of entirely new coatings technologies, the reformulation of coatings, and the creation of new surface preparation and paint application methods. High solids coatings, eg, those of epoxy and urethane, have displaced alkyds and are now the principal marine coatings, but some have short pot lives. Alkyd coatings have been extensively reformulated and are still important but dry more slowly than their forebears and are not used as extensively as in the 1970s. Coatings that contain high levels of solvents, such as vinyl and chlorinated rubber coatings, are disappearing from the marine industry.

VOC-conforming paints are more demanding than their predecessors, and attention to application conditions and techniques is imperative. The coatings can be more viscous and harder to apply, wet films have poorer leveling, and coatings of uniform thickness are more difficult to achieve.

2.2. Heavy-Metal Pigments. Lead (qv) and chromate pigments (qv), used for many years as corrosion inhibitors in metal primers and topcoats for marine coating systems, have been linked to adverse health and environmental effects (see CHROMIUM COMPOUNDS). Inhaling or ingesting droplets of lead- or chromate-containing coatings is a potential source of poisoning of paint applicators. Regulations concerning the removal of lead-based coatings require that existing coatings be analyzed before removal for toxic metals and that all debris be contained during removal. The air in the vicinity must also be monitored during removal to ensure safe conditions, and old paint and blasting abrasive must be disposed of as toxic waste.

Because of these concerns, lead- and chromate-containing pigments are not used in marine coatings. Chromate pigments, which contain the metal in the +6 valence state, are proscribed, but pigments containing chromium in the +3 valence state, such as chromium oxide, Cr_2O_3, are unregulated and continue to

Table 1. **Active Pigments in Anticorrosive Coatings**

Pigment	CAS Registry number	Molecular formula
	Prohibited	
red lead	[1314-41-6]	Pb_3O_4
white lead	[1344-36-1]	$PbCO_3$
lead chromate	[7758-97-6]	$PbCrO_4$
zinc chromate	[13530-65-9]	$ZnCrO_4$
strontium chromate	[7789-06-2]	$SrCrO_4$
basic lead silicochromate	[11113-70-5]	$PbCrO_4 \cdot n SiO_2$
	Allowed	
zinc oxide	[1314-13-2]	ZnO
zinc phosphate	[7779-90-0]	$Zn_3(PO_4)_2$
zinc phosphosilicate		$Zn_3(PO_4)_2 \cdot n SiO_2$
zinc molybdate	[13767-32-3]	$ZnMoO_4$
calcium borosilicate		$CaO \cdot B_2O_3 \cdot n SiO_2$
calcium phosphosilicate		$Ca_3(PO_4)_2 \cdot n SiO_2$

be used. The corrosion inhibitive pigments that were commonly used and those which have replaced them are listed in Table 1.

2.3. Organotins. In the mid-1970s compounds based on derivatives of triphenyl- or tributyltin (see TIN COMPOUNDS) known generically as organotins, were found to be much more effective than cuprous oxide paints in controlling fouling, and numerous products were introduced. These fell into two classes. Free-association coatings contained a tributyltin salt, eg, acetate, chloride, fluoride, or oxide, physically mixing into the coating. These were available in a variety of resins and characterized by a leach rate of organotin which is quite high when the coating is new, and which falls off rapidly until insufficient to prevent fouling. In contrast, copolymer coatings contain organotin which is covalently bound to the resin of the coating and is not released until a tin–oxygen bond hydrolyzes in seawater (1). This controlled hydrolysis produces a low and steady leach rate of organotin and creates hydrophilic sites on the binder resin. This layer of resin subsequently washes away and exposes a new layer of bound organotin. These coatings are also known as controlled release, self-polishing, or ablative coatings, and last for five years when applied at a dry-film thickness of 375 μm.

However, there is now considerable evidence that sufficiently high concentrations of organotins kill many species of marine life and affect the growth and reproduction of others. Thus many nations restrict organotin coatings to vessels greater than 25 meters in length. In the United States, laws prohibit the retail sale of copolymer paints containing greater than 7.5% (dry weight) of tin, and of free-association paints containing greater than 2.5% (dry weight) of tin, but do not restrict the size of the ship of which the paints may be applied (2). Organotins must be used on vessels with aluminum hulls, because copper is cathodic to aluminum and causes rapid pitting and perforation when used on an aluminum hull. Regulations to minimize the exposure of workers and protect the environment during the application and removal of organotin coatings also exist.

2.4. Abrasive Blast Cleaning. Removal of paint by abrasive blasting may lead to adverse health effects for workers who breathe dust formed during the operation. Regulations restrict blasting operations to such procedures as blasting within enclosures, using approved mineral abrasives, using a spray of water to reduce dust, and blasting with alternative materials such as ice, plastic beads, or solid carbon dioxide. A military specification (3) describes abrasives that are approved for use in U.S. naval shipyards. Limits are placed on carbonates, gypsum, and free silica, all of which are not abrasive but only contribute to dust, and on the amount of arsenic, beryllium, cadmium, lead, and 13 other toxic materials in blasting abrasives.

Debris from the removal of paint may contain lead, chromium, or other heavy metals. Collection of such debris is required to prevent release of these metals into the environment and to avoid exposure and contamination of workers. Blasting debris is contained in two ways: by use of containment systems, eg, screens, panels, tarpaulins, and shrouds, which enclose the removal area, and by paint removing machines equipped with vacuum collection devices. The latter include both powered mechanical tools, eg, grinders, brushes, and sanders, and self-contained abrasive blasting equipment. Blasting enclosures that draw in air help to contain particles of paint but do not ensure worker safety, and these are seldom more than 85% effective in preventing dust and debris from escaping from the system. In order to evaluate the efficiency of the containment method, periodic medical examinations of workers for respired air contaminants are required.

Hazardous waste generated by removal of toxic paints may be stored for only a limited time and must be disposed of in conformance with prevailing regulations. The amount of hazardous waste can be greatly reduced by cleaning and recycling the abrasive.

2.5. Reactive Coatings.

Coatings that cure by chemical reaction of two component parts are the most widely used in marine applications and protection of workers from the reactive ingredients is required. For example, urethane coatings may contain isocyanates that may cause respiratory difficulties, and epoxy coatings may contain glycidyl ethers which are skin sensitizers. This danger is diminished in modern coatings when the reactive groups are bound to oligomers having low vapor pressures and the likelihood of exposure to vapors is considerably reduced.

3. Surface Preparation for Marine Painting

Surface preparation, always important in obtaining optimal coatings performance, is critical for marine coatings (see METAL SURFACE TREATMENTS). Surface preparation usually comprises about half of the total coating costs, and if inadequate may be responsible for early coating failure. Proper surface preparation includes cleaning to remove contaminants and roughening the surface to facilitate adhesion.

3.1. Standards for Cleaned Steel Surfaces.

The most important standards (4) used to specify and evaluate cleaned steel surfaces are summarized in Table 2 in order of increasing cost. Photographic standards consistent with the written standards in Table 2 are also available (5).

Table 2. **Steel Surface Preparation Standards**[a]

Number[b]	Title	Intended use
SSPC-SP-1	Solvent Cleaning	removal of oil and grease prior to further cleaning by another method
SSPC-SP-2	Hand Tool Cleaning	removal of loose surface contaminants before spot repair
SSPC-SP-3	Power Tool Cleaning	removal of loose surface contaminants before spot repair
SSPC-SP-7	Brush-Off Blast	removal of loose surface contaminants before spot repair
SSPC-SP-6	Commercial Blast	for interior steel to be coated with alkyd paint
SSPC-SP-10	Near-White Metal Blast	for most exterior surfaces, decks, water, fuel tanks, etc
SSPC-SP-5	White Metal Blast	for the most demanding coating conditions and for those products, ie, inorganic zinc primers, thermal sprayed metals, and powder coatings, which require an uncontaminated surface

[a] Ref. 4.

[b] SSPC = Steel Structures Painting Council, Pittsburgh, Pa.

3.2. Abrasive Blasting. Blast cleaning using mineral abrasives (qv) is the preferred method for cleaning steel prior to applying marine coatings. Blasting not only provides the highest level of cleanliness but also roughens the surface to provide for good adhesion of the primer. As much blasting as possible is done in purpose-built enclosures to minimize the amount of particulates produced and to provide better and less costly cleaning. Shop blasting is accomplished by equipment having high speed rotating wheels that propel shot or grit abrasive onto steel. Portable closed-cycle vacuum blasting equipment is available for field use. Special machines have been made for steel decks and hulls which recycle the abrasive several times, saving costly abrasive and reducing the amount of blasting waste.

Abrasive blasting of steel ships using conventional equipment is usually accomplished at a nozzle pressure of about 700 kPa. Abrasives can completely remove rust, scale, dirt, and old coatings, but grease and oil are smeared and driven into the surface. Abrasive blasting must, therefore, be preceded by solvent cleaning if any grease or oil is present.

To reduce the amount of dust produced, water can be added to the abrasive from a circular water sprayer around the nozzle. Chemical corrosion inhibitors must be dissolved in the water to prevent flash rusting of the steel. Newer methods to reduce dust include the use of ice, solid carbon dioxide (dry ice), or plastic beads as abrasives. Blasting with dry ice is inexpensive and effective, but the accumulation of carbon dioxide must be avoided in enclosures. Plastic beads are inexpensive, but the cutting efficiency is low and paint removal is slow; the beads can be cleaned of paint particles and reused.

Softer metals such as aluminum and its alloys can be blast cleaned using abrasives that are not as hard as those used on steel. Garnet, walnut shells, corncobs, peach pits, glass or plastic beads, and solid carbon dioxide have been used successfully.

3.3. Other Cleaning Methods. Solvent cleaning, ie, degreasing, is chiefly used to remove grease and oil. Solvent is applied to rags which are replaced when they become contaminated. The final rinse is always made using fresh solvent. Individual ship components can be solvent-cleaned by dipping in tanks of solvent.

Hand and power tool cleaning is used on ships mostly for spot repair of damaged areas. Hand tools include scrapers, wire brushes, and sanders. Electric and pneumatic power tools, which include grinders and needle guns, clean faster and more thoroughly than hand tools. Most power tools have vacuum lines connected to collect paint debris.

Blast cleaning with water, sometimes called hydroblasting, is used to remove marine fouling and sometimes to clean metal surfaces for coating. The water may be heated and detergent may be added to facilitate removal of oil, dirt, and marine slimes. Cleaning bare steel for coating may be achieved using pressures over 200 MPa (30,000 psi) and water volumes of only 8 to 56 L/min. Abrasive may be injected into the stream of water or used in a second operation to produce the rough surface needed for adhesion. Corrosion inhibitors must be used in the water, and extreme caution must be maintained using these high pressures.

Steam cleaning may also be used to remove grease and oil. On large surface areas such as the hulls of ships, steam cleaning is usually more economical and efficient than solvent cleaning. Detergents are sometimes brushed onto the hull before steam cleaning.

4. Types of Coatings

Coatings ingredients fall into four principal classes. Resins form a continuous solid film after curing, bind all ingredients within the film, and provide adhesion to the substrate (6). The properties of a coating are determined principally by the resins it contains. Pigments are metals or nearly-insoluble salts that impart opacity, color, and chemical activity to the coating. Solvents are used primarily to facilitate manufacture and application, but are lost by evaporation after application and are not a permanent part of the coating. Additives used in small (1–50 ppt) amounts give the coating such desirable additional properties as ease of manufacture, stability in shipment and storage, ease of application, or increased performance of the dried film.

These ingredients may be formulated to give coatings that protect against corrosion in different ways (7). Barrier coatings physically separate oxygen, water, ions, and other corrosive agents from the steel surface. Inhibitive coatings prevent corrosion by absorbing or neutralizing corrosive agents, or by slowly releasing protective ions. Sacrificial coatings contain a metal (usually zinc) that is oxidized more rapidly than steel, thereby providing protection for the substrate by electrochemical action. Conversion coatings chemically oxidize the surface of the substrate to a depth of 7–10 μm, producing a passive layer which resists corrosion better than the metal itself.

Modern marine coatings fall into eight generic categories, each named for the principal resin it contains. Significant variation in each category is achieved by varying pigments and other ingredients. The categories are discussed in rough order of importance.

4.1. Epoxies.

Epoxy coatings are the workhorse materials for premium marine applications (8). High performance primers and anticorrosive coatings that conform to VOC regulations are widely available (9). The cured coatings are durable, tough, and smooth, and demonstrate excellent resistance to solvents, alkalies, and abrasion. Multiple-coat systems are applied before a preceding coat cures completely, in order to obtain chemical reaction between coats. Fully-cured epoxies have a hard finish that is difficult to topcoat. Epoxy resins (qv) photolyze in sunlight, leaving a dust of unbound pigment known as chalk. Thus they are always topcoated, usually using urethanes, alkyds, or vinyls, for exterior use.

The coatings are usually formulated using an epoxy resin in a first component and a polyamide, amine adduct, or polyamine curing agent in a second component. The coatings cure by a chemical reaction between the components, and curing time depends primarily on temperature. Epoxy–polyamide coatings can tolerate some surface dampness and contamination during application and a near white blast is satisfactory, although the best possible surface preparation is always desirable. Organic zinc primers containing about 30% epoxy and polyamide resins and about 69% zinc metal provide long-lasting corrosion protection but are not suitable for immersion service.

4.2. Urethanes.

Urethane coatings are comparatively expensive and are used almost exclusively as topcoats over epoxy or inorganic zinc primers. Urethanes containing aliphatic polyisocyanates as curing agents are the best choice for excellent high gloss cosmetic topcoats where prolonged resistance to ultraviolet radiation and retention of appearance are important. Coatings containing aromatic polyisocyanates lose gloss and become yellow in sunlight, but give excellent service as tank linings and in other interior applications. Both types of curing agents produce tough, durable, smooth coatings with excellent resistance to chemicals and abrasion, and both can be formulated to give highly flexible elastomeric coatings if desired.

Urethane coatings are formulated in two components (10). The first contains a polyester polyol, pigments, additives, and solvents, and the second contains a polyisocyanate curing agent. Modern curing agents have low vapor pressures, which minimize worker exposure to isocyanate fumes. Yacht finishes that may be applied by brush are available for the individual user not wishing to apply the coating by spray. Use of urethanes requires careful attention to worker safety and application procedures but, when properly applied, they are the best finishes available for most exterior marine surfaces (see URETHANE POLYMERS).

4.3. Alkyds.

Alkyd resins (qv) are polyesters formed by the reaction of polybasic acids, unsaturated fatty acids, and polyhydric alcohols (see ALCOHOLS, POLYHYDRIC). Modified alkyds are made when epoxy, silicone, urethane, or vinyl resins take part in this reaction. The resins cross-link by reaction with oxygen in the air, and carboxylate salts of cobalt, chromium, manganese, zinc, or zirconium are included in the formulation to catalyze drying.

Alkyd coatings were the standard products in the marine industry for atmospheric service until they were superseded by epoxies in the early 1970s. Alkyds dry reasonably fast, are easy to apply, and demonstrate good weathering in mild environments but are not suitable for immersion service. They have a high moisture vapor transmission rate and to be effective must contain inhibitive pigments (Table 1). The elimination of lead and chromate pigments has made the formulation of an effective alkyd coating challenging but not impossible.

4.4. Inorganic Silicate Coatings.

Inorganic silicate coatings are available for marine use in diverse formulations, which cure by different mechanisms. A silicate binder is formed when sodium, potassium, or lithium silicates in alkaline aqueous solution polymerize. Partially hydrolyzed ethyl silicate in an alcohol–water solution is also used in these coatings. Water is necessary for curing to take place but must evaporate before a film can form. High humidity, low temperature, or poor air circulation may retard evaporation and film formation, but very low humidity retards curing.

The coatings demonstrate excellent abrasion resistance, hardness, and toughness, but they are not flexible. Inorganic zinc-rich coatings containing more than 80 wt% metallic zinc in a silicate binder are used in automated blasting and priming operations as preconstruction primers for steel plate. They are also used near the seashore as primer coatings on bridges, electric power transmission towers, and structural steel but are not suitable for immersion service. A single coat of 75–125 μm provides galvanic protection to steel. These coatings are almost always topcoated. Vinyls, epoxies, and urethanes are suitable, but alkyd coatings are not stable to the alkaline surface of zinc and should not be used as topcoats.

4.5. Vinyls.

Vinyl resins are thermoplastic polymers made principally from vinyl chloride; other monomers such as vinyl acetate or maleic anhydride are copolymerized to add solubility, adhesion, or other desirable properties (see MALEIC ANHYDRIDE, MALEIC ACID, AND FUMARIC ACID). Because of the high, from 4,000 to 35,000, molecular weights large proportions of strong solvents are needed to achieve application viscosities. Whereas vinyls are one of the finest high performance systems for steel, many vinyl coatings do not conform to VOC requirements (see VINYL POLYMERS).

Vinyl coatings are lacquers, that is, they form films solely by the evaporation of solvent. Thus throughout their lives they are soluble in the solvents used to apply them, allowing for good intercoat adhesion when solvents in a later coat soften the resins in an earlier coat. Vinyl coatings have been widely used on bridges, locks, ships, dams, and on- and off-shore steel structures. They are tough, flexible, adherent coatings. Excellent primer, anticorrosive, and antifouling formulations are available. The coatings have a low moisture vapor transmission rate, and inhibitive pigments are rarely used. These coatings are particularly useful where fast drying at low (0–10°C) temperatures is required, and they require only a short curing time before being placed in service, but they do not tolerate surface moisture. Vinyls are excellent for immersion service only if applied over a near white or white blast. They have good weather resistance but are softened by heat and are not suitable for prolonged use above 65°C.

The wash primer is a special type of vinyl coating. This material contains a poly(vinyl butyral) resin, zinc chromate, and phosphoric acid in an alcohol-water solvent. The coating is so thin it is literally washed onto a freshly blasted steel surface, where it passivates the metal surface by converting it to a thin iron phosphate-chromate coating. The alcohol solvent makes it possible to apply the coating over damp surfaces. The coating forms the first coat of an all-vinyl system and can also be used to preserve a freshly-cleaned steel surface until an epoxy or other primer coat can be applied. These coatings contain chromates and are very high in VOC.

4.6. Chlorinated Rubber. Chlorinated rubber coatings are lacquers. These thermoplastic materials have low moisture vapor transmission and excellent acid, water, salt, and alkali resistance. They dry under very cold conditions but do not tolerate surface moisture. They are useful at extreme service temperatures (−35 to 120°C) and are easily repaired. Toughness and high chemical resistance are similar to vinyls. Chlorinated rubber coatings are widely used in Europe and are common in the United Kingdom, where coatings pigmented with micaceous iron oxide are used by British Railways. They find fewer applications in the United States, primarily as topcoats on exterior steel exposed to high humidity.

4.7. Coal Tar. Coal-tar resins are made from processed coal-tar pitch (see TAR AND PITCH). They undergo rapid and severe cracking in sunlight and thus are suitable only for underground use on steel and saltwater immersion. Coal-tar resins are frequently combined with epoxy resins to add the chemical and abrasion resistance of the latter. Coal-tar epoxy coatings cured with polyamides are widely used on marine structures because of low water permeability. All of these are cost-effective coatings but are available only in black or dark shades and demand a white or near white blast for long life. The U.S. Navy does not use coal tar or coal-tar epoxy coatings because low levels of carcinogens may be present in processed coal tar.

4.8. Powder Coatings. Coating films can be formed from dry thermoplastic powder (see COATING PROCESSES, POWDER TECHNOLOGY). Small objects may be dipped in a fluidized bed of powder or grounded and coated by electrostatic spray; the object is then heated to fuse the particles and form a film. The powder may also be melted as it is sprayed; molten droplets coalesce and form a film on the object before cooling. Epoxy, polyester, and vinyl resins are widely used, and the particular properties of the coating depend on the type of resin. These coatings are used on electrical junction boxes, motor housings, hatches, and other small pieces of equipment, which are usually removed from the ship and coated in a shop.

5. Application Methods

The application of marine coatings is a critical factor in achieving maximum performance. Protective clothing and breathing equipment should be worn during application. Because of large surface areas, ships are usually spray painted (see COATING PROCESSES, SPRAY COATINGS). Three techniques are widely used: air, airless, and electrostatic spraying. In air spraying, paint is forced by 200–400 kPa (30–60 psi) of compressed air into a spray gun where a second stream of air atomizes the paint and carries it onto the surface. Paint losses can be as high as 40%

because some paint misses the surface (overspray) and some rebounds from the surface. Nearby objects must be protected from inadvertent painting.

Airless spray uses hydraulic pressure to deliver the paint. Paint is brought to the spray gun under 7–40 mPa (1000–6000 psi), where it is divided into small separate streams and forced through a very small orifice to produce the spray. Airless spray is faster, cleaner, and less wasteful than air atomization, but demands good technique because it delivers paint very quickly.

Electrostatic spraying is used in shops to coat conductive objects. It is very useful for odd-shaped objects such as wire fence, cables, and piping. An electrostatic potential of 60,000 volts on the object attracts oppositely-charged paint particles; the spray can wrap around and coat the side of the object opposite to the spray gun. This technique produces very uniform finishes and has the least paint loss of the three methods. However, it is slow, requires expensive equipment, produces only thin coats, and is sensitive to wind currents.

Manual painting occurs mostly during touch-up or repair, and is best suited for piping, railings, and other hard to spray places. The conventional tools for manual application are brushes, rollers, paint pads, and paint mitts. These methods are very slow but are suitable for unskilled applicators and allow the painter to work the coating deeply into the surface being painted.

6. Transfer Efficiency

Many components of ships and marine structures are now coated in the shop under controlled conditions to reduce the amount of solvents released into the atmosphere, improve the quality of work, and reduce cost. Regulations designed to limit the release of volatile organic compounds into the air confine methods of shop application to those having transfer efficiencies of 65%. Transfer efficiency is defined as the percent of the mass or volume of solid coating that is actually deposited on the item being coated, and is calculated as

$$\text{transfer efficiency (\%)} = \frac{\text{mass of solid coating on item} \times 100}{\text{mass of solid coating consumed}}$$

or

$$= \frac{\text{volume of solid coating on item} \times 100}{\text{volume of solid coating consumed}}$$

The principal factors affecting transfer efficiency are the size and shape of the object, the type of application equipment, the air pressure to the spray gun, and the distance of the spray gun from the object. The transfer efficiency becomes lower as the object becomes smaller or more complex. The transfer efficiency increases when the spray gun is brought closer to the object and when the atomizing pressure is reduced. The transfer efficiency of different types of application equipment in descending relative order is manual > electrostatic spray > airless spray > conventional atomized air spray.

7. Selection of Coatings

7.1. Underwater Hull. Hull coatings consist of two layers of an anticorrosive coating topped with one layer of an antifouling coating. The coating system must resist marine fouling, severe corrosion, the cavitation action of high speed propellers, and the high current densities near the anodes of the cathodic protection system. Epoxy and coal-tar epoxy systems are commonly used as anticorrosive coatings. The U.S. Navy uses two coats of epoxy polyamide paint (11), each 75 μm thick when dry. Epoxy and coal-tar epoxy systems are used extensively on commercial ships. Coal-tar epoxy systems (12) are usually applied in two coats to give a total dry film thickness of 200 μm.

Anticorrosive systems require an antifouling topcoat. Marine antifouling coatings (13) contain materials that are toxic to fouling organisms and are the only effective way to prevent the growth of marine organisms on the hull. The nature of the toxic substance is heavily regulated in Europe, Japan, and the United States. Arsenic, cadmium, and mercury are proscribed and organotins are severely restricted. Cuprous oxide has always been and remains the most widely used toxicant.

The system of hull coatings, including antifouling paint, must be compatible with the cathodic protection system. Thus the coating system must have good dielectric properties to minimize cathodic protection current requirements and must be resistant to the alkalinity produced by the electric current. The cathodic protection system should prevent corrosion undercutting of coatings that become damaged, and the current density should be able to be increased easily to meet the increased electrical current needed as the coating deteriorates.

Antifouling paints containing a vinyl-rosin base and cuprous oxide (14) were used beginning in the 1940s but are being discontinued because of their high VOC levels. They provided about two years of protection against fouling but needed to be cleaned about every three months, depending on operational schedules and the waters in which the vessel operated. Organotin antifouling paints effectively prevent fouling for much longer periods, and the copolymer paints containing covalently-bound tin furnish about five years of protection when applied at a dry film thickness of 375 μm (15 mils).

Hull coatings having low surface energies, known as fouling release coatings, provide fouling protection without the use of toxins (15). These coatings form only weak bonds with fouling organisms, and the fouling loses adhesion by its own weight or by the motion of the ship through the water. Heavily fluorinated urethane coatings were tested for some years, but toughened silicone coatings are now providing superior performance. Foulant release coatings are environmentally benign and promise extended service lives.

Epoxy and polyester systems filled with flake glass provide a finish that is tough and resistant to abrasion. One commercial system is filled with copper flakes to provide intrinsic antifouling action. These systems are applied at a total dry film thickness of about 625 μm and are used on pleasure boats.

7.2. Boottop and Freeboard Areas. The boottop is that part of the hull that is immersed when the ship is loaded and exposed when the ship is empty. The freeboard is the area from the upper limit of the boottop to the main deck. The boottop suffers mechanical damage from tugs, piers, and ice, and experiences intermittent wet and dry periods with nearly constant exposure to sunlight. Thus coatings for this area require resistance to sunlight and mechanical damage, good adhesion, and flexibility. Frequently the hull coating system is used in the boottop area, and one or two extra topcoats are applied for added strength.

In the freeboard areas, commercial ships use organic zinc-rich primers extensively and usually topcoat them with a two- or three-coat epoxy system. U.S. Navy ships use an organic zinc-rich primer, two to three coats of an epoxy-polyamide coatings, and a silicone-alkyd topcoat (16); the entire dry system is 150–225 μm thick.

7.3. Weather Decks. Coatings for decks must be resistant to abrasion by pedestrians and small vehicles, and must be slip-resistant. Inorganic zinc primers overcoated with epoxy coatings for additional corrosion protection perform well on steel decks, or a multiple-coat all-epoxy system can be used. Nonskid coatings are used on aircraft carrier landing and hangar decks and in passageways of all ships to maintain traction during wet and slippery conditions. The coatings contain epoxy resins and a coarse grit and are applied using a roller over epoxy primers to produce a textured finish. Nonskid coatings are 6 to 10 mm thick when dry.

Aluminum and galvanized steel are widely used in equipment on weather decks. Historically, galvanized steel and aluminum surfaces have been treated using a thin coat of wash primer after cleaning and before coating. For environmental reasons, the wash primer is omitted and these metals are coated directly with an epoxy primer. An aliphatic polyurethane, alkyd or silicone-alkyd enamel provides improved weather resistance. Galvanizing can best be cleaned by water blasting if no rusting is present or a light brushoff blast can be used if rusting exists. The same blast technique can be used to clean aluminum surfaces. Alkyds must not be used on galvanized steel because zinc and moisture rapidly hydrolyze the resin, producing zinc soaps that destroy adhesion.

7.4. Superstructure. Coatings for superstructures must have good resistance to sun, salt, and corrosion, and good gloss and appearance retention properties. In addition, coatings on antennas and superstructures must be resistant to acidic exhaust fumes and high temperatures. Deck hardware and machinery, masts, and booms are coated with an inorganic zinc primer, an intermediate coat of epoxy, and a finish coat of aliphatic polyurethane or silicone-alkyd enamel. Powder coatings are used effectively on antennas and other equipment on the superstructure. This equipment, as well as exhaust stacks, steam riser valves and piping, and other hot surfaces, can also be coated using thermal-sprayed aluminum. Powder coatings and sprayed metallic coatings (qv) are applied in shops under controlled conditions. Inorganic zinc primers are becoming widespread in new construction.

7.5. Tanks. Coatings for liquid cargo tanks are selected according to the materials that the tanks (qv) are to contain. Tank coatings protect the cargo from contamination and must be compatible with the material carried. Epoxy systems are most frequently selected because they perform well with both aqueous and organic products. A carefully applied three-coat epoxy system having a dry-film thickness of 225–300 μm can be expected to last for 12 years.

Coatings for potable water tanks must not impart taste or odor to the water and must not allow corrosion products to enter the water. Epoxy coatings are usually used. In the United States these coatings must be approved by the National Sanitation Foundation, acting as agent for the U.S. Environmental Protection Administration. Complete cure is very important and up to two weeks at 20°C may be necessary.

Petroleum products far exceed all other substances carried aboard ship, as cargoes or as fuel. Fuel tanks have specialized requirements because they may be filled with seawater ballast after the fuel is consumed. The coating must resist attack by both fluids, and seawater is much more corrosive than hydrocarbons. A three-coat epoxy system totalling 250–300 μm dry thickness gives good service in U.S. Navy ships. Zinc primers are not permitted in fuel tanks because, in addition to being unsuitable for seawater immersion, zinc may dissolve in automotive or aviation fuels causing damage to the engines in which the fuel is subsequently used. The same three-coat epoxy system used in fuel tanks is used in a variety of other tanks, including ballast tanks, sanitary holding tanks, and hydraulic fluid reservoirs. Fluorinated polyurethane coatings pigmented with 24% of poly(tetrafluoroethylene) give exceptionally long service in fuel tanks (17).

7.6. Machinery Spaces, Bilges, and Holds. Machinery spaces and bilges are so inaccessible that surface preparation is a significant problem and damage to machinery that cannot be removed must be avoided. Chemical cleaning by aqueous citric acid solutions, followed by degreasing using a nonflammable solvent, is widely used. Surfaces are best protected using a two- or three-coat epoxy-polyamide system having a total thickness of 250–300 μm. Alkyd enamels perform well in dry machinery spaces. Holds for carrying cargo may be painted with either of these systems, but the epoxy system is preferred for chemical and abrasion resistance.

The interior of piping has been protected from corrosion and abrasion by aromatic amine-cured epoxy coatings (18). These coatings are forced through intact piping systems by compressed air and cure within 10 minutes, forming a hard impervious lining. They have been used to protect 70:30 and 90:10 copper:nickel pipes in sanitary systems from sulfide corrosion, and are also suitable for use in potable water piping systems.

7.7. Living Areas. Coatings for living areas must be easily cleaned and resistant to bacteria, soiling, and fire. Living areas are generally painted with nonflaming coatings, or with intumescent coatings which foam when heated and produce a thick char that lessens damage to the substrate. For ceilings and walls in living and sleeping areas the U.S. Navy uses coatings based on highly chlorinated alkyd resins (19) or on aqueous emulsions of vinylidene chloride (20). Epoxy systems are generally used in damp areas such as galleys, washrooms, and showers where moisture deteriorates enamels.

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