FIELD APPLICABLE PVDF CORROSION PROTECTION COATING FOR MARINE ASSETS

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ABSTRACT

Marine environments are highly corrosive to ships and other assets that are made out of steel. Novel field applicable PVDF coating solutions have been developed to provide immediate relief when used as top coating or over-coat over existing protective coatings.

This field applicable, patent-pending PVDF corrosion protection coating technology have the following key attributes:

1) At 30-50μm thickness, the corrosion protection coating is 100x more efficient than 500μm (20mils) of epoxy coatings in blocking moisture and moisture-carrying dissolved salts and acidic gases.
2) At 70% PVDF in the coating, it has been proven to withstand direct UV exposure for more than 60 years. The patent-pending 100% PVDF corrosion protection coating is now available to further the longevity of corrosion protection when applied over the epoxy coating as over-coat protection.
3) The inherent hydrophobic property of the PVDF polymer is maintained in the patent-pending field applicable coating technology to provide antifouling protection for below seawater line naval and marine assets.

As top coatings in protecting the underlying coating, these field applicable PVDF coatings not only to resist, but also block UV light from damaging the underlying UV vulnerable epoxy and polyurethane coatings.

Key words: field applicable PVDF coating, corrosion protection, over-coat, moisture blocking, UV protection, UV resistant

INTRODUCTION

Preventing and slowing corrosion are key to assuring the availability of naval and marine assets and lowering the costs of maintenance. The U.S. Navy spends $3 billion a year fighting rust, according to Military.com. Corrosion takes place both at sea and onshore, affecting cruisers, helicopters, and fighter jets. A deep fix of corrosion issues on just two ships, cost the service $170 million alone[1].

A coating that can prevent moisture and water laden with dissolved salts and other corrosive gases from reaching the steel surfaces, with or without traditional epoxy coating, will be an effective solution in preventing corrosion damage to the ship. If the coating can provide the inherent ability to resist, or dramatically slow the attachment of barnacles and zebra mussel growth[2], it would be an ideal solution and measurably extend the service duration between maintenance.

In this paper, we present data showing dramatic corrosion protection of bare steel, and steel coated with traditional epoxy coatings, using field applicable modified PVDF coating technology. PVDF is known to be molecularly structured to provide an outstanding barrier to moisture and water permeation. However, because of its relative low surface energy, it cannot be used in the field as an effective coating.

In this paper we present data of roll/brush/spray PVDF coatings that can be air-cured to bond to bare steel, traditionally prepared, and epoxy coated steel with 5B cross-hatched coatings, that provide good adhesion while maintaining a low surface energy on the side exposed to the sea water and salt-spray.

Figure 1: Marine and naval assets show significant corrosion both above and below the sea waterline after just a few hundred days at sea.

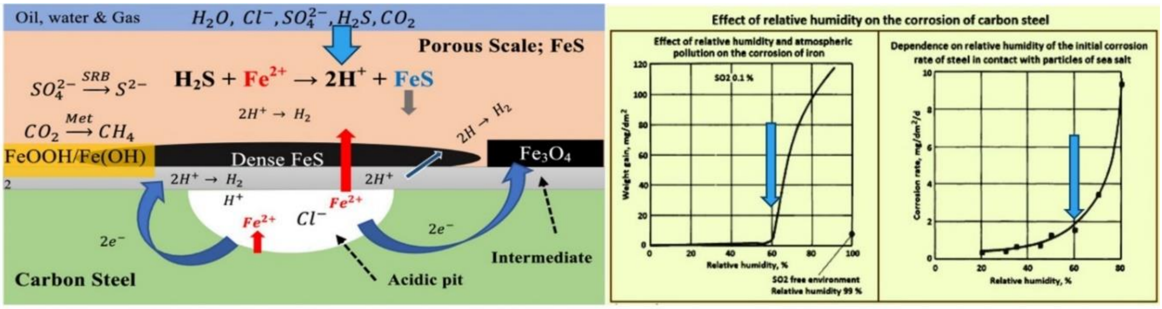
CORROSION MECHANISM IN MARINE ENVIRONMENT

Corrosion to steel and other base metals are primarily caused by acidic and/or galvanic mechanism with water as ionic carrier. The following discussion illustrates the pitting type corrosion mechanism[3] in water with dissolved CO_2 and H_2S. A similar mechanism of corrosion occurs with acidic gases, from industrial exhausts such as SO_2, etc., that form an electrolyte that accelerates corrosion. A similar corrosion mechanism applies to microbial and bio-growth that generate acidic byproducts during their life cycles.

When ships and other marine assets that are submerged into seawater, the dissolved sodium chloride and other chlorides provide a natural corrosive electrolyte causing corrosion.

These corrosion mechanisms are kinetic chemical processes that increase exponentially with temperature. That is, corrosion in tropic zones will be much faster than temperate zones. For many aqueous reactions, a 30°C temperature change results in a 10-fold change in corrosion rate, while a 20°C change will approximately double the corrosion rate[3]. Figure 2 below illustrates the corrosion mechanism with acidic gases and dissolved ions carried by moisture and water[4]. Dissolved ions in seawater are extremely corrosive to carbon steel when they get through the protective coating into the coating-steel interfaces. As seen in Figure 3, the corrosion rate is relatively constant over time[5].

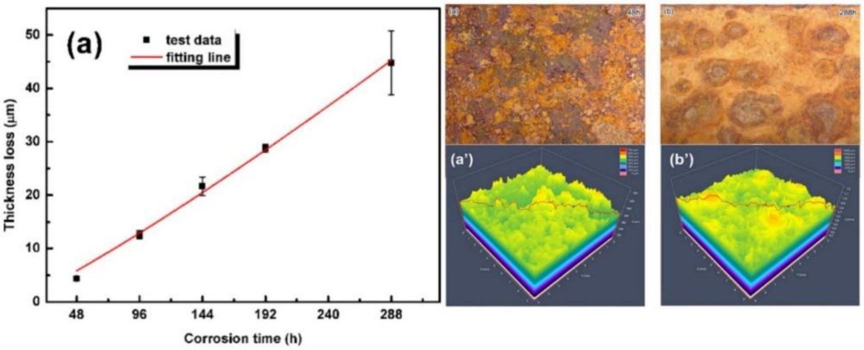
Corrosion being primarily chemical kinetic process, the increase in corrosion rate with increasing temperature. In addition, the environments that are laden with dissolved ions, as in submerged into seawater or the splash zone near the water level, where salt-fog and salt-spray provide a more efficient means of carrying corrosive Cl^- ions to the metal surfaces.



Shokri, A., Sanavi Fard, M.; Under deposit corrosion failure: mitigation strategies and future roadmap. *Chem. Pap.* 77, 1773–1790 (2023). https://doi.org/10.1007/s11696-022-02601-6

https://www.ispatguru.com/corrosion-in-carbon-steels/

Figure 2: Marine and naval assets show significant corrosion both above and below the sea waterline. The seawater is highly corrosive when combined with dissolved salt ions and laden with dissolved corrosive gases.



Thickness loss of carbon steel samples as a function of corrosion time

Influence of Seawater on the Carbon Steel Initial Corrosion Behavior; Yuwei Liu, Zhenyao Wang, Yinghua Wei;
http://www.electrochemsci.org/papers/vol14/140201147.pdf

Figure 3: If corrosion is not stopped with protection, the rate of corrosion does not seem to stop.

That is, in simple terms, the following elements must be present to induce corrosion:

1. Moisture and/or water in combinations with other corrosive elements
2. Acidic gases such as CO_2, SO_2, H_2S, etc. that can be dissolved in water and carried by moisture or water to direct contact with the base metal
3. Corrosive ions dissolved in water and moisture such as chlorides, sulphates, sodium, potassium, etc. that are carried by moisture and/or water to direct contact with base metal
4. Higher concentrations of one, or all three ingredients in the environment, or more importantly, those that can pass through the protective coating, will accelerate the corrosion
5. Higher temperatures accelerate corrosion

To prevent naval and marine steel assets from corrosion damage, the protective coating must provide the following capabilities:

1) Possess good adhesion to the steel substrate in all seasons from temperature changes and all dynamic ocean conditions. That is, good adhesion prevents delamination of the coating which forms voids along the steel-coating interfaces, that retain the corrosion electrolytes causing corrosion. Corrosion will only happen when corrosive electrolytes are in contact with steel substrate.
2) Block moisture from penetrating into the steel-coating interfaces. Moisture penetration carries with it the corrosive chlorides, sodium and corrosive acidic gases dissolved and laden in the moisture.

3) Block corrosive gases such as CO_2, SO_2, H_2S, etc. from penetrating the polymer molecular pores into the steel-coating interfaces and any moisture retained in the polymer pores. Different polymer molecular structures have different molecular packing density and thus different capability in blocking the penetration of these corrosive gases.
4) Prevent moisture retention within the molecular pores resulting in small pools of water. That is, provide as close to zero moisture absorption as possible. The affinity to retain moisture, or moisture absorption, depends on the sizes of the molecular pores (or "free-volume" in polymer technology) and the polarity of the molecular structure. This is reflected in the level of hydrophobicity. Retained moisture combined with corrosive gases form corrosive electrolytes which induce corrosion.
5) For those exposed surfaces, such as the ship hull and marine assets above the seawater line, the coating must be resistance to UV degradation. UV damage to the polymer coating, results in embrittlement and fractures causing delamination and exposing the steel structure to corrosion.
6) The protection coating should have high antifouling capability for the ship hull submerged in seawater. Bio-growth not only reduces the ship movement efficiency, increasing fuel costs, but also causes corrosion from acidic gaseous byproducts of its natural growth processes.

Commonly used epoxy coatings, polyurethane coatings and silicone coatings in naval and marine assets all have substantial differences between coating types and sometimes observable differences within its own class as well. They have different moisture and corrosive gases permeability rates and water absorption percentages. Even with the best modes of protection, ships have to be maintained with at least 2 dry dock services in 3-5 years depending on the usage conditions.

ENHANCING THE PROVEN MARINE PROTECTION COATINGS TO EXTEND THE MAINTENANCE INTERVAL AND IMPROVE OPERATIONAL EFFICIENCY

Marine and Naval protective coatings have been proven over a long period of usage and practices. Their capability in protecting steel hull of ship have been proven and maintenance requirements are well established.

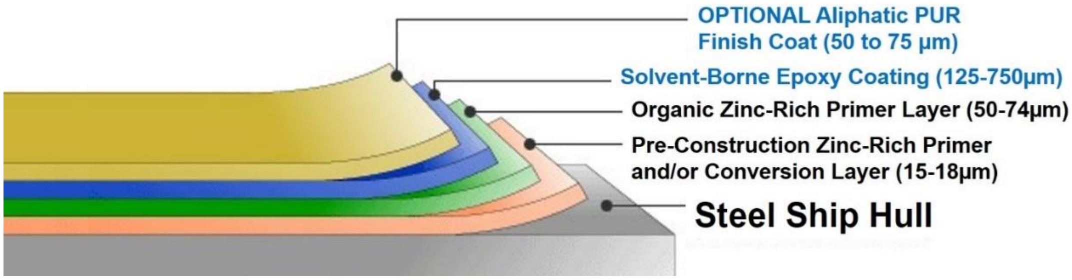


Figure 4: Representation of traditional coating protection for typical ship hull structure. Extension treatments along with heavy epoxy or other structural and corrosion protection are used. Yet, the corrosion of marine assets still occurs in a matter of less than a year and must be reworked at least twice in 5 years in according to SOLAS guidelines.

"As per SOLAS (Safety of Life at Sea) requirements, all merchant vessels require a complete survey of the hull in a dry dock twice within 5-year period and an intermediate survey within not more than 36 months.[6] This includes maintenance of hull, propeller, rudder etc. and other parts which are immersed in water and are normally inaccessible by staff when the ship is sailing.

For a passenger vessel, the inspection of the ship's bottom is to be done annually. Two of such inspections in a period of five years must be carried in dry dock and the maximum intervals between these inspections should be 3 years.[6]"

Naval and marine protection coatings for steel hull and other structures are primarily epoxy-based, modified polyurethane-based, acrylic-based, and silicone-based coatings, with high build-up to provide the mechanical and corrosion protection. The following improvements, if achieved, will dramatically improve the protection duration:

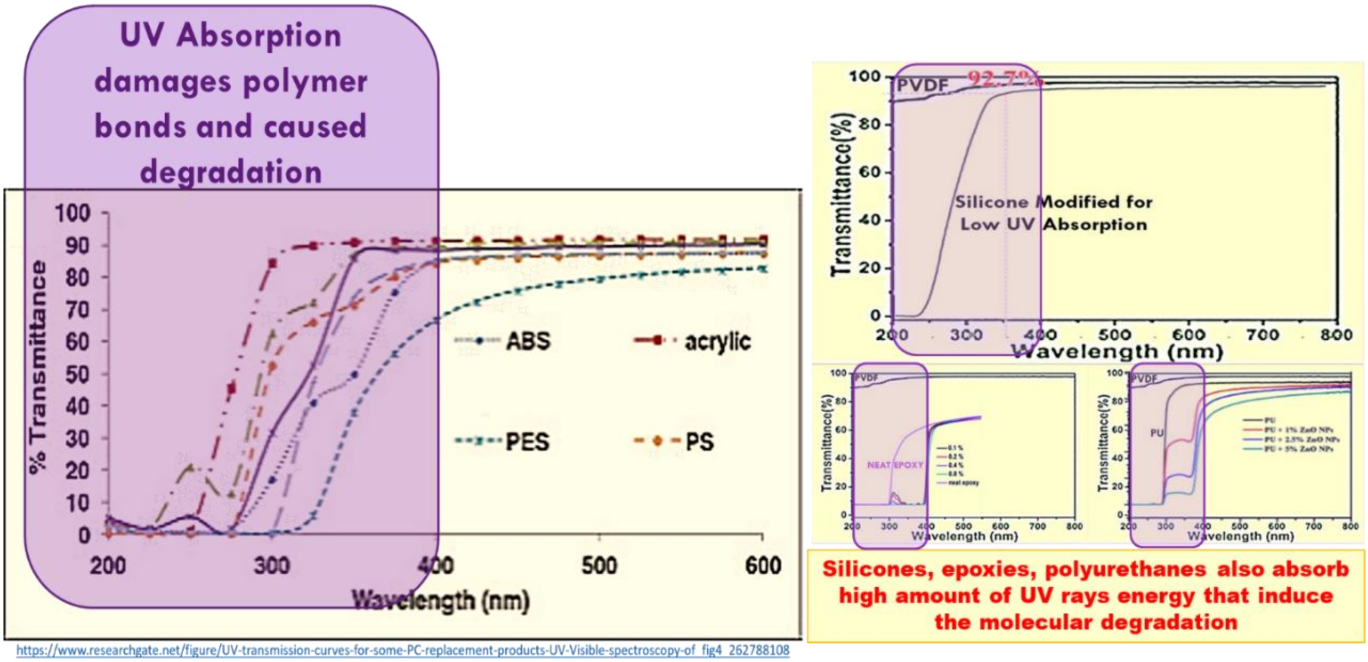
1) Adding UV exposure protection to epoxy, polyurethane, and acrylic coatings. This capability can dramatically reduce molecular damages to the coating that results in coating embrittlement and delamination.
2) Adding moisture blocking capability to existing coatings. There is room to improve the existing coating by several orders with a moisture blocking top coating. Along the same technical consideration, low moisture retention or water in along the steel-coating interface and inside the coating is also important factor in preventing corrosion.
3) Adding corrosive gas blocking capability to the existing protection coatings.
4) Addition of an antifouling component to the existing protection coatings.

The following provides a more detailed explanation of these solutions:

Sun UVA-UVB-UVC energy from 200nm[RG1] to 400 nm wavelength damages most Polymer with molecular bonds that absorb in this range of solar energy:

Exposure to ultraviolet (UV) radiation may cause significant degradation of most plastic (polymeric) materials. UV radiation causes photooxidative degradation which results in breaking of the polymer chains, produces free radicals and reduces the molecular weight, causing deterioration of mechanical properties and leading to useless materials, after an unpredictable time[8].

Figures 4A and 4B, represent the vulnerability of different polymers that are commonly used for naval and marine protection coatings. While fillers such as carbon black and/or TiO_2 and other absorptive and reflective properties help to slow down the degradation, the fundamental vulnerability still persists and results in the need for timely repaints and reworks.



https://www.researchgate.net/figure/UV-transmission-curves-for-some-PC-replacement-products-UV-Visible-spectroscopy-of_fig4_262788108

Silicones, epoxies, polyurethanes also absorb high amount of UV rays energy that induce the molecular degradation

Figure 5A: Acrylic and silicone polymers absorb UVB and UVC energy that cause relatively fast degradation. Epoxy and polyurethane, with their aromatic molecular structures, absorb UVA and UVB solar energy, causing even faster degradation.

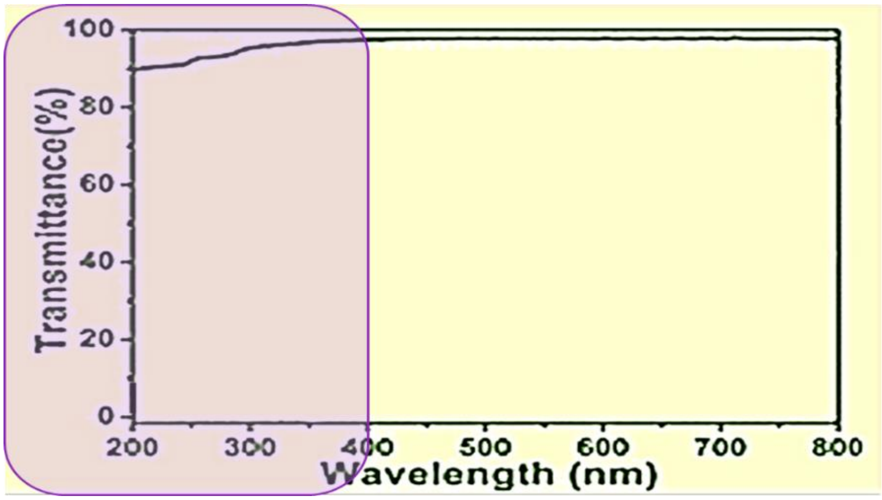


Figure 5B: PVDF polymer with its higher energy molecular bonds of C-F absorbs very little UVA, UVB and very slight UVC energy. That is the reason why PVDF coatings with 30% acrylic have been proven to last over 60 years or more, when used under the Florida sun.

Traditionally, PVDF coatings (with up to 30% acrylic) have be applied in the factory requiring extensive high temperature drying to cure the protective coating. That is, they are not easily “field applicable”. While specialty PVDF coatings have been developed for small field repairs, they are not suitable for large area field applications.

PTFE and other fluoropolymers are similarly difficult to apply and adhere to metal substrates without higher temperature processing and sometimes extensive surface treatments.

Field applicable patent pending PVDF coatings with up to 100% PVDF have been recently developed and proven for use in corrosion protections. They can be brushed, rolled, or sprayed coats onto metals and more importantly onto typical naval and marine epoxy and polyurethane coating with 5B crosshatch adhesion results. With additional engineering, these field applicable PVDF coatings are not only resistant to UV, but also provide years of UV blockage - with or without UV reflective additive oxides.

These new PVDF coatings can be used as transparent top coatings, or as color matched top coatings, to provide UV protection to the underlying epoxy and/or polyurethane of traditional naval and marine protection coatings as shown in Figure 6.

Field applicable PVDF as top coating can help block moisture ingress into the steel through the existing epoxy or polyurethane corrosion protection coating:

Moisture permeability, or the rate of moisture in penetrating a fixed layer thickness of polymers, have been extensively studied for their use in food freshness protection. In balancing the costs and performance, PET polyester is used for bottling of liquid and drinks while PVDC (instead of PVDF where instead of fluoride, chloride is used in forming the polymer) is used for preserving fruit and food freshness (e.g., “SARAN” wrap).

Figure 7 is a representation of the various common polymers and their relative permeability. Epoxy, polyurethane, and acrylics, with their amorphous molecular structure and conformation, have a similar permeability as polycarbonate and polystyrene (data filled in by the author). Silicone with its amorphous structure and large free volume, has order of magnitudes higher moisture permeability (data added by the author).

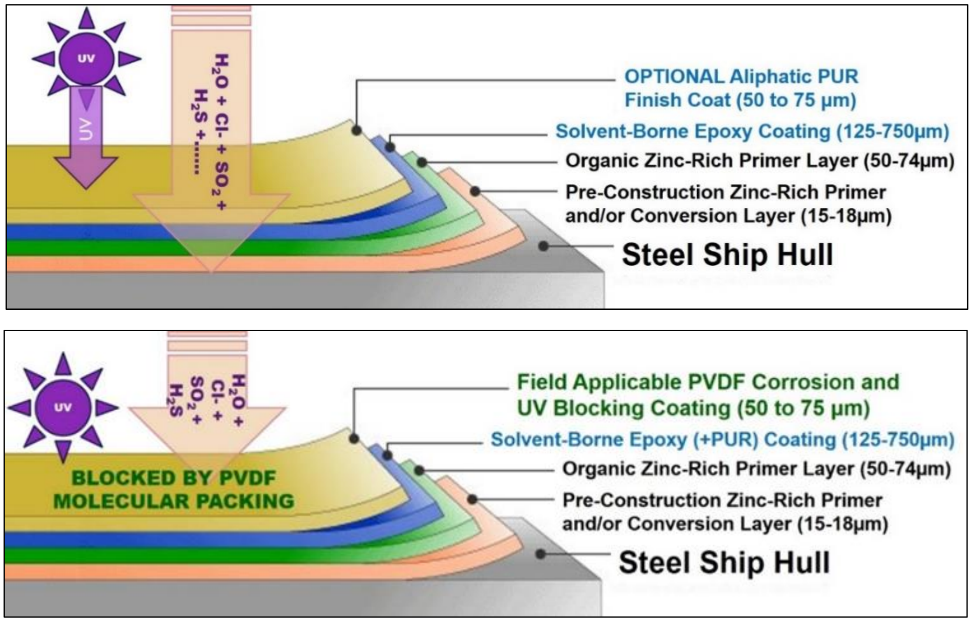
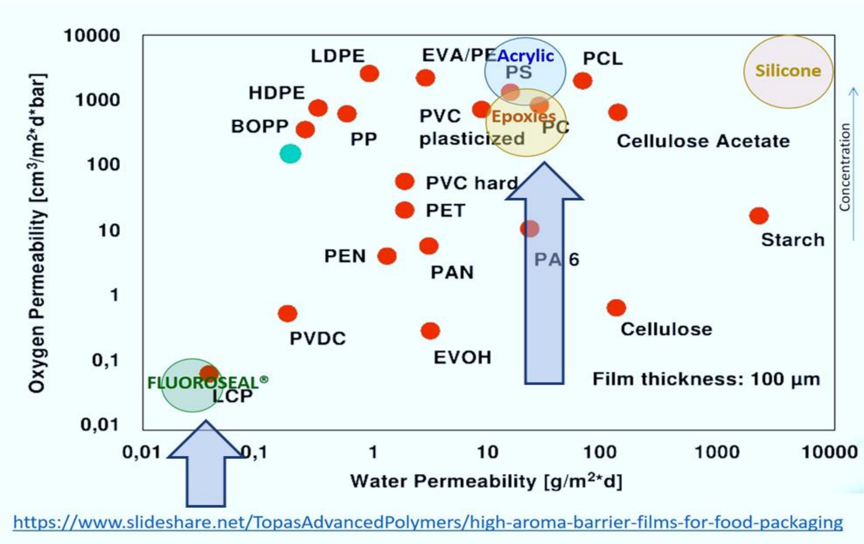


Figure 6: The top drawing is a representation of traditional coating protection for typical ship hull structure under typical environmental attack. The bottom drawing represents the addition of a top coating of PVDF that is resistant to, and blocks, UV as well as blocking corrosive gases and dissolved ions laden in the moisture from getting into the steel primer interfaces.



https://www.slideshare.net/TopasAdvancedPolymers/high-aroma-barrier-films-for-food-packaging

Figure 7: A representation of the various common polymers and their relative permeability. Epoxy, polyurethane and acrylics with their amorphous molecular structure and conformation have similar permeability as polycarbonate and polystyrene as filled in by the author. Silicone with its amorphous structure and large free-volume has order of magnitudes higher in moisture permeability as depicted by the author. The field applicable 100% PVDF top coating can provides a few hundred times more effectiveness in blocking moisture and moisture laden with dissolved ions and corrosive gases.

Pure, 100% PVDF, is slightly better than LCP polymer in blocking moisture. Thus, even with 30% acrylic, PVDF coatings have a very low moisture permeability - as represented by the circular zone in Figure 8. That is, a thin (100µm) 100% PVDF top coating provides 3 orders of magnitude (1,000 times) better moisture blocking capability than epoxy of the same thickness. Thus, even if one uses a high build coating of 500µm, the 50µm PVDF top coating still provides 2-3 orders, or 100-1000 times, better moisture blocking capability.

Moisture can carry dissolved salts (chlorides, sodium, potassium, etc.) that form corrosive electrolytes that permeate through the epoxy coating and get into direct contact with the steel, along the steel-coating interfaces or delaminated areas. So, blocking moisture penetration through the protective naval and marine coating by 100-fold means 100 times better protection of the steel.

Blocking moisture penetration into the coating lowers the amount of water retention along the steel-coating interfaces and within the coating:

Figure 8 below represents a compilation of the moisture-water absorption of common polymers often used for corrosion protection. Moisture absorption and water retention contribute to the corrosion of underlying metal, such as steel and copper.

First and foremost, moisture carries dissolved ions that pass through the coatings and reaches the metal at the metal-coating interface. Chloride, sulfates, sodium, and others are well-known elements that cause corrosion of base metals, such as steel and coppers.

Secondly, the absorbed moisture forms small water pockets inside the coating, and along the metal-coating interface, can dissolve corrosive gases such as carbon dioxide, sulfur dioxide, etc. and cause corrosion of the underlying metals. Acidic water solutions are also known main causes of corrosion of base metals.

PVDF has one of the lowest moisture absorption and retention levels, on par with PTFE and slightly better than LCP (liquid crystal polymers), at less than 0.01% (Figure 9 left side). In comparison, typical epoxies absorb 2% while more flexible polyurethane absorbs 3-5% (Figure 9 right side). Thus, PVDF as top coating, added over existing epoxy marine and naval coatings, can greatly reduce the moisture passing through the epoxy layer getting into contact with the steel at the steel-coating interfaces.

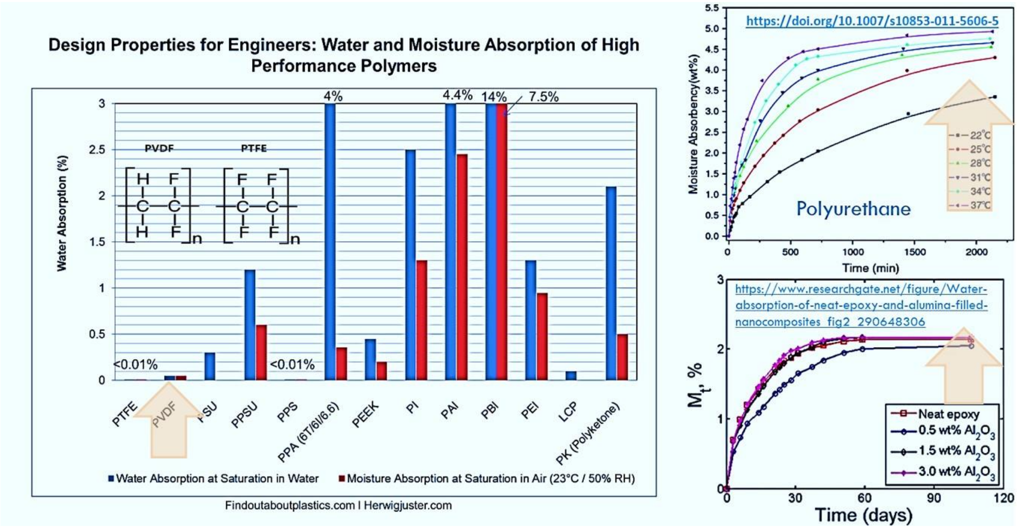


Figure 8: The figure illustrates the moisture-water absorption of common polymers commonly used for corrosion protection. Moisture absorption and water retention contribute to the corrosion of underlying metal, such as steel in structural applications and coppers in electronic applications. PVDF has one of the lowest moisture absorption and retention, similar to PTFE and slightly better than LCP (liquid crystal polymers), at less than 0.01% (chart on the left). By comparison, typical epoxies absorb 2% while more flexible polyurethane absorbs 3-5%.

Interfacial stress and stress concentration consideration of thick epoxy coating on steel hull and other naval and marine asset:

Stress concentration is a critical factor in all structural failures. This is particularly applicable for steel structures that are protected by protective coatings. When a protective coating is not providing adequate protection, corrosion happens. Among all the corrosion phenomena, pitting corrosion is among the most damaging. In particular, the phenomenon of pitting is crucial, as it leads to local stress concentrations and thus affects the fatigue life of structures. Maximum local stress concentration factor ranging from 3.0 to 5.3 with mean value of 3.55. [7]

Figure 9 is a picture from a public source [8] depicting excessive corrosion of the USS ARLEIGH BURKE DDG51 in the Black Sea in 2021. The present authors have highlighted the most corroded areas to illustrate the effects of stress concentration on areas with sharp edges.

In fact, stress concentration at scratch surfaces and structural discontinuity areas, such as corners and drilled holes, etc., induces in the high strength epoxy coating, areas of high stress concentration.

Localized stresses that are several times higher than flat surface areas tend to delaminate locally, allowing moisture laden with dissolved salt ions to cause more corrosion. The corrosion is accelerated and exasperated at coating delamination areas.

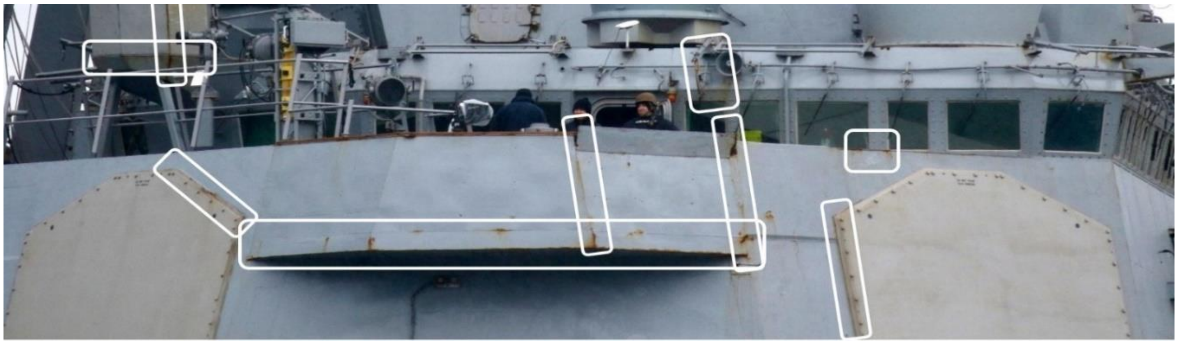


Figure 9: The above public picture depicts excessive corrosion of the USS ARLEIGH BURKE DDG51 in the Black Sea in 2021. The highlighted areas of excessive corrosion are mostly at the edges and corners where stresses tend to concentrate to cause the protective paints failure to allow moisture laded with dissolved salts to get into the interfaces between steel and coating.

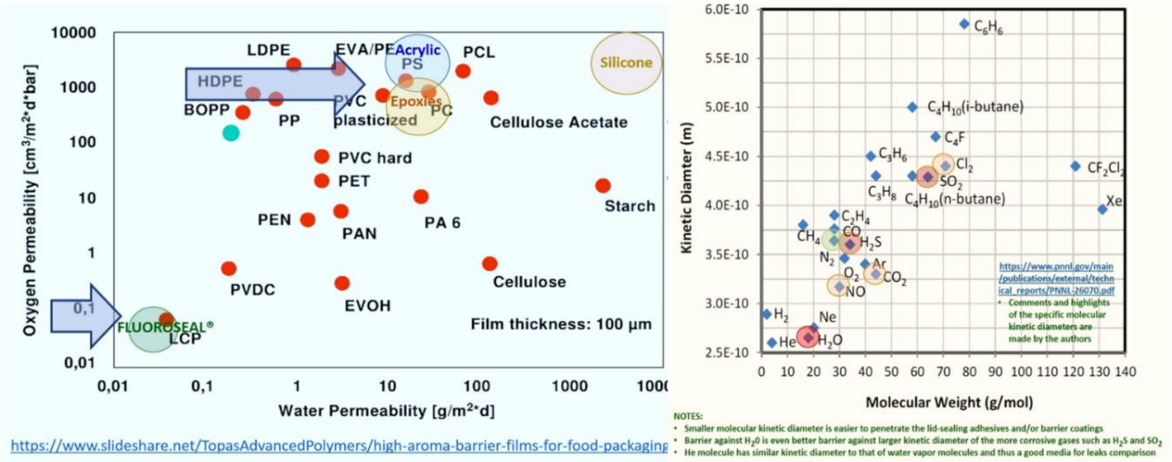
Delamination depends somewhat on the coating capabilities to comply or to absorb coefficient of expansion (CTE) differences between the metal and coating induced interfacial stresses. Properly molecularly structured coatings will do better than others. For example, steel has a CTE of 11 ppm/°C while most high strength polymers such as epoxies, acrylics and polyurethanes expand and contract at approximately 45-60 ppm/°C. With changing seasons, the interfacial stresses can be quite substantial.

While a top coating cannot mechanically help to minimize the localized steel-epoxy interface delamination at the stress concentrated areas, it can still block the ingress of the moisture laden with dissolved salts.

Field applicable PVDF as top coating can help block corrosive gases from penetrating and migrating to the steel being protected by epoxy coating:

The exhausts from burning fuels in naval and marine ships, produces a large amount of exhaust acidic gases such as CO_2, SO_2, etc., and is similar to refinery, high vehicular traffic, and underground parking garage environments.

The ability of polymers to act as a barrier to these corrosive gases is illustrated in Figure 10. The corrosive gases permeability mechanism is the same as that of moisture. It depends on the molecular diameters. Liquid H_2O, or water in its gaseous form, has one of the smallest kinetic diameter gases as seen in the right-side chart of Figure 8. Nitric oxide and carbon dioxide are slight bigger, and like bigger bouncing balls, are slower to permeate through. Corrosive gases when penetrated into the coating pores reacts with the retained moisture in the form of water can form electrolytes to provide the agents for corrosion.



https://www.slideshare.net/TopasAdvancedPolymers/high-aroma-barrier-films-for-food-packaging

https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-26070.pdf

- Comments and highlights of the specific molecular kinetic diameters are made by the authors

NOTES:

- Smaller molecular kinetic diameter is easier to penetrate the lid-sealing adhesives and/or barrier coatings
- Barrier against H_20 is even better barrier against larger kinetic diameter of the more corrosive gases such as H_2S and SO_2
- He molecule has similar kinetic diameter to that of water vapor molecules and thus a good media for leaks comparison

Figure 10: Corrosive gases permeability mechanism is the same as that of moisture. They depend on their intrinsic kinetic diameters. The left chart summarizes the relative permeability of O_2, having similar to or smaller kinetic diameter than corrosive gases such as NO, CO_2, H_2S, SO_2, Cl_2 (right chart). new PVDF coating has intrinsic density (molecular packing density) of 1.6-1.8 is similar to PVDC (1.6) afford one of the best thin coatings in blocking these corrosive gases.

EXPERIMENTAL PROCEDURE

Simulating Below Seawater Line of Corrosion Protection with new PVDF Coating as Top Coating or Over-Coating over Epoxy Coated Steel Bars

Two different steel bars coated with different epoxy coatings are used for comparative effectiveness of epoxy coatings and epoxy coatings with the new field applicable 100% PVDF corrosion protection coating. Each of the steel bars coated with different epoxy coatings are divided into two sections with one of the sections coated with field applicable 100% PVDF top coat (~50µm thickness).

To simulate and accelerate the corrosion tests below the seawater line, they are submerged into 5% saline water (instead of 3% in seawater) and temperature of 60°C.

Simulating Above Seawater Line of Corrosion Protection with new PVDF Coating as Top Coating or Over-Coating over Epoxy Coated Steel Bars

To accelerate the corrosion tests above the seawater line, the same steels with partial top coating with the field applicable PVDF coating are exposed to 60°C/95-100% salt-fog (with 5% salinity) enclosure. In addition, samples of aluminum foils that have been coated with the same field applicable coating, a commercial acrylic conformal coating, and uncoated aluminum are also exposed to the similar corrosion environment of sulfur and chlorine with water 60°C/95-100% conditions for comparative testing.

Simulating Biofouling Protection Potential with new PVDF Coating as Top Coating or Over-Coating over Epoxy Coated Steel Bars

In this case, the same epoxy coated steel is cut into two halves. One of them is top coating with the field applicable PVDF coating while the second one retains its original epoxy coating only. They were submerged in Maryland seawater for 30 days during June, 2023. Biofouling conditions are examined in comparison.

RESULTS

Simulating Below Seawater Line of Corrosion Protection with new PVDF Coating as Top Coating or Over-Coating over Epoxy Coated Steel Bars

Figure 10 and Figure 11 are pictures of the effect of PVDF coating applied as an over-coat to steel fused bonded with epoxy (FBE). The side with round edges is coated with epoxy only. The sharp side is a cut with an exposed steel edge that simulates the situation when epoxy coated ship hull is scratched through.

The round edge side with epoxy coating are not over-coated. The cut-side edge is brush coated with the new PVDF coating from the exposed steel side to the middle of the bar - with a demarcation clearly visible. The top coating is air dried. The thickness of the top coating of PVDF is approximately 30μm. The new PVDF coating over the FBE steel is transparent. The whole bar was submerged in 5% salt solution and placed in a 60°C oven for the accelerated corrosion test of approximately 50 hours. The following are the observations and results:

- Extensive corrosion starts at the edges of the bar that is protected by FBE and the corrosion started to migrate and propagate into the edge of the flat part of the steel bar.
- The epoxy coating may not be as uniform along the edges. The sharp discontinuity of the steel bar edge also produces stress concentration of up to 3-5 times that along the flat surfaces. Thus, localized micron delamination and weakening of the FBE causes the steel-epoxy interface to allow faster permeation of the dissolved salt ions causing more corrosion.
- The cut side with the exposed steel, coated with 30μm thick brush-coated new PVDF coating showed no sign of corrosion from edge to inside. That is, the top-coating not only protected the FBE areas from corrosion, by itself as direct coating over cut steel, but also provided better corrosion protection than FBE steel.
- The new PVDF coating has a compliant molecular structure, with glass transition temperature (Tg) of about -45°C, provides protection even at the sharp cut steel edges.

Figure 11: FBE coated edges corrode quickly upon exposure to 5% salt water at accelerated temperature of 60°C after 50 hrs. The corrosion quickly propagated outward to other areas. The new PVDF Corrosion Protection Coating is used to coat on the side that was cut with exposed bare steel. No sign of corrosion is seen under the same salt water condition. The new PVDF Corrosion Protection Coating is transparent having a thickness of approximately 30μm, applied by brush and ambient dried.

Figure 12: Steel bars coated with epoxy coatings, are partially coated with field applicable 100% PVDF top coat (~50µm thickness). The portion protected by epoxy coatings only when exposed to salt-water (water with dissolved corrosive ions) suffered extensive corrosion in 65 days under the accelerated conditions of 60°C-5% saline solution. By comparison, epoxy coated steel when top coated with field applicable PVDF coating showed no sign of corrosion. The accelerated conditions are roughly equivalent to 2-3 years of ambient temperature seawater submersion condition.

<u>Simulating Above Seawater Line of Corrosion Protection with new PVDF Coating as Top Coating or Over-Coating over Epoxy Coated Steel Bars</u>

Figure 13 is a picture of the effect of PVDF coating as an over-coating over steel fused bonded with epoxy. In this experiment, both sides of the FBE steel bar are cut. One side is left exposed to simulate an epoxy coated structure that was scratched to expose the bar steel without epoxy coating protection. The second cut side with exposed cut steel edge is coated over with a new crosslinked PVDF corrosion protection coating to the middle of the bar. The top coating is brush coated with a thickness of ~50µm, air-dried and cured for 5 days at ambient.

The steel bar with FBE coating and top coating on half of the bar is exposed to a saturated moisture atmosphere created with water and a 5% Clorox solution and sulfur solid at 60°C for 10 weeks. Figure 10 represents the results after the exposure:

- The side not coated with top coating showed substantial corrosion starting at the steel edge.
- The propagation into the FBE flat areas is relatively minor other than at edges.
- The side coated with PVDF corrosion protection coating as over-coating or top coating showed no sign of corrosion.
- PVDF corrosion protection coating provided the blocking of the corrosive gases and moisture laden with dissolved salt ions and chloride ions.

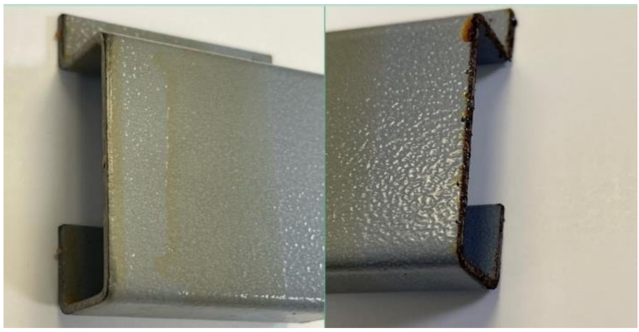


Figure 13: Uncoated cut edge shows obvious corrosion on the steel edge and under the FBE coating near the cut edge. Steel with FBE Epoxy coating suffered corrosion from moisture laden with corrosive gases quickly when any coated surfaces are scratched or peeled away exposing the bare steel surfaces.

The ability for the corrosion protection coating to block ingress of moisture laden with corrosive gases, is important for the hull and structural areas near the fuel exhaust. With global acidification and warming, this capability is becoming increasingly more important even for not directly exposed areas of the ship hull and structure.

To further illustrate the capability of the PVDF coatings, they have been used for the last 5 years in some of the most critical electronic circuits used in the more stringent aircraft control electronics that fly into more aggressive environments (i.e., Florida). Figure 14 below is a “sulfur flower” test comparing aluminum surfaces that are exposed to moisture carrying more aggressive dissolved sulfur-based gases. The new PVDF coating showed dramatically better protection than the more established acrylic based conformal coating.

The molecular structure of PVDF used as coating clearly demonstrates orders of magnitude better capability in blocking moisture and moisture laden with dissolved acidic gases.

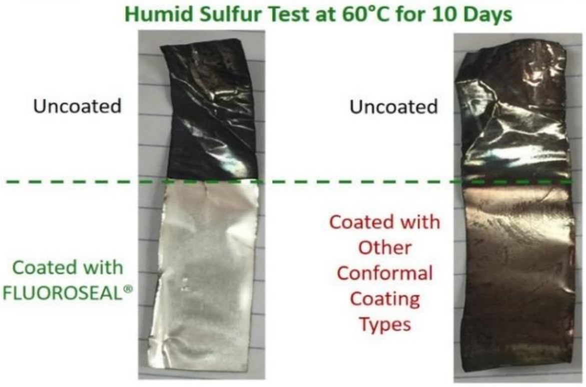


Figure 14: The experimental results of aluminum surfaces that are protected by traditional acrylic conformal coating and new PVDF type coating. The surface area not protected showed obvious tarnishes. The aluminum surface that are coated with PVDF coating showed almost no tarnishes in comparison to the same surface that was coated with traditional acrylic coating.

<u>Biofouling Reduction and Protection with new PVDF Coating as Top Coating or Over-Coating over Epoxy Coated Steel Bars</u>

Figure 15 shows the results of marine exposure of epoxy coated steel coated with field applicable PVDF after 30 days submersion in the Chesapeake Bay, Maryland during the month of June 2023,

Figure 15: The top piece of epoxy coated steel coated with field applicable PVDF after 30 days submersion in Chesapeake Bay, Maryland during the month of June. The cut edge showed corrosion and initiated with some biofouling growth and starting to migrate to the other edge. The bottom piece of the other half of epoxy coated steel without PVDF top coating showed substantially more biofouling growth along with more obvious brownish corrosion coloring.

CONCLUSIONS

Marine environments are highly corrosive to ships and other assets that are made out of steel. The dissolved salt ions and corrosive gases in the seawater and sea moisture from fuel exhaust and increasingly acidic ocean are highly aggressive in penetrating even the toughest protection coatings using epoxy and/or polyurethane polymers. The warming of the ocean raises the kinetic corrosion rate that will continue to increase the costs of maintenance and costs of the loss of availability during the maintenance period.

A novel field applicable PVDF coating solution has been developed to provide immediate relief when used as top coating or over-coat over existing established protective coating. This paper presented data and proof of its efficacy in preventing corrosion orders of magnitude better in blocking moisture and moisture carrying dissolved salt ions and corrosive gases.

This field applicable patent-pending PVDF corrosion protection coating technology provides a hydrophobic film and surface that has been proven both scientifically and experimentally with the following key attributes:

1) At 30-50μm thickness, the corrosion protection coating is 100x more efficient than 500μm (20mils) of epoxy coating in blocking moisture and moisture carrying dissolved salts and acidic gases.
2) Even at 70% PVDF in the coating, it has been proven to withstand direct UV exposure for more than 60 years. The patent-pending 100% PVDF corrosion protection coating is now available in furthering the longevity in corrosion protection when applied over the epoxy coating as over-coat protection.
3) The inherent hydrophobic property of PVDF polymer is maintained in the patent-pending field applicable coating technology to provide antifouling protection for below seawater line naval and marine assets.

These novel PVDF corrosion protection coatings can be used without changing long-established corrosion protection standards with epoxy or polyurethane coating. It is applied as a thin over-coat or top coating over the new and old protection coating to provide 100x corrosion protection. The inherent flexibility of the PVDF polymer with a Tg of -45°C does not induce substantial mechanical or interfacial stresses or other deleterious effects on the underlying coating.

As a top coating in protecting the underlying coating and thus the steel ship hull and other marine infrastructure that are exposed to the marine environment, they have built-in capability not only to resist but also block UV from penetrating through to damage the underlying UV vulnerable epoxy and polyurethane coatings.

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