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PROTECTIVE COATINGS

Solution to Marine Corrosion Protection

Technology Focus focuses on the technological achievements in the organization covering the products, processes and technologies.

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Laboratory Correspondents

From the Desk of Special Editor

I am immensely proud to highlight the groundbreaking advancements in protective coatings technology developed by the scientists at the Naval Materials Research Laboratory (NMRL), Ambernath. This pioneering research not only underscores our commitment to excellence but also represents a crucial step forward in ensuring the longevity and resilience of Naval assets and other Defence infrastructure.

The importance of protective coatings cannot be overstated. These innovations play a critical role in safeguarding various naval platforms, including ships and submarines, from the harsh marine environment, significantly enhancing operational life, reliability and performance. The research and development efforts at the NMRL have led to the creation of advanced coatings that are designed to withstand extreme conditions such as corrosion and biofouling. These coatings, developed using state-of-the-art materials and nanotechnology, are among the finest examples of indigenous solutions for the Indian Navy and the broader defence sector.

Our focus on protective coatings is not limited to enhancing the lifespan of Naval assets but also contributes to cost efficiency, reducing the need for frequent maintenance and ensuring readiness for operational tasks. These innovations are also aligned with our national objectives of self-reliance in defence technologies, as articulated under the 'Make in India' initiative. By leveraging home-grown expertise and cutting-edge research, we are reducing dependency on foreign technologies and fostering a culture of innovation within our Defence ecosystem.

The teams at NMRL have demonstrated exceptional dedication, creativity, and technical prowess in developing these coatings, which stand as a testament to our capability to lead in specialized fields of materials science. Their efforts are directly contributing to the modernization of India's Defence capabilities and ensuring the safety and effectiveness of our armed forces.

As we continue to push the boundaries of technology, it is crucial to recognize the collaborative spirit and passion for innovation that drives these successes. I extend my congratulations to the NMRL team and encourage them to continue their pioneering work, which is setting new standards for the Defence sector.

Together, we are forging a stronger, more resilient future for India's defence infrastructure, and I am confident that the advances made by NMRL in the fields of protective coatings will serve as a cornerstone for further innovations in the years to come.

RV Hara Prasad

Distinguished Scientist and DG (NS&M)

From the Desk of Guest Editor

Corrosion is regarded as a slow creeping enemy to all of us and it is affecting our day-to-day lives. Military assets like warships, submarines, weapons, platforms, arms, ammunition, off-shore installations, bridges, sensors, etc. are exposed to very harsh corrosive environment. Corrosion is a huge problem not only for civilian sector but also for the armed forces as the war equipment are deployed in very aggressive environments which causes significant stress on them. Corrosion leads to disintegration of almost 5 tons of steel every second worldwide and about 40 % of all produced steel is used to replace corroded steel.

The cost of corrosion is huge for our nation and we are spending @ 4.2% of GDP in combating corrosion. It's a big issue for the armed forces as we spend nearly 25 % of the budget allocated for maintenance on corrosion management alone. If we can address some part of it, it is going to provide big saving not only in the expenditure but it will also lead to longer life of military assets, increased availability, improved safety, and employment of lesser number of crew.

Military assets face complex operating environments which triggers all possible types of corrosion to include general corrosion (of metals in the corrosive media like seawater, chemicals, acids, gases), galvanic corrosion, bio-fouling driven corrosion, graphitisation of cast iron, stress corrosion, dezincification, fretting corrosion, pitting corrosion, intergranular corrosion, corrosion fatigue, biofouling and microbial influenced corrosion, etc.

Naval Materials Research Laboratory (NMRL) since its inception in 1953 has contributed extensively in the field of corrosion protection of assets of Indian Navy. NMRL has been providing solutions for corrosion protection needed by our Armed Forces and has successfully developed Coatings which includes speciality paints, complex concentrated alloy powders and nano crystalline amorphous powders, Surface treatments, Corrosion-resistant materials, Corrosion inhibitors, Sacrificial anodes, Electrochemical protection which includes Impressed Current Cathodic Protection (ICCP) and Active Shaft Grounding (ASG), etc. Today, Indian Navy's warships, submarines and Indian Coast Guard ships are protected by the anti-corrosion technologies provided by the NMRL.

This issue of Technology Focus highlights NMRL's contributions towards development of various corrosion protective technologies.

Prashant Rojatkar

Outstanding Scientist and Director, NMRL

PROTECTIVE COATINGS

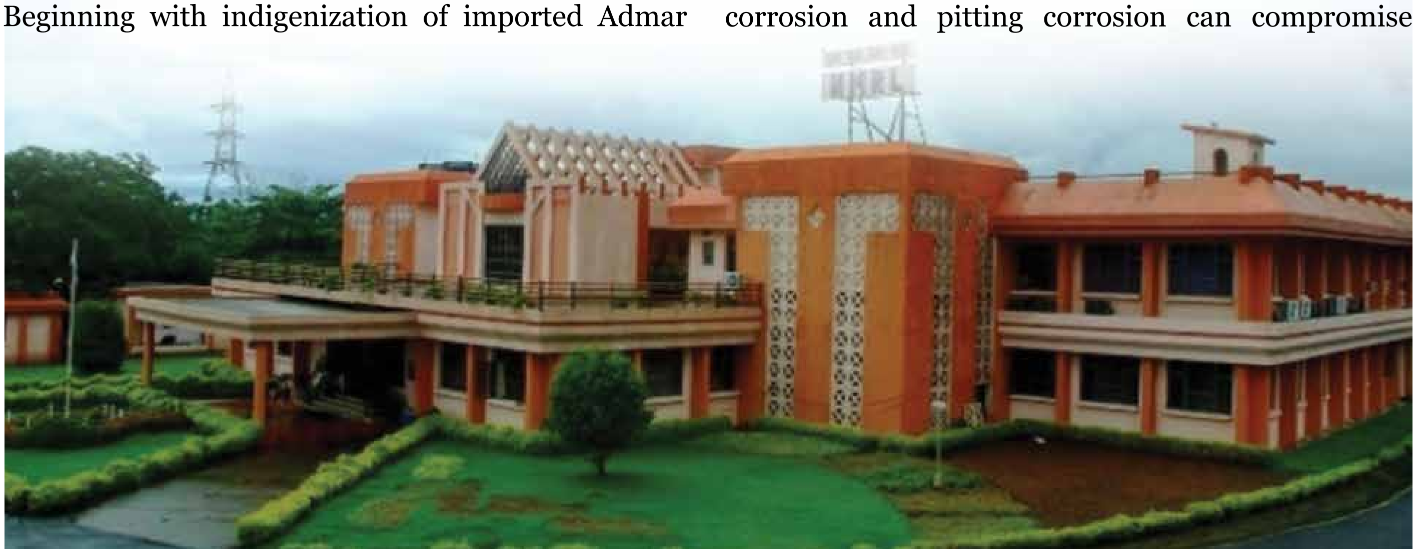
Solution to Marine Corrosion Protection

Naval Materials Research Laboratory (NMRL), Ambernath, is one of the oldest R&D Laboratory of Defence Research and Development Organisation (DRDO), dedicated for development of cutting-edge materials and energy systems for the Indian Navy and other armed forces. Founded in 1953 as Dockyard Laboratory in Mumbai, its initial focus was on routine fuel and oil sample testing and providing support to the Indian Navy. The laboratory's mission gradually expanded from fleet support to import substitution and research and development activities. This shift enabled development of advanced materials, including high-strength steel, piezo-composites, specialty coatings and polymers. The expertise gained in material R&D, along with a successful track record of delivering numerous products, prompted further expansion of the laboratory's scope, culminating in its renaming to the Naval Materials Research Laboratory in 1995.

One of the core competences of NMRL is development of coating technologies for protection of naval platforms from corrosion and fouling. Marine coatings serve as protective barriers for materials employed in naval vessels, thereby prolonging their longevity and ensuring optimal performance. Beginning with indigenization of imported Admar anti-corrosive paint, the laboratory has been engaged in development of corrosion protection coatings for almost seven decades.

Steel is the most common material used in shipbuilding because it is strong, resistant to fatigue and inexpensive. Steel makes up to 80% of a ship's weight. Warships and submarines are deployed in seawater which is one of the most corrosive liquids naturally occurring on earth. The presence of seawater and salty humid air forms perfect environment for corrosion of various parts of warships and submarines.

Corrosion is a process of degradation of materials due to reaction between the material and its surrounding environment. The primary function of marine coatings is to safeguard vessels from corrosion induced by continuous exposure to saline seawater and harsh marine environment. These coatings create a protective interface that prevents direct contact between seawater and metal substrates, effectively reducing ingress of corrosive agents thereby preventing/ minimising the corrosion. Various areas of ships and submarines require protection against several forms of corrosion. The hull is a primary focus due to its constant exposure to seawater, where general corrosion and pitting corrosion can compromise



structural integrity. Microbiological organisms and biofouling further aggravate corrosion problem in underwater hull. The superstructures and deck areas are generally exposed to splashing of seawater, humidity, and salt laden air leading to corrosion. Galvanic corrosion is another threat, particularly for the weld regions. Ballast tanks are prone to corrosion as they are filled with seawater. Crevice corrosion is predominant in propeller shafts seal areas. The bilge area often has accumulation of water and oil mixtures, and is highly prone to corrosion. The propeller blades undergo pitting corrosion in areas where repair work during manufacturing stage is carried out. Biofouling, the accumulation of marine organisms like algae and barnacles on submerged surfaces, increases drag and reduces fuel efficiency of ship. Additional challenges arise in areas like the battery compartments of submarine, where corrosion is induced due to spilling of battery acid.

In addition to the corrosion issues described above, the warships and submarines have few specialized functional requirements, viz. non-skid surfaces, radar stealth, fire safety, hygiene, heat insulation, wear resistance, etc.

To address the aforementioned issues, NMRL has developed a wide range of specialized coatings. The protective coating technologies developed by NMRL primarily for the warships and submarines are described in the following sections.

PROTECTIVE COATINGS DEVELOPED BY NMRL FOR WARSHIPS AND SUBMARINES

The protective coating development efforts are organised in the following manner:

- Paints/-coatings inducted into the Services
- Paints/coatings successfully completed User trials
- Other paints/coatings developed by the NMRL

Protective Coatings Developed

- Underwater hull: Anti-corrosive coating, fouling release coating, paint for underwater application
- Flight-deck: Non-skid paint
- Superstructure: High performance exterior paint, Radar absorbing paint
- Engine room: Intumescent fire-retardant paint,self-cleaning coating
- Deck area: Overlay coating for dry and wet areas
- Bilge areas: Solvent free epoxy coating, nano-material based bilge coating
- Battery pit: Acid resistant paint,rubber coating
- Submarine hull: Acoustic rubber tiles
- Fasteners: Peelable coating

Paints/Coatings Inducted into the Services

After successful conduct of User trials, following paints/coatings developed by the NMRL have been inducted by Indian Navy. ToTs of these paints/coatings are given to various Indian paint manufacturing agencies. These products are under bulk production and are safeguarding several assets of the Indian Navy and the Indian Coast Guard.

- High-performance paint for exterior of ship superstructures
- Heavy-duty non-skid coating
- Paints for underwater application
- Solvent free anti corrosive paints for tanks and battery pit
- Intumescent fire-resistant paint
- Nano-material based bilge coating
- Hydrophobic self-cleaning coating
- Paints for protection of submarine acoustic rubber tiles

Paints/Coatings Successfully Completed User Trials

NMRL has successfully completed development and User trials of following products. These products are expected to be formally inducted into services shortly.

- Deck overlay coating
- Acid resistant rubber lining
- Bulk metallic glass coatings

Other Paints/Coatings Developed

Development of the following paints/ coatings has been completed by the NMRL. User trials of these are expected to commence soon.

- High temperature resistant non-skid coating
- Anti-corrosive foul release paint
- Anti-microbial coating for internal compartments of ships
- Heat barrier coating
- Anti-icing coating
- Transparent coating for aircraft canopy
- Peelable coating
- Thermally sprayable organic coating
- Self-healing smart coating
- Corrosion sensing coating
- Alkali resistant coating

PAINTS/COATINGS INDUCTED INTO SERVICES

The details of the paints/coatings which are inducted into services are given below:

High-performance Paint for Exterior of Ship Superstructures

The laboratory has developed high performance exterior paint based on silicone-alkyd copolymer, the process for synthesis of the copolymer has been established. This paint is single pack system and available in white, dark admiralty grey and light grey shades. Modification of alkyd resins with silicone improves its mechanical properties and resistance to UV-radiation. This paint has been evaluated extensively for its exterior durability. The developed paint has shown more than 50% retention of gloss after 1000 hours of exposure when tested in QUV-weatherometer. The paint has service life of more than 5 years. The high-performance exterior paint can be manufactured using sand mill and high-speed mixer.

Naval ship painted with high performance exterior paint

The technology of high-performance exterior paint includes processes viz. preparation of long oil alkyd resin, modification of alkyd resin with silicone followed by preparation of paint in different shades. The User trials of this paint has been successfully completed onboard TRV 17 and INS Gomati. The ToT has been transferred to industries and the paint is currently under bulk production.

Heavy Duty Non-Skid Paint

The flight/ helo decks of naval ships require application of heavy-duty non-skid coatings to provide resistance to slippage/skidding during movement of aircraft and personnel. An epoxy-based heavy duty non-skid paint composition has been developed by NMRL to meet the requirements of flight deck coatings for aircraft carrier as well as helo-decks of other type of ships. This coating contains coarse aggregates of varying particle sizes along with suitable pigments. This coating provides desired texture (roughness) and frictional properties.

Features of the coatings include low Volatile Organic Compound (VOC), thermal resistance up to 250 °C, impact resistance against arresting cables, wear and durability. User trials of this paint has been completed on various Naval platforms (INS Hansa, INS Brahmaputra, INS Aditya, etc.) and the Navy has accepted the paint for induction. NCD for this paint has been issued by Navy. The ToT of this paint has been given to various paint industries and currently under production.

Paints for Underwater Application

The marine environment is highly corrosive to metallic structures due to the presence of salts (chlorides) and dissolved oxygen in seawater. The submerged structures such as platforms, jetties and ship hulls are protected against corrosion by applying anti-corrosive anti-fouling paint. However, coatings are vulnerable to mechanical damage due to abrasion/impact against underwater objects. The affected areas (damaged paint) need to be repaired and repainted which calls for dry docking of ship. Dry docking of a ship is a time consuming and labour-intensive activity and in fact some installations in the sea cannot be brought to the dry condition.

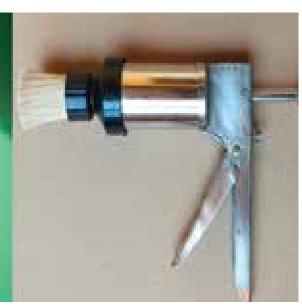
The laboratory has developed two epoxy-based anti-corrosive paint and anti-fouling paint which can be applied directly on underwater/submerged surfaces of structures without need for dry-docking. Coat of anti-corrosive paint is applied first on the damaged surface followed by application of anti-fouling paint. Developed compositions are solvent free and provide a dry film thickness of 225 ± 25 µm in a single coat.

These paints can be applied to submerged areas by using a hand-held applicator specially developed by the laboratory. Two to three coats of the paints are recommended, at intervals of 24 h between each coat. Post successful completion of User trials (INS Trishul, INS Trikhand and INS Aditya) and induction by the Indian Navy, ToT of these paints have been given to various paint manufacturing industries.

Heavy duty Non-skid paint

Heavy duty non-skid paint applied on flight deck (Representative image)

Diver applying underwater paint



Hand held paint applicator

Solvent Free Anti-corrosive Paints for Tanks and Battery Pit

Naval ships/submarines have several interior tanks for storing fluids like fuels, lubricants, seawater, fresh water, etc. Also, there are compartments which are used for storing lead acid batteries. Many of these stored fluids are corrosive in nature, especially the battery acid which invariably gets spilled during battery filling operation and leads to severe corrosion. Hence there is a requirement of coating/paint to protect the metallic surfaces of the storage tanks and battery pit compartment against corrosion. This paint system apart from anti-corrosion properties, is also expected not to contaminate the stored fluids. To address this issue, NMRL has developed solvent-free anti-corrosive paint compositions, EP-1 and EP-2 for protecting tanks and battery pits. These paint compositions are thixotropic in nature and provides a dry film thickness of 250 ± 50 μm in single coat. They possess good resistance to several fluids, such as seawater, fresh water, diesel, aviation fuels, battery electrolyte, etc.

These solvent-free anti-corrosive paints are based on blends of epoxy resins, pigments, extenders and are cured using speciality hardener. These paints are available as two component system, base and hardener, which are mixed in specified ratio prior to application and has a pot life of 2 hours. Absence of solvent or any volatile matter in the paint makes it safe from fire hazards during application in confined areas like tank interiors. These paints are available in two shades, white and light pink. Solvent-free anti-corrosive paint EP-2 is used for corrosion protection of surfaces from acid attack, such as in battery compartments, while EP-1 is used for protection of other areas. These paints have been inducted into services and are being extensively used by the Indian Navy.

Solvent-free anti-corrosive paint applied in battery pit of submarine

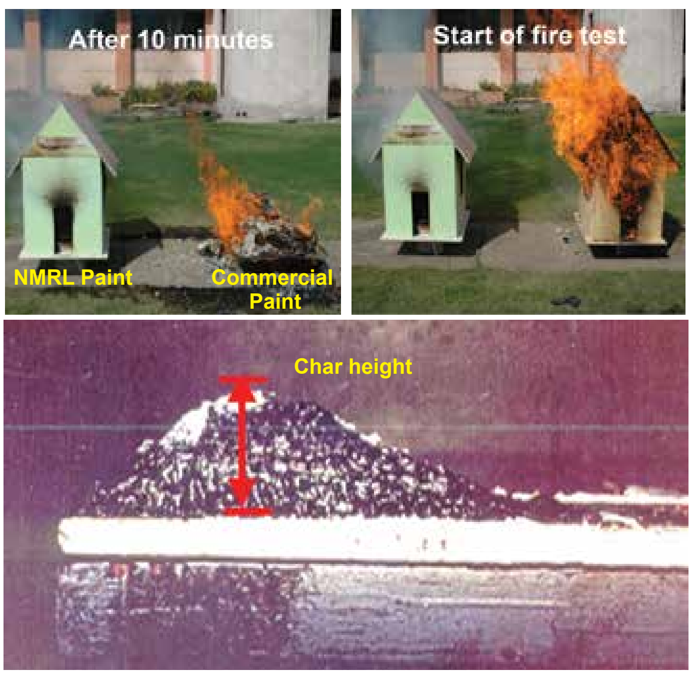
These paints can be applied on manually cleaned surfaces without the application of a primer. The paint system has a service life of > 5 years in battery pits of submarines and > 6 years in engine room, aviation fuel tanks and other interior compartments of ships. The technology for these paints has been transferred to various paint industries to meet Navy's bulk requirements.

Intumescent Fire-Resistant Paint

Fire in buildings and installations, both in Defence and civil sectors can cause extensive damage to property and human life. One of the most efficient ways of fire-retardant treatment is application of intumescent fire-retardant paint. Fire-retardant paint, in case of fire, swells or foams to produce a cellular carbonaceous char which provides heat insulation and acts as an oxygen barrier which prevents ignition of combustible substrate materials. An intumescent fire-resistant paint has been specially developed by NMRL for the Indian Navy. Further, transparent version of this coating has also been developed for substrates where original texture of surface is required to be maintained.

Intumescent fire-retardant paints developed by the NMRL are based on water-based acrylic polymer emulsion it are designed for both interior and exterior applications. Specialty additives have been employed for producing intumescence. Titanium dioxide has been incorporated as a pigment. The paint is applied in three coats to provide a dry film thickness of 750 μm. The coating on exposure to fire, swells 70-80 times its original thickness. Transparent coating compositions have been developed using a phytic acid modified resin synthesized in the laboratory. The viscosity of these coatings can be adjusted by diluting with water.

These paint compositions have undergone extensive evaluation in the laboratory and have demonstrated exceedingly good fire protection properties on various substrates, viz. plywood, aluminum, steel, electrical cables, and false ceiling materials. The paint has also shown good heat insulation property on aluminum substrate. The heat insulation properties of intumescent fire-retardant paints are immensely useful in maintaining the mechanical integrity of ship superstructures in case of fire. The fire-retardant paint can be applied directly on non-metallic substrates. On metallic substrates, application of suitable primer is necessary for corrosion protection. Fire retardant paint, on outdoor surfaces, can be overcoated with appropriate exterior paint. User trials of intumescent fire-retardant paint have been completed successfully at Nuclear, Biological and Chemical Defence (NBCD) facility at INS Shivaji, Lonavala and has proven its effectiveness. This paint has been accepted and inducted by Indian Navy. The ToT has been given to several paint manufacturers.

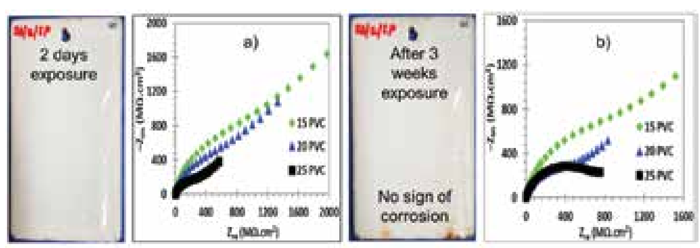


Demonstration of fire-retardant property of paint

Nanomaterial-based Bilge Coating

Bilge compartments are the bottom most area of machinery compartments of ship. These are generally confined spaces, which remain contaminated and filled with seawater, oil/grease, other substances released from various machinery and equipment. Apart from these, the environment in bilges always remains highly humid. All these factors lead to severe corrosion. As the bilge areas are confined, they have very limited or no access for surface preparation using abrasive blasting or power tool cleaning which is essential before application of any protective coating. Furthermore, conventional paints are generally solvent based, hence there is always a hazard of accidental fire due to poor ventilation in bilge areas. An improved protective paint system was required by the Indian Navy with good adhesion and resistance to various liquids in bilge areas for improved corrosion protection.

Taking note of these requirements, NMRL developed a nano-material based two pack, high solid paint system comprising of epoxy resin, reactive diluents, pigments, extenders, nanofillers and other additives. It can be applied by paint brush or roller directly to the substrate with nominal surface cleaning and does not require a separate primer. Some important features of the paint are low volatile content of <5 % by weight, pot life 2 h and drying time 6-8 h. The developed paint has shown excellent corrosion resistance.

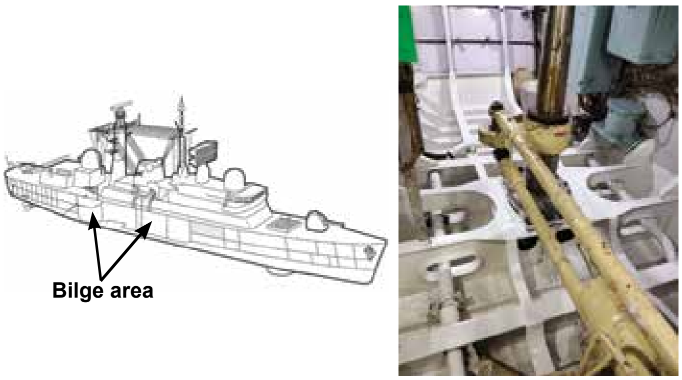


Nyquist plots after a) 2 days and b) 3 weeks of exposure in humidity

Nyquist plots for coatings (Pigment Volume Concentration, PVC: 15, 20 & 25) indicates that they exhibit requisite polarization resistance of >1 MΩ. cm^2 necessary for corrosion protection. Twenty PVC paint composition was selected as it showed better mechanical properties. The covering capacity of the paint is 3.5 sq.m. per litre for a dry film thickness of 225-250 µm. Two coats of this paint are recommended at an interval of 16 to 24 h.

The developed paint system has a service life of >5 years (when applied on manually cleaned surfaces). Being high solid composition and low VOC, the paint has very less fire hazards during application. After satisfactory Users trial scarried out on INS Abhay and INS Vipul, the nano-material based bilge coating has been inducted into services.

The technology of this paint has been transferred to paint industry for bulk production. It is being regularly used by Navy for protecting the bilge compartments of various ships from corrosion.

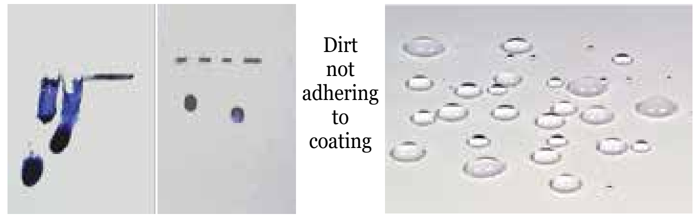


Bilge area of ship coated with nano-material based coating

Hydrophobic Self-Cleaning Coating

Hydrophobic self-cleaning coating is a functional material which keeps the coated surface dirt-free and maintains its original appearance. Such coatings can find application in maintaining hygienic conditions in kitchens, storage rooms and medical facilities of a Naval ship. The laboratory has developed a self-cleaning coating using low surface energy siloxane-based polymers with a novel crosslinker. This low surface energy silicone-based coating does not allow dust, dirt, oil, grease, etc. to adhere on to it. These coatings are very easy to clean. The developed coating has shown good adhesion with the substrate, scratch resistance, and excellent self-cleaning properties.

User trials of Hydrophobic self-cleaning coating have been completed on Yard Craft Pushkar and INS Vikramaditya. After the successful field trials, this coating has been inducted by Indian Navy. ToT of this paint has been given to three paint manufacturing industries and is currently under bulk production.



Non-hydrophobic coating(blue dye sticks on the surface) | Self-cleaning coating (blue dye rolls down without sticking on the surface) | Water droplets beading on self-cleaning coating

Demonstration of self-cleaning ability of coating

Engine room hatch area of ship coated with self-cleaning coating

Paints for Protection of Submarine Acoustic Rubber Tiles

A specialty paint has been developed by the laboratory for protection of acoustic rubber tiles of submarines. It is a single coat system for direct application on rubber substrate. The coating provides a dry film thickness of 40 ± 15 µm in a single coat.

The essential ingredients of this paint are elastomeric polymer (Styrene Ethylene Butylene Terpolymer, SEBS), pigments, solvents and additives. These specialty additives in the paint formulation provide superior adhesion, thixotropic nature, good wettability, dispersion and defoaming properties. The paint can be applied using brush/rollers and dries in 2 hours to form a hard and tough barrier coating to protect the rubber tiles from seawater as well as environmental weathering. This paint has been formulated in black and white shades. The paint has an adhesion strength of 1 MPa (on rubber surface). It has excellent flexibility, impact strength as well as resistance to seawater and weathering.

Black shade paint is applied on above the watermark/level of the submarine whereas the white shade is used for marking purposes. The User trials of this paint have been carried out on INS Shindhukeshari and INS Sindhuvijay. Post successful User trials, this paint has been inducted by Indian Navy. ToT of this paint has been given to paint manufacturing industry for production in bulk quantity for the Indian Navy.

Field trials of black and white protective paint onboard Submarine

PAINTS/ COATINGS SUCCESSFULLY COMPLETED USER TRIALS

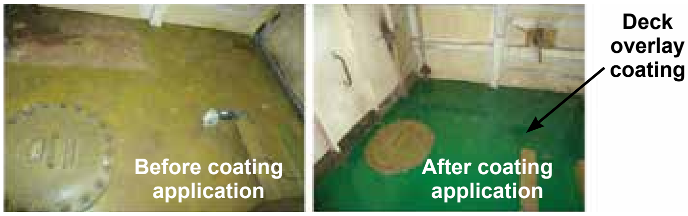
Details of various products which have successfully completed User trials are given below. These products are expected to be inducted in to the Services shortly.

Deck Overlay Coating

The metallic, concrete, or wooden floor surfaces of the ship deck area experiences lot of movement of people, material, and vehicles. This results in the material loss due to erosion and corrosion, leading to uneven thickness and appearance. Development of an appropriate coating was essential to minimize wear and tear as well as erosion. The deck overlay coating used on floor surfaces is expected to possess good toughness, resistance to abrasion and corrosion as well as resistance to harmful effects of chemical spillage and cleaning detergents. Additionally, it is essential to maintain good aesthetic appearance of floorings.

To meet these properties, NMRL has developed a paint composition, that utilizes in-house synthesized hyperbranched resin based on fatty acid and commercially available epoxy resin. The resin has been pigmented using different pigments at various concentrations. Developed paint has good adhesion strength, high abrasion, and scratch resistance.

Furthermore, it has safer limits of limiting oxygen index, smoke density, toxicity index, electrical resistivity, and thermal conductivity, as per the naval standards. Coating has been developed in four colours with high gloss retention suitable to various surface applications. The trials of this coating have been carried out onboard INS Kora, INS Brahmaputra, and INS Vasudha. The coating has shown promising results.



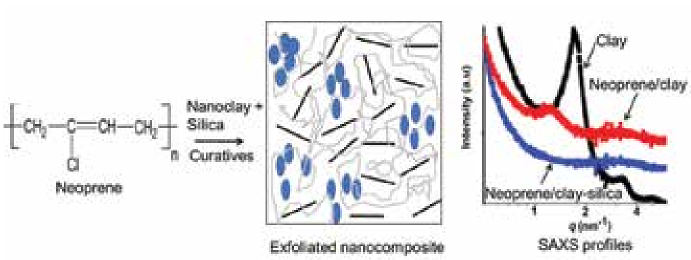
Deck overlay coating applied onboard ship deck area

Characteristics of NMRL developed deck overlay coating

Characteristics	Indian Navy Requirement (NCD 1471)	NMRL developed coating
Density (g/cc)	< 1.70	1.5
Moisture absorption (%)	< 0.5	< 0.2
Adhesion strength, MPa	> 1.75	> 3
Flexibility (½ inch Mandrel)	Should not crack or detach	No cracking or detachment
Volume resistivity, Ohm.cm	$> 100 \times 10^6$	2.45×10^{12}
Smoke density, %	-	65.8
Limiting oxygen index	-	25
Toxicity index	-	0.7
Resistance to salt spray test, 500 h	No sign of rusting or corrosion	No sign of rusting or corrosion
Fire resistance test	Self-extinguishing after removal of fire source	Self-extinguishing after removal of fire source

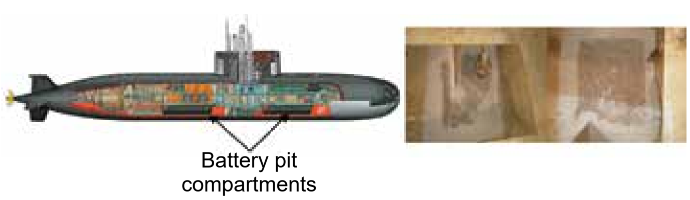
Acid Resistant Rubber Lining

Diesel electric submarines are powered by series of batteries placed in its battery pit compartment. These batteries are filled with an acidic electrolyte (battery acid). This electrolyte invariably spills during the filling operation. This spillage from the batteries results in severe pitting corrosion of submarine steel hull. To protect this, NMRL has developed a nano composite-based rubber (neoprene) lining which incorporates specialty Nanoclay having platelet-like structure in a polymer matrix. Inclusion of specialty Nanoclay resulted in improved mechanical properties and acid resistance characteristics of polymer matrix.



Exfoliated neoprene clay nanocomposites along with SAXS profile

Sheets of acid-resistant rubber lining material are applied on the bottom surface of the battery pit compartment to provide protection against battery acid corrosion. The rubber lining has shown excellent adhesion strength and acid resistance characteristics for extended period of over 24 months. Furthermore, lining can be applied over already coated surfaces to enhance overall corrosion resistance. After successful long duration User trials on INS Sindhu Shashra, INS Sindhu Vijay, SPV and INS Salki, the acid-resistant rubber lining has been accepted by Indian Navy for induction. NCD is expected to be issued shortly. Developed rubber lining has found spin-off in civil applications as well, as it can be used for protection of chemical tanks, reaction vessels, piping and other installations from corrosive effects of several mineral acids, viz. sulfuric acid in various chemical industries, etc. Acid-resistant rubber lining technology has been transferred to two industries.



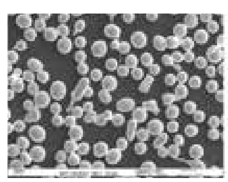
Rubber lining applied in battery pits of submarines

Bulk Metallic Glass Coatings

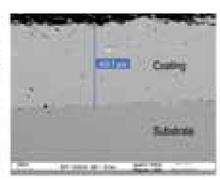
Bulk metallic glasses are an emerging field of materials with many desirable and unique properties, such as high strength, good hardness, excellent wear resistance and high corrosion resistance. A series of iron based metallic glass have been developed in laboratory using melting and melt spinning process. Furthermore, these have been produced in larger batch sizes, with the help of industry using melting and atomization technique.

Developed Fe-based Bulk Metallic Glass (BMG) coatings have been applied using HVOF technique. These coatings have hardness ranging from 750 to 900 VHN, high erosion-corrosion resistance equivalent to wrought super duplex stainless steel. These coatings possess good adhesion strength of more than 60 MPa, porosity of less than 2 per cent, a surface finish of 0.3 µm after grinding. These coatings may be used as replacement for hard chrome plating.

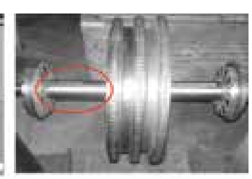
User trials of this coating have been carried out on steam turbine rotors of naval ships (INS Brahmaputra and INS Beas) and it has shown satisfactory performance with excellent erosion-corrosion resistance property. This coating has been accepted by the Indian Navy for induction and its NCD is expected to be issued shortly.



BMG powder morphology



BMG coated by HVOF technique



Coated Rotor Shaft

OTHER PAINTS/COATINGS DEVELOPED

Navy has been entrusting the job of protective paint/coating development for wide variety of applications on NMRL. Taking note of these requirements, NMRL has taken dedicated efforts to develop various paints/coatings. These development efforts are enumerated below:

High Temperature Resistant Non-Skid Coating

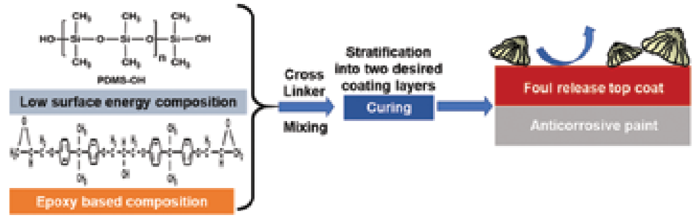
To improve the service-temperature range (up to 300°C), durability and overall performance of existing (Mk-I) in-service epoxy-based heavy duty non-skid paint, a two-component siloxane epoxy hybrid non-skid coating (Mk-II) has been developed by the laboratory. This coating contains silicon-oxygen (Si–O–C) bonds, which provide greater bond strength than carbon-carbon (C–C) bonds in normal epoxy coatings, thereby providing greater exterior durability against UV radiation (from sunlight). In addition, the siloxane-epoxy hybrid non-skid coating has lower VOCs content, it repels hydrocarbons, detergents and does not blush or bloom after application due to its hydrophobic nature. Due to Si–O–C bonds, it has thermal resistance up to 300°C and possesses an excellent impact resistance against arresting cables, wear, and durability. User's trials of the coating were first conducted at SBTF, Goa.

The coating formulation has been modified based on the feedback received from SBTF trials. Second series of User trials of the coating would be undertaken by Indian Navy on the weather deck of INS Kolkata and are expected to commence shortly.

User trials of coating SBTF, INS Hansa Goa

Anti-corrosive Foul Release Paint

The laboratory has developed a siloxane-epoxy pigmented fouling-release coating composition which impart anti-corrosive and fouling release properties in a single coat application. This coating is formulated based on self-stratification concept of thermodynamically incompatible polymers, which differ widely in their solubility parameter values, to produce a multilayer coating in a single coat application. During curing the low surface energy polymer enriches the air interface while the polymer with a higher surface energy preferentially migrates towards the substrate. The low surface energy hydrophobic top surface ensures foul release property, while the underneath epoxy coating layer ensures anti-corrosive property.



Self-stratification mechanism of the foul release coating

The main advantages of this coating over conventional sequentially applied multi-layer coatings are higher inter-coat adhesion between two layers of resin owing to interdiffusion and reduced VOC emission because of the single coat application.


Existing coating after 90 days of immersion


Foul release coating after 90 days of immersion

Field evaluation of anti-corrosive foul release paint

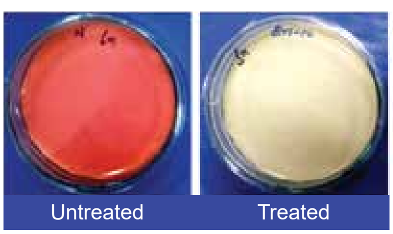
The performance evaluation of anti-corrosive foul release coating has been carried out in dynamic flow channel test setup at IGCAR, Kalpakkam where in the coating has shown satisfactory performance. The certification of this paint has also been completed by the NMRL through Indian Registry of Shipping (IRS), Mumbai. The field trials of this paint are expected tocommence soon.

Anti-Microbial Coating for Internal Compartments of Ships

Microbes are microscopic living organisms that usually thrive in the moist interiors of ship or submarine compartments. Many of them are pathogenic and infectious. Through skin contact, inhaling polluted air, consuming contaminated food or water, etc., they have the ability to infect humans with disease. These bacteria have the potential to proliferate rapidly in the right circumstances and eventually harm their surroundings and structures. Anti-microbial coatings are used to protect interior and humid surfaces from bacterial and fungal attack. It helps in maintaining hygienic conditions and aesthetic appearance.

Utility of anti-microbial coating in various locations of ship

The laboratory has developed an anti-microbial paint based on silicone modified alkyd resin, speciality fillers and antimicrobial additives. Prior to paint development, bacteria and fungi samples were collected from affected areas of naval ships and tested in the laboratory. Various antimicrobial agents were evaluated for confirming their effectiveness in inhibiting microbial and fungal growth. Stearate based additive showed excellent antibacterial properties and essential oil-based additive showed excellent anti-fungal properties as compared to other additives.



Coating without and with antibacterial agents

Coating without and with anti-fungal agents

These two additives were blended in silicone soya alkyd paint which showed excellent resistance to bacterial and fungal attacks. These additives either breaks the cell wall of bacteria or fungi and spills the active contain within cell wall or binds to S-Ribosomal unit of RNA. This results in killing or inhibition of growth of bacteria or fungi. The ratings for antibacterial and anti-fungal properties of paint prepared with and without antimicrobial additives are given in the tables below. After successful completion of anti-microbial coating development an Indian patent has been filed by the laboratory.

Antibacterial property of coating without and with antimicrobial additives

Bacteria	Observations after 48 h	
	Coating without additives (Untreated)	Coating with additives (Treated)
Staphylococcus cohnii	3	0
Bacillus cereus	4	0
Bacillus paramycoides	4	0
Staphylococcus sciuri	3	0
Serratia marcescens	4	1

Ratings: 0, 1, 2, 3 and 4 represent complete inhibition, less than 10%, 10-30%, 30-60% and flat bacterial growth (> 60%), respectively.

Anti-fungal property of coating with and without antimicrobial additives

Fungi	Observations after 30 days		
	Filter paper (positive control)	Coating without additives (Untreated)	Coating with additives (Treated)
Aspergillus niveoglaucus	3	2	0
Aspergillus terreus	4		0
Chaetomium globosum	4	2	0
Penicillium chrysogenum	4	3	0
Aspergillus niger	3	2	0

Ratings: 0, 1, 2, 3 and 4 represent complete inhibition, less than 10%, 10-30%, 30-60% and flat bacterial growth (> 60%), respectively.

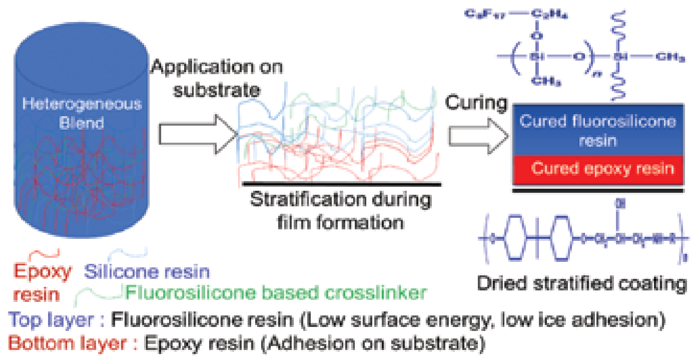
Heat Barrier Coatings

Heat barrier coatings, viz. acrylic emulsion and silicone epoxy based have been developed for application on aircraft carriers on the structures which are exposed to aircraft jet engine exhaust. The coating minimizes the heat transfer by acting as barrier for conduction, convection, and radiation. This heat barrier coating is also fire-retardant in nature and can withstand a temperature of up to 300°C. Coating can be applied by brush, roller and spray. It provides a dry film thickness of 200-250 µm in single coat application. It acts as a barrier type heat insulation coating. This coating is formulated with low thermal conductivity materials, viz. microsphere, pigments, fillers, additives etc. The development work of this coating has been completed. The heat barrier coating developed by the laboratory has shown substantial temperature reduction compared to imported coating.

Heat barrier coating

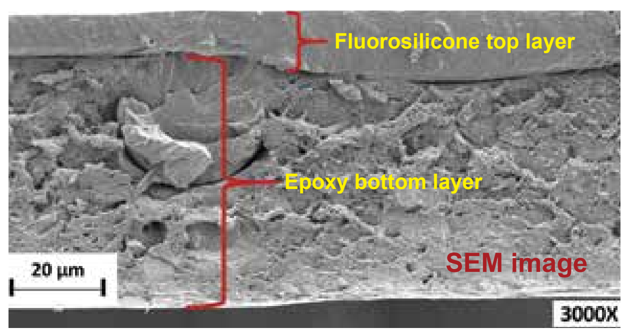
Anti-Icing Coatings

Ice accretion over leading edges (wings) and horizontal tails of Unmanned Aerial Vehicle (UAV) can lead to reduced endurance and flight instability due to addition of unwanted weight. Removal of ice from such surfaces in flight is difficult. Complex mechanisms are required to be employed for ice removal in flight which also adds to the structural weight. The laboratory has developed a self-stratifying paint system containing silicone epoxy resin, pigments, fillers, thinners, fluorine-based additives, wetting and dispersing agents, and curing agents. The coating has been prepared in two colours: grey and orange. It is applied in a single coat of 60 ± 5 µm thickness. After application, epoxy resin settles at the bottom and low surface energy silicone resin at the top. The mechanism of two-layer separation (stratification) is illustrated in figure given below,



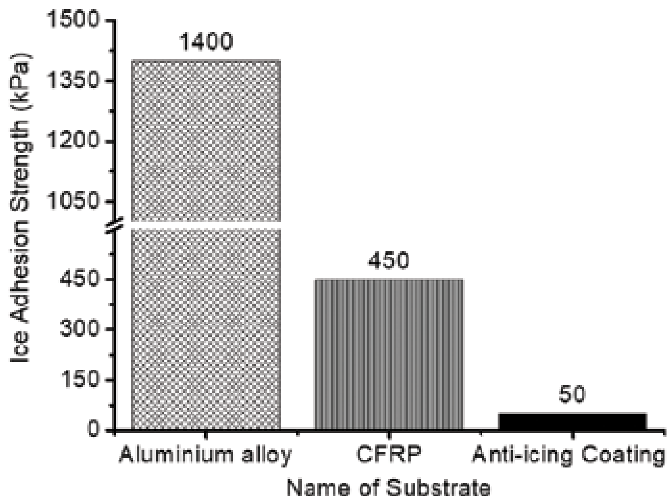
Schematic representation of stratification

Scanning Electron Microscopy (SEM) analysis revealed that the bottom layer contains epoxy resin and top layer fluorosilicone resin.



Confirmation of stratification by SEM

The anti-Icing coating is ambient temperature curable, robust, sprayable and provides anti-icing property for 12 months. This coating is hydrophobic in nature (high contact angle of >110°) and also has very low ice adhesion strength (50-52 kPa) which minimizes ice accretion. It exhibits excellent mechanical properties, thermal cycle resistance as well as ease in maintaining cleanliness. The coating has resistance to various fluids such as ethylene glycol, propylene glycol, ethanol, phosphate ester hydraulic oil, pyrolyzed oil, battery acid and mineral-based hydraulic oil. Application of anti-icing coating has been completed on three airframes of UAV TAPAS.



Ice adhesion strength on various substates

UAV TAPAS

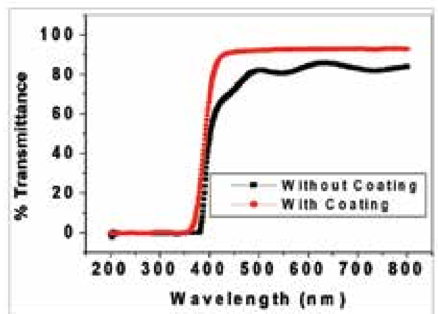
Anti-icing coatings being applied on leading edges and horizontal tail of UAV

Transparent Coating for Aircraft Canopy

The windscreen and canopy of aircraft are made of transparent materials. It covers the cockpit to provide a weather proof and secure environment for the pilot. These are made of special kinds of polymers due to their easy processability and moldability to provide desired aerodynamic shape. Stealth canopies are coated with a thin layer of conducting material to prevent the build-up of static charges and to provide radar attenuation inflight. However, this coating has limited scratch resistance.

LCA Tejas

The laboratory has developed optically transparent protective coating which is applied over the conducting stealth coating without compromising its radar reflecting properties or optical transparency. Coating has been developed using siloxane-based resin. After curing and drying, it produces a hard and transparent layer. It does not interfere with radar absorption characteristics of the conducting stealth coating. Transmittance of canopy substrate coated with NMRL-developed transparent coating was measure using UV-Visible spectrophotometer in 200-800 nm range. NMRL coating exhibited requisite transmittance of > 90%.



Transparency of coating

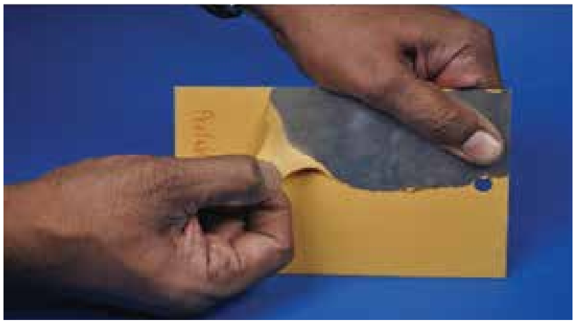
Perspex acrylic sheet coated with transparent coating

Characteristics of the transparent coating	
Parameter	**Observation**
Appearance	Clear colour less to light straw liquid
Viscosity, mPa.s	40-50
Specific gravity, g/cc	1.155
Molecular weight, g/mole	< 1000
Theoretical silicone content, w/w%	70-74
Surface tension, mN/m	24.42

Peelable Coating for Temporary Corrosion Protection

Peelable coating can be used for temporary protection of structures/parts/ fasteners from corrosion/scratches/seepage of water, etc. This coating film can be peeled off manually as and when required. It can protect surface beneath from corrosion for 6-10 months depending on the environment. Peelable coating can be directly applied on metallic and non-metallic substrates. It can be even applied on articles coated with epoxy polyurethanes, etc. The peelable coating is employed for temporarily protecting painted structures/parts/fasteners from scratches and corrosion during storage and transit. The coating can be easily be peeled off as and when required.

The laboratory has developed a Styrene Ethylene Butylene Styrene Terpolymer, SEBS rubber-based peelable coating used for temporary protection of structures/ parts/ fasteners from corrosion/ scratches/seepage of water. It can be applied by brush or spray techniques, at dry film thickness of about 45 to 50 µm. Coated items can be protected from corrosion for six months. As coating has been formulated to have low adhesion, it can be easily peeled off whenever required. NMRL has filed an Indian patent for this coating.



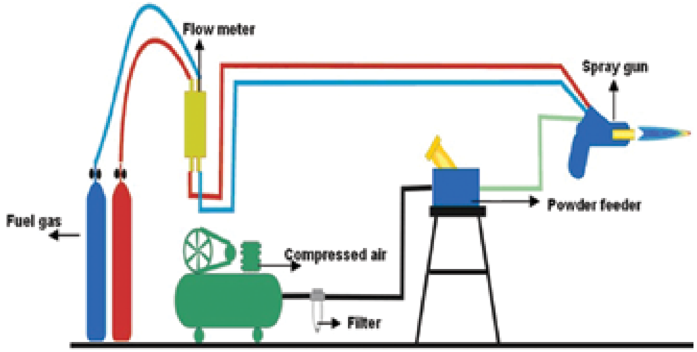
Rubber based peelable coating

Thermally Sprayable Organic Coating

Thermally sprayable polymeric coating is one of newer technologies where high molecular weight polymers are melted and applied in coating form to protect metallic surfaces from adverse environment. As these polymers cannot be dissolved in common solvents, flame spraying is used to melt and deposit in coating form onto a surface. These coatings have high chemical resistance and superior mechanical properties as compared to powder coatings. They can be applied on large metallic structures with instantaneous film formation. The coating has overcoat ability and is easy to repair. Being a solvent free coating, there are no fire hazards during its application in confined areas unlike conventional paints.

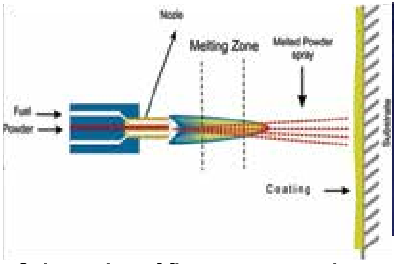
The laboratory has pioneered in development of this technology using organic polymer powder blends. Commercially available polymer granules are grinded to powder form, approximately to 250 µm particle size to facilitate spraying. The powder is then blended with various pigments. Additives are also incorporated to improve flowability and coalescence of hot splats released from the thermal spray gun.

Pigmented polymeric powder is applied on cleaned and contamination free metallic surface, using thermal spray system. It includes a flame spray gun, feed stock material container and feeding mechanism, fuel gases, carrier gas with flow meters and pressure regulators and air compressor. In this process, the feed stock material is fed continuously to the tip of the spray gun where it is melted in a fuel gas flame and propelled to the substrate in a stream of carrier gas. During application, the temperature is controlled and maintained below the decomposition temperature of the polymer. Within a few minutes of application, the coating solidifies and surface is ready for use.



Schematics of flame spray system

Thermally sprayable polymeric coating can be used on large structures, intricate shaped objects, chemical handling vessels, non-flammable surfaces, etc. Coating application setup is portable and can be used in open atmosphere. The concept of thermal spray coating has been proven at laboratory level. Application of this coating for the naval use is being explored.



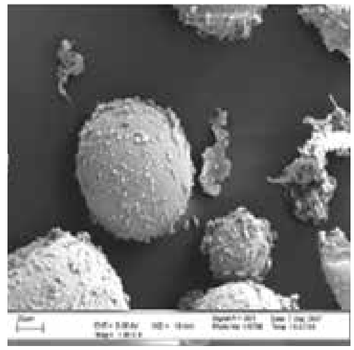
Schematics of flame spray torch

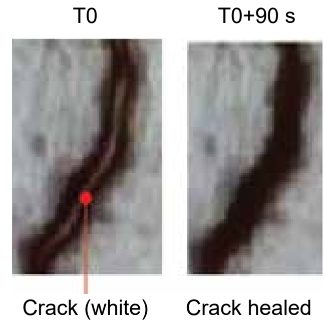

Coating on intricate shaped objects by flame spray method

Self-Healing Smart Coatings

Paints are commonly used for decoration and protection. During service, these undergo various degradation processes and reach to a condition when coatings require renewal. One of the most common coating defects is generation of cracks in the paint film during service. These cracks allow moisture and other corrosion inducing agencies to reach the metal surface and initiate corrosion process. Subsequently, delamination of the paint film occurs, exposing bare metal to the environment. If microcracks could be healed as soon as they are generated, further damage to the coating can be avoided and the service life of the paint film can be increased which in turn enhances the life of structures. This has been achieved by incorporating microcapsules filled with healing agents in the paint. When a crack is generated, healing agent is released due to the rupture of microcapsules and the crack is sealed/ healed. This built-in smart property enhances the service life of coatings.

The laboratory has developed a paint system having silicone modified alkyd-resin based top coat and epoxy-resin based primer. Air drying silicone modified alkyd-resin based paint has microcapsules, containing healing agent. When there is damage in the top coat, capsules get ruptured and the core material (healing agent) is released. This undergoes oxidative polymerization and repairs the crack. Corrosion inhibitors encapsulated into alkali sensitive microcapsules were incorporated in the primer. Release of corrosion inhibitors takes place under alkaline pH conditions which is generated during the onset of the corrosion reaction at metal coating interface. Self-healing coating system has been successfully developed and its functioning has been demonstrated in the laboratory.


Shell morphology of microcapsules

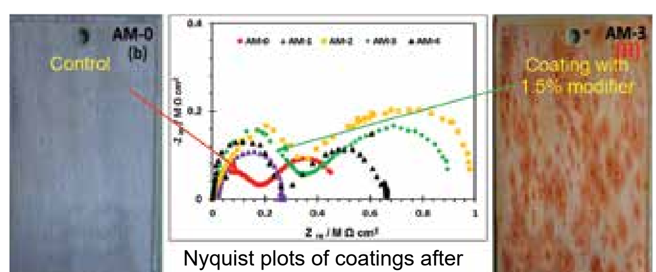


Healing of crack

Corrosion Sensing Coatings

Paint application is the most economical method for corrosion protection of metallic structures. Failure of paint/coating before the anticipated service life, may result in catastrophic accidents leading to economic and manpower loss. Being passive in nature, the conventional paints do not exhibit corrosion sensing properties that can indicate degradation of the paint coating and onset of corrosion at the metal-coating interface.

The laboratory has developed two types of smart corrosion sensing coatings for early detection of corrosion underneath the coating film. The developed paints act as sensors for corrosion and detects cathodic and anodic reactions at early stages of corrosion. Coatings detect onset of corrosion either via colour change or fluorescence change. Colour changing coating uses phenanthroline-modified epoxy resin which shows colour spots wherever corrosion sets in at the metal-coating interface.



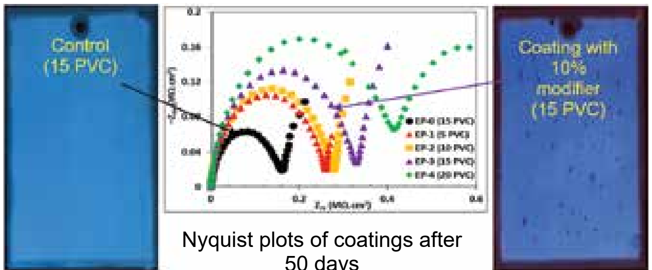
Coating without corrosion

Nyquist plots of coatings after 7 days

Red coloured spots due to onset of corrosion

Colour changing corrosion sensing coating

Similarly, fluorescent-modified coating shows fluorescent spots at places where corrosion occurs underneath the paint film. The coating acts as early corrosion warning and highly useful for taking appropriate measures to tackle the onset of corrosion.



Nyquist plots of coatings after 50 days

Coating under UV light without corrosion

Fluorescent spots in coating (under UV light) due to onset of corrosion

Fluorescence-based corrosion sensing coating

Initially, the Nyquist plots for coated samples indicates that they exhibit requisite polarization resistance of > 1 MΩ cm² necessary for corrosion protection. The coatings after immersion in corrosive seawater successfully showed colour or fluorescence spots due to the onset of corrosion. The polarisation resistance was measured once again after onset of corrosion which was observed to be < 1 MΩ cm² which corroborates with the colour or fluorescence spots seen on the coated samples.

Alkali Resistant Coating

NMRL has developed an alkali resistant coating for metal, glass, ceramic and polymeric substrates. This coating composition is based on blend of synthetic rubber copolymer and epoxy resin, and cured with a suitable hardener. It produces a clear coating on the surfaces with a dry film thickness of 100 ± 5 µm. This coating can be applied on containers used for storing the highly alkaline substances. The coating has been developed for sodium borohydride storage tank (being used in AIP system) lining application. The laboratory level trials of this coating have been completed and performance was observed to be satisfactory. NMRL has filed Indian patent for this coating.

NaBH4 storage tank lined with clear alkali resistant coating

TEST FACILITIES FOR CORROSION PROTECTION COATINGS

The laboratory has a full-fledged facility for research, development and testing of paints for corrosion protection of structures. It is well equipped with equipment for preparation of resins for paint formulation. Paint preparation facilities include Ball mill, Attritor Mill, Ultrasonicator, Three Roll Mill and High-Speed Disperser. Hard drying apparatus for drying properties, Paint viscosity cups, Brook field viscometer, and Roto-viscometer for viscosity, air and airless spray systems for paint application are used for determining paint properties.

Dried film characteristics are measured using, dry film thickness gauge, gloss meters for shining properties, conical and cylindrical bend testers for flexibility, universal tensile machine for tensile strength, elongation and adhesion properties, tabor abrasion tester for abrasion resistance, coefficient of friction tester for frictional properties of non-skid coatings, scratch resistance tester for coating toughness, portable adhesion tester for field measurement are used for coating characterization. Various environmental chambers like, paint corrosion oven, seawater immersion tanks, impressed-current cathodic protection set-up, salt spray chamber, UV weatherometer are used for assessing corrosion resistance properties. Electrochemical impedance analyzer is used for determining pore resistance, capacitance, water uptake and adhesion properties of coatings, cathodic disbondment for coatings under electrochemical conditions. A specialised facility, ice adhesion tester has been set up for studying adhesion properties of ice on painted surfaces.

In addition to above, modern characterisation techniques such as, Particle size analyser, Scanning Electron Microscope, X-Ray Diffraction, Atomic Force Microscope, DSC, DMA, TGA are also available in the laboratory for examination of paint and raw materials.

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