

Surface-Preparation Chemicals for Salt Decontamination or Flash Rust Inhibition

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Surface preparation methods and standards are under a lot of scrutiny and are subject to significant revisions because of premature coating failures. Nonvisible surface salts have been considered a leading cause of these failures. Cost-effective chemical removal using products with the proper chemical functionality is summarized. Formulated acidic products can lower the salt levels to threshold levels, whereas alkaline formulations provide surface inhibiting properties that can mask salts remaining on the substrate.

The coatings industry is focusing much attention on surface preparation because of excessive premature coating failures. An analysis of premature coating failures may provide evidence that residual surface salts remain during surface preparation and are a root cause of the failures. According to corrosion authorities H.H. Uhlig and R.W.

Revie, "Tests have shown that the most important single factor influencing the life of a paint is the proper preparation of the metal surface. This factor is generally more important than the quality of the paint that is applied. In other words, a poor paint system on a properly prepared metal surface usually outperforms a better paint system on a poorly prepared surface."¹

The corrosion-inducing effect of soluble salts on metal surfaces is well documented.²⁻³ The presence of soluble salts on steel substrates, when in contact with moisture, forms electrolytic cells that generate deep and narrow micropits from the cyclic reaction of the acid and iron salt products formed. This process can be demonstrated by exposing a steel surface to a neutral solution of sodium chloride (NaCl), which will form a fluid in the crevices of that steel with three to 10 times as many chloride ions as the dipping solution and a pH of 4 rather than 7.⁴ An important objective during surface preparation is to eliminate or reduce the level of corrosion-inducing soluble salts (most commonly chlorides, sulfates, and nitrates) to recognized threshold levels that will not influence the performance or significantly effect the life of a coating. Because these salt anions are most prevalent in the deep and narrow pits developed by surface abrasive blasting and further accentuated during the chemical transformations occurring in the electrolytic cells, removing the salt anion from the electrolytic cell is the key to stopping corrosion and potential for coating failure.

Traditional Salt Removal

The corrosion-inducing anions are literally sandwiched between the steel substrate and a rust layer formed by the corrosion products. In the testing and identification of soluble salts during surface preparation, the steel substrate must be fully exposed to extract the salt anions.⁵ Exposure alone, however, does not necessarily translate into easy removal. Dry abrasive blasting may remove some of the salt anions, yet the size of the blast particles limits penetration into the deep

crevices where the salt anions are concentrated. A traditional yet insufficient method of reducing soluble salt levels on surfaces that have been abrasive blasted to remove mill scale, pack rust, or the layer of insoluble oxides formed over the substrate surface has been to wash these surfaces with high-pressure water. Repeated water washings, even at high pressure after grit blasting, has been found to be only slightly effective, however.⁶ Experience shows that with each water wash or sequential blast and water wash cycle, fewer contaminating salts are removed with each pass—and the desired limit may not be reached after a specified number of passes. Cost-effectiveness and time must be considered also.

Ultrahigh-Pressure Water and Salt Decontamination

An ultrahigh-pressure water was used by a coatings contractor on a U.S. Navy project to replace the antiskid deck coating of the USS *Saipan* helicopter carrier. This project demonstrated the limitations of water, even at 40,000-psi (276-MPa) pressure, to remove surface-reacted salts during surface preparation.⁷ Because of the capillary action in deep and narrow pits, a slow diffusion action may be more appropriate than high-pressure water blasting.⁸ This last statement adds some relevance to the approach outlined by W.C. Johnson, where the capillary action from deep pits was observable.⁹ It is evident that with the threshold levels of salt permissible prior to coating, the overnight capillary drainage is insufficient to achieve the specified limits.

Industry Trends and Emphasis

NACE and SSPC committees have been preparing and reviewing various updates to existing documents and new documents and guides addressing the impact of salts on coating performance, their identification, and methods for removal. These documents, including “Evaluating Nonvisible Soluble Salt Contaminants on Coated and Uncoated Metallic Surfaces Immediately Prior to

Coating Application,”¹⁰ “Methods for Retrieval and Analysis of Soluble Salts on Steel and Other Nonporous Substrates,”¹¹ and “Surface Preparation of Contaminated Steel Surfaces,”¹² will generate changes to traditional methods of decontaminating surfaces that: 1) maximize the protective function of a coating, 2) minimize life cycle costs, and 3) preserve asset value.¹³

Chemical Surface Treatment

The choice of a specific chemical product for surface treatment will depend on the desired outcome. The removal of corrosion-inducing surface reacted salts is a major objective toward ensuring the extended life of coatings. Generally speaking, the products for salt removal and rust inhibition (passivation) are mutually exclusive due to their chemical functionality. Except for pickling acids, which have significant environmental limitations, specifically formulated acidic products will effectively react and decontaminate surfaces of corrosion-inducing salts; alkaline products will effectively accelerate the formation of a barrier layer on a metal surface to inhibit the formation of flash rust.

Surface Rust Without Salts

Under the right conditions of temperature, humidity, and moisture, the presence of salts will accelerate the presence of flash rust. However, rust can still form without the presence of soluble salt anions. This form of “waterline corrosion” occurs between the interface of the metal and waterline because it is at that point that there is a concentration of oxygen from the atmosphere and oxygen from the water to promote oxidation or rust.

Passivation

Surface passivation of metals, also described as the formation of a surface barrier layer, is a naturally occurring phenomenon in alkaline or near-neutral environments. Specifically, “oxygen in air can adsorb directly on iron and passivate it in aerated alkaline solutions, or in near-

neutral solutions if the partial pressure of oxygen is increased sufficiently.”¹⁴ The application of an alkaline solution to a metal surface will accelerate the formation of a diffusion-barrier layer, forming a direct barrier between the substrate and the atmosphere.¹⁵ The films formed are too thin to be detected even by high-energy electron diffraction. The barrier slows down the rate of reaction between oxygen and the steel surface to prevent metal oxides or rust from forming.¹⁴

Forming an Alkaline Surface Barrier Layer

The formation of a surface barrier layer on steel with the application of an alkaline treatment, commonly known as an inhibitor, will mask salt anions that may be present on the substrate. This process was verified in an in-house, controlled laboratory experiment using salt fog contaminated panels that were washed with commercially available, water-soluble alkaline surface treatments after an initial dry abrasive blasting. Multiple coupons were contaminated in a salt fog cabinet for 29 days to simulate the effect and concentration of salt contamination of weathered steel.¹⁶ These coupons were all abrasive-blasted to a near-white visual appearance with a nonchloride-containing dry abrasive. Control coupons were randomly selected and boiled in deionized (DI) water using the Mayes method to obtain an average level of surface chlorides from the chlorides remaining in the DI water. The other abrasive-blasted panels were separated randomly into two groups and pressure washed at 3,500 psi (24 MPa) with a 2% solution of the two alkaline passivation water solutions using local tap water. The pH of both alkaline solutions was >9.2. The alkaline solution-washed samples were allowed to dry and then boiled in the same fashion as the control coupons. The level of chlorides extracted from the boiled, DI water test coupons was <25% (22% for one alkaline product and nil for the other) of the average chlorides removed from the control coupons that had not had the alkaline prewash. It was

concluded that a temporary barrier layer was formed on the test coupon surfaces from the application of the alkaline passivation wash, under which remained the substrate metal-reacted chloride ions.

Surface Barrier Layers and Salts

It is important to note that the formation of a surface barrier layer to prevent flash rust will fail if the salt anions remain on the substrate surface. From the Uhlig and Revie text, "...iron and stainless steels are not readily passivated anodically in solutions containing an appreciable concentration of chlorides. Instead, the metal continues to dissolve at high rates both in the active and passive potential ranges.... Breakdown of passivity by chloride occurs locally rather than generally, the preferred surface sites being determined perhaps by small variations in the passive-film structure and thickness."¹⁷ This conclusion ties back to the earlier observation that chloride ions concentrate in the crevices of steel panels after being dipped in a neutral solution of NaCl. The concentration of these anions leads to the formation of a corrosion cell through the surface barrier layer (which can also be a protective coating), leading to rust formation (and osmotic blistering under a coating).

Effective Salt Decontamination with Acid

Specific acidic chemical mixtures are scientifically sound for the effective removal of surface-reacted salt anions. S.K. Boocock has shown that an acidic extraction media will remove a higher level of the residual salts than water.¹⁸ Alkaline extraction media will not, however, provide accurate measurements of salt anions that may be present. Concentrated acids, such as sulfuric acid (H₂SO₄) and nitric acid (HNO₃), are known to develop a film on steel, providing a film or surface passivation layer. The pipe coatings industry has historically used phosphoric acid (H₃PO₄) to remove residual chlorides prior to coatings. The H₃PO₄ is applied in an 8 to 12%

concentration along with a buffering agent and surfactant. The dilute acid releases the surface-reacted salt anions, displacing corrosion-inducing chlorides, and forming insoluble, ferrous phosphate compounds. Ferric phosphate (FePO₄·2H₂O) that may be formed is partially soluble in water and can be removed with a final DI water wash. The NACE book on FBE for pipeline corrosion protection outlines the acid wash step.¹⁹

Summary

The removal of residual corrosion-inducing surface salts is very important to the performance and life-cycle of a coating. It is a primary objective for the long-term protection of the substrate surface. Using a specifically formulated, dilute acidic cleaning product, which can be applied without specialized equipment and without an environmental impact, will achieve the desired objective cost-effectively. Acids that may contain H₂SO₄ or HNO₃ in water-diluted form only replace existing corrosion-inducing chloride salt anions with sulfates or nitrates, which are corrosion-inducing as well.

If the formation and presence of flash rust cannot be tolerated prior to coating, testing for and removal of the salt anions is always the first step because the presence of the salt anion can accelerate the formation of flash rust. The masking effect of a barrier layer formed by treatment with an alkaline chemical product, temporary though it may be, creates the risk of blanketing the salt anions present. This masking effect ultimately may cause a coating to fail because of the breakdown discussed earlier.

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