Cost Effective Chemical Removal of Corrosion Inducing Surface Salts

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ABSTRACT

It is well documented that the single largest contributor to premature coating failures are non visible surface contaminating soluble salts, which go undetected prior to coating application. In large part this is due to the fact that contaminating levels of the salt are not visible. Other considerations are insufficient or inadequate testing of the surface and surface preparation materials, and the lack of proper surface cleaning steps. Quite simply, surface reacted soluble salts will cause corrosion because osmotic forces develop from the hygroscopic affinity of the soluble salts below the coating. Moisture, along with the presence of contaminating salts on the substrate metal provides all the necessary ingredients for electrolytic reactions and the formation of the microscopic corrosion cells.

When surface reacted soluble salts are detected through quantitative testing, the use of a chemically active, acidic, nonhazardous, noncorrosive soluble salt remover, applied very simply with a pressure washer (3500 to 4000 psi) will cost effectively remove these surface contaminants to prevent premature coating failures caused by the salts.

Corrosion escapes few industries. Industrial, marine, transportation, aerospace and military assets and hardware, to name a few, all face the insidious problem of surface corrosion which result in their reduced productivity arising from more frequent downtimes for maintenance repairs. Consequently, life cycle costs increase, yielding a lower investment return.

BACKGROUND

The removal of lead from coatings has dramatically increased surface corrosion problems and coating failures, raising awareness about the detrimental effect of salts, even at low levels. Lead in coatings rendered soluble salts inactive by producing insoluble compounds. Coatings have gone through several generations since the mandated ban on lead paint in the 1970's. Unfortunately, many, if not most, surface preparation standards used today are the same as those originally developed in the 1940's when lead coatings were the norm. In summary, surface preparation is not compatible with subsequent coating systems. Uhlig and Revie, in their text Corrosion and Corrosion Control[1] confirm the importance of surface preparation: "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 that the quality of the paint that is applied."[2]

Recoats are failing long before the experience with lead based coatings. This is forcing asset owners to reassess their standards. Specifications are being revised to take into consideration the testing for and remediation of corrosion inducing soluble salts. The NACE and SSPC organizations are working through joint committees to develop industry guides for the field testing of surface soluble salts (Guide X15X) and for the evaluation of non-visible salts on nonporous surfaces (TG259). These documents are being followed closely by ISO, ASTM and API, which will be issuing their own documents

The summary results of an exhaustive survey sponsored by the U.S. Government under the auspices of NACE which was presented at the 2002 NACE Conference, estimate the identifiable cost of corrosion in the U.S. to be $275 billion annually.[3] The actual cost was estimated to be closer to $500 billion. These estimates parallel the 1995 study by Battelle which estimated the cost of corrosion at $300 billion annually, with $100 billion being avoidable.

SOURCES OF SALTS

Our environment is filled with sources of contaminants, both natural and produced by man. From numerous monitoring sites, the EPA reports rain water pH ranging from 4.3 to 6.0 across the U.S. A pH of 5.8 or less is defined as acid rain. CO_2, SO_2, and NO_X calculated emissions in the U.S. for 2001 were 2.39 billion tons, 10.63 million tons, and 4.69 million tons, respectively.[4] The sources of these are well known, and their oxidation to form weak acids reverses the formation of the slightly alkaline to neutral passivation surface barrier layer on metals.

CORROSION PROCESS

The most common soluble salts that contaminate surfaces are the chlorides, and sulfates of sodium, magnesium and calcium.[5] Nitrates from ammonium and fertilizer salts are also prevalent. Left on the metal surface, these salts will absorb moisture because of their affinity to water. The permeability of coatings permits the migration of moisture to the metal substrate. We are reminded that corrosion is an oxidation process. And, oxidation is any process which increases the proportion of oxygen or acid forming element or radical in a compound. Acids originating from emissions, as described above, will react with the iron to produce unstable ferrous ions that will in turn convert to ferric ions in the presence of oxygen. The extremely reactive ferric ions will react with the chlorides and sulfates to produce hygroscopic ferric salts. The ferric salts will convert to ferric oxide, or rust, and produce acids (hydrochloric, sulfuric or nitric). The presence of the acid will make the reaction cyclic, causing the pitting which is easily identifiable from this form of corrosion. A simple experiment to demonstrate this phenomenon is to dip a piece of steel into a neutral solution of sodium chloride. A fluid is formed in the crevices of the dipped steel which shows a pH of 4 rather than 7 and a chloride concentration that is 3 to 10 times that of the original solution.[6]

Metal surfaces are given an anchor profile for coating adhesion. The microscopic troughs are ideal for corrosion cell formation. The corrosion process consists of series of electrochemical reactions in an acidic environment between soluble salts and substrate steel surfaces in the presence of moisture. The dynamics of the reactions are dependent on the relative electrochemical bonding strengths between ions. As the corrosion and permeation process continues, these active microcells deteriorate the substrate and become large enough to reach a critical size, forming osmotic blisters that will rupture the coatings physical adhesion with the metal substrate. Research indicates that the internal pressure created from the surface reacted salts under a coating can be as high as 22,000 p.s.i. Most coatings have a tensile bonding strength from 500 to 2500 p.s.i., so it is not surprising that coatings will disbond from the substrate and eventually fail.

DETECTION

Most surface preparation specifications today reflect only visual cleanliness requirements, such as abrasive blasting to a white metal or near white metal, SP-5 or SP-10. Since the corrosive effect of invisible soluble salts is well known, the need for quantitative testing is critical. Metal surfaces cannot tolerate the presence of these salts.

Zero tolerance levels of these soluble salts on the surface would be ideal. For reasons of practicality, standards are being set on chloride ion limits. The U.S. Navy, for example, after exhaustive testing has set 3 $\mu g/cm^2$ as the limit for immersion service and 5 $\mu g/cm^2$ for atmospheric service.[7] These values have since been verified by various other entities.

Testing is critical before, during and after surface preparation because of the tremendous impact invisible soluble salts have in diminishing the life and effectiveness of protective coatings.

REMEDIATION

The key to soluble salt decontamination is to combine physical and chemical actions in proper sequence. The corrosion rate is a function of the concentration of oxygen present. The electrolytic cell in which we find metal (anode and cathode), metallic pathway (between the anode and cathode) and the electrolyte (dissolved salt anion in water) becomes active in the presence of oxygen. Activation with oxygen begins the process of pitting.

Oxygen displaces the chloride ion from the soluble iron salts to form insoluble rust on the substrate surface.[8] Rust caps are formed over the corrosion cell in which the corrosion inducing products remain. The insoluble layer of rust formed on the substrate surface includes products such as magnetite.

The removal of the contaminating salts with abrasives has limitations.[9] The blending of different sizing of grit can improve physical attack on the uneven surface profile, yet there is no assurance that this method will reduce the salts to acceptable levels. Furthermore, the amount of time taken to physically remove layers of the substrate surface to accomplish this task may be impractical and costly. Combined abrasive blasting and water washing steps generally requires multiple cycles with no assurance of achieving the threshold acceptable levels. The cost of time, labor and materials must be considered.

Ultrahigh water pressure (35,000 to 40,000 p.s.i.) has become a more common method of surface preparation with more affordable equipment available for contractor use. It is an excellent method for removing old coatings and pack rust, yet documented field cases exist where the hydraulic action of the ultra high pressure water jetting is insufficient for removal of soluble salts to threshold levels. For example, the use of several passes of ultra high water jetting (40,000 p.s.i.) was insufficient to meet the chloride limits of the U.S. Navy specification on a recent project involving the removal of the antiskid coating and surface preparation of the flight deck on the carrier U.S.S. Saipan.[10]

The speed at which hydroblasting passes over the surface may be a key reason why the contaminating salts are not removed from the deep and narrow crevices of the surface profile and corrosion pits.[11] The use of an acidic chemical to draw the salt anions from the deep and narrow (microscopic) crevices provides the chemical antidote required to effectively decontaminate.

It is well known that the insoluble oxide products which form on the surface are a layer above where the contaminating salts can continue the corrosion cycle. Imperfections in the insoluble layer allow oxygen to penetrate the corrosion cell to perpetuate the debilitating reactions. Removing the insoluble layer with physical pressure to achieve the acceptable visual appearance standard becomes only a part of surface preparation. Uncovering the corrosion cells in which the salts can be found facilitate their removal through chemical action.

ECONOMICS

All coating projects have cost performance objectives. Surface preparation, as a critical key to the success of coating performance, should not only be given a great deal of attention but also be allowed to claim a significant share of the project cost. Important factors also include service downtime, not only because of the loss of asset productivity but also incremental administrative expenses and additional insurance costs associated with days of exposure during project implementation.

A list of the major factors which are to be accounted for in most maintenance include:

Tangible cash costs:

1. Access
2. Mobilization (personnel, equipment, materials)
3. Training (safety, work conditions, emergency procedures)
4. Security (badges, control)
5. Liability insurance and occupational hazard insurance (for owner and contractor)
6. Resources (water, air, power, sewer, sewage)
7. Site preparation (tenting, sludge removal, volatiles control, scaffolding)
8. Site conditioning (drop cloths, DH, heat)
9. Environmental (lead, waste disposal, testing, regulatory compliance)
10. Safety equipment (hard hats, airpacks, clothing)
11. Site storage
12. Inspection (training, equipment, consultants)
13. Raw material cost (abrasives, coatings, surface treatments and solvents)
14. Equipment use and amortization

15. Equipment rental (trucks, pumps, scaffolding, cranes, cherry pickers, trailers)
16. Labor and supervisory costs (wages + benefits)
17. Dismantling, demobilizing, and cleanup.

Intangible expenses:

1. Project management (bidding, supervision, control)
2. Disruption control
3. Inspection
4. Accounting
5. Security
6. Utilities

Contingency planning and risk management are major consideration. Unscheduled or early shutdowns due to coating failures lower capital investment returns and raise the administrative costs necessary to return the asset to service. The allocated cost of a maintenance coating project, for example, usually does not include the non cash cost for administrating the project, increased insurance liability, and loss of asset utility. In the event of a premature coating failure, multiples of the original project cost are the norm. For example, third party testing and failure analysis, legal fees, process interruption and administrative costs are incurred even before the coating failure is repaired. When all the costs, both tangible and intangible, are taken into account, the cost of a failure can easily exceed the original project cost. The list of project items to be considered in dealing with a failure, then, not only include most if not all of those listed above for the original project but are compounded by legal and arbitration time and expenses.

Essentially, the importance of thinking through, executing, and ensuring the contractor follows the detailed project specifications and completes these without preagreed exceptions, cannot be overlooked because of the tremendous financial burden placed on the asset owner in the event of a coating failure.

PERFORMANCE AND SOLUBLE SALT REMOVERS

The concept of using a chemical to react with nonvisible soluble salts on surfaces requires substantiation with performance measured field tests and results. Certified third party lab testing, which simulates actual field conditions and performance endorsements in field projects should be verified.

Various products are offered as salt removers. It is very important to verify efficacy from endorsements in field trials in addition to scrutinizing the product information on the MSDS. Unfortunately, some so called “salt removers” have little or no effect and others replace one problem ion with another during application. Acids will react with bonded surface reacted soluble salts, yet health concerns and disposal costs are important considerations. Products with a high concentration of sulfuric acid, for example, will replace the chloride ion with contaminating sulfate salts. High pH products can produce a blanketing ferric hydroxide which will mask the contaminants still left on the substrate.[12] Residual salt anions left under topical treatments of high pH will react preferentially with the substrate metal and cause eventual coating failure.[13] In essence, the passivating hydroxide layer will form over the corrosion inducing salts. Metal surfaces to be coated which have not been effectively decontaminated prior to the application of the passivating hydroxide layer will eventually corrode because the salt anion will preferentially react with the substrate metal, displacing the hydroxide.

CONCLUSION

The long term benefit of obtaining the full life of a protective coating by properly engineering the surface with the use of an effective chemical to remove soluble salts far outweigh the nominal \$0.15 - \$0.19/ft^2 full cost of application. Cycles of abrasive blasting and water washing have been an alternative for removing soluble salts yet with less than certain final results for reducing contaminating soluble salts and at a total cost approximating \$2.10/ft^2 per cycle which can be significantly greater than the methodology proposed with a specific chemical solution wash.

Testing for salts during the surface preparation process is critical. Verification of removal of the salts to specified limits is important because the tolerance levels under coatings are extremely low. For example, 3 µ/cm^2, a common chloride limit for immersion service, is the equivalent of 0.17 oz/1,000 ft^2.[14] Thus, the use of exacting field testing methods should be employed to ensure ion specific species are quantitatively identified.

A known and proven soluble salt remover is CHLOR*RID®. It has the proper chemistry and pH to cost effectively and efficiently remove the contaminating salts. In combination with the blasting step (wet abrasive blasting, for example) or immediately following abrasive blasting, the chemical is applied with a pressure washer. The physical water pressure used helps penetrate the crevices of the surface profile in order to allow reaction with the salts found most prevalently in the bottom of the corrosion pits, flushing the salts from the surface in a 1 to 2% water solution.

References:

1. Uhlig, H.H. and Revie, R.W., *Corrosion and Corrosion Control*, Third Edition, John Wiley & Sons, Inc., New York, NY (1985).
2. Ditto, p 253.
3. *The United States Cost of Corrosion Study*, NACE International sponsored study contracted to CC Technologies from 1999 to 2001 with a grant from the U.S. Congress, presented at the NACE International Conference in Denver, CO, April 2002.
4. Environmental Protection Agency, National Atmospheric Deposition Program, Progress and Results, Clean Air Markets (2001).

5. Morcillo, M., Rodriguez, F.J., Bastides, J.M., "The influence of chlorides, sulphates and nitrates at the coating-steel interface on underfilm corrosion," *Progress in Organic Coatings*, **31**, 245-253 (1997).
6. Flinn, R.A., Trojan, P.K., *Engineering Materials and Their Applications*, Second Edition, Houghton Mifflin Company, Boston, MA, 507 (1981).
7. NAVSEA PPI 63101-000 (latest revision), "Preservation of Ships In Service" (Washington, DC: NAVSEA).
8. M. Morcillo, S. Feliu, J.C. Galvan, J.M. Bastidas, "Some Observations of Painting Contaminated Rusty Steel," Journal of Protective Coatings and Linings (JPCL)(1) 4, 9 (1987).
9. Morcillo, M., "Soluble salts: their effect on premature degradation of anticorrosive paints," *Progress in Organic Coatings,* **36**, 144 (1999).
10. Letter from Ronnie Kinsel, Production Manager, United Coatings, Portsmouth, VA of 7/18/99 to Mr. Jerry Colahan of CHLOR RID International, summarizing the U.S.S. Saipan non-skid coating removal project.
11. Dasgupta, D., Ross, T.K., *British Corrosion Journal*, **6**, 238-239 (1971).
12. Uhlig, H.H. and Revie, R.W., *Corrosion and Corrosion Control*, Third Edition, John Wiley & Sons, Inc., New York, NY (1985), p72.
13. Ditto, page 109.
14. G.C. Soltz, "The Effects of Substrate Contaminants on the Life of Epoxy Coatings Submerged in Sea Water," NSRP Report, TASK No. 3-84-2, March 1991.
