RELEASE PROPERTIES AND ELECTROCHEMICAL CHARACTERIZATION OF ENCAPSULATED CORROSION INHIBITORS FOR ENVIRONMENTALLY FRIENDLY SMART COATINGS

B.P. Pearman, L.M Calle and X. Zhang
NASA, Kennedy Space Center, FL 32899, USA

W. Li, J.W. Buhrow, M.N. Johnsey, E.L. Montgomery, L. Fitzpatrick, and J.M. Surma
ESC-QNA, Kennedy Space Center, FL 32899, USA

SUMMARY

The NASA Kennedy Space Center's Corrosion Technology Lab at the Kennedy Space Center in Florida, U.S.A. has been developing multifunctional smart coatings based on the microencapsulation of environmentally friendly corrosion indicators, inhibitors and self-healing agents. This allows for the incorporation of autonomous corrosion control functionalities, such as corrosion detection and inhibition as well as the self-healing of mechanical damage, into coatings. This paper presents technical details on the characterization of inhibitor-containing particles and their corrosion inhibitive effects using electrochemical and mass loss methods.

Three organic environmentally friendly corrosion inhibitors were encapsulated in organic microparticles that are compatible with desired coatings. The total inhibitor content and the release of one of the inhibitors from the microparticles in basic solution was measured. Particles with inhibitor contents of up 60 wt% were synthesized. Fast release, for immediate corrosion protection, as well as long-term release for continued protection, was observed.

The inhibition efficacy of the inhibitors, both as the pure materials and in microparticles, on carbon steel was evaluated. Polarization curves and mass loss measurements showed that, in the case of 2-MBT, its corrosion inhibition effectiveness was greater when it was delivered from microparticles.

INTRODUCTION

The corrosion of metals is a problem with great economic and social impact. It is estimated to have cost the world economy over $2 trillion dollars in 2010[1] and the loss of the structural integrity of buildings, bridges, automobiles, airplanes, etc. poses a significant safety issue to society.

One approach to preventing corrosion is the incorporation of inhibitors within coatings.[2] In recent years, the use of some highly effective corrosion inhibitors, such as chromates, is in the process of being phased out or have been banned outright, due to their negative impact on human health and wildlife ecosystems.[3] In the quest to find suitable replacements, as well as a general societal & industrial trend towards using "green" technologies, environmentally friendly alternatives are being investigated.[4] Some promising materials, however, due to too low or too high solubility or coating incompatibility cannot be used as drop-in replacements.

In an effort to overcome the limitations of these promising candidates, multiple approaches to the development of delivery systems for these materials have been taken.[5-6] This has involved the encapsulation into nanoparticles, microparticles and microcapsules,[7-10] the absorption into meso- and macroporous synthesized or naturally occurring materials,[11-15] as well as the incorporation into double-layer hydroxides[16] and layer-by-layer polymer structures.[17-19]

The NASA Kennedy Space Center's Corrosion Technology Lab has been developing multifunctional smart coatings based on the microencapsulation of environmentally friendly corrosion indicators, inhibitors and self-healing agents for several years. This paper focuses on the evaluation of three different compounds, both in their pure form and encapsulated in microparticles, as corrosion inhibitors for carbon steel using electrochemical methods and mass loss experiments.

EXPERIMENTAL PROCEDURE

Encapsulation procedure

Three different inhibitors, phenylphosphonic acid (PPA), 8-hydroxyquinoline (8-HQ) and 2-mercaptobenzothiazole (2-MBT) were encapsulated into pH-sensitive organic microparticles using emulsion polymerization.[20]

Total Inhibitor Content and Release Studies

The total inhibitor content of 2-MBT particles was determined using elemental analysis. Approximately 5 mg of particles in tin sample vessels were placed in a Vario EL III CHNS Elemental Analyzer instrument. The samples were combusted in oxygen with helium as the carrier gas. The carbon, hydrogen, nitrogen and sulfur content was determined by a thermal conductivity detector. Sulfanilic acid was used to calibrate the instrument.

The release of 2-MBT from microparticles was determined. Microparticles were dispersed in 20 ml of 0.01 M KOH at a concentration of 1000 mg/g and continually stirred at 300 rpm. Aliquots of samples were taken after 1 h, 24 h, 1 week, 2 weeks, 4 weeks and every following 4 weeks until no further release was observed. Samples were filtered through a 0.2 μm nylon filter and appropriately diluted with acetonitrile. The concentration of the inhibitors was measured using a

Thermo Fisher Scientific Accela HPLC with a Varian Polaris C18-A column and a diode array detector. A gradient run was performed at 200 μl/min with 0.1% phosphoric acid in water and acetonitrile as the mobile phase. The concentrations of the inhibitors were determined at a wavelength of 320 nm.

Polarization curves

One inch (2.54 cm) diameter 1018 carbon steel coupons were embedded in epoxy stubs with an attached, insulated copper connection. The samples were immersed in 200 ml of 3.5% NaCl solutions/suspensions containing inhibitors, added directly or in microparticles, at the concentrations shown in Table 1. To maximize dissolution, the pure inhibitor solutions were heated to 90 °C and cooled to room temperature. The pH of the solutions were adjusted to 5.5 using either HCl or NaOH prior to steel immersion. A silver/silver chloride (SSC) electrode was used as the reference and a graphite rod as the counter electrode. The samples were left in solution for 17 hours to allow them to reach open circuit potential (OCP), before beginning polarization measurements. Anodic and cathodic polarization curves were obtained for freshly polished samples each time. The coupons were polarized from 30 mV below OCP to 1.5 V (for anodic scans) and 30 mV above OCP to -1.5 V (for cathodic scans). Triplicate samples were run for each condition.

Mass Loss Testing

3 in (7.62 cm) x 1 in (2.54 cm) x 0.06 in (0.15 cm) 1018 carbon steel panels were cleaned using 0.025 M hexamethylene tetramine in 18.5% HCl (based on ASTM G1-90 and G3-03) and weighed to 0.1 mg. The panels were immersed in 200 ml of 3.5% NaCl solutions/suspensions containing inhibitors, added directly or in microparticles, at the concentrations shown in Table 1. To maximize dissolution, the pure inhibitor solutions were heated to 90 °C and cooled to room temperature. The pH of the solutions were adjusted to 5.5 using either HCl or NaOH prior to steel immersion. Triplicate samples were removed from solution after 3 days, 10 days and 28 days. The panels were photographed, cleaned using the same procedure described above, and weighed to 0.1 mg.

Table 1
Concentrations in wt% of inhibitors and particles in 3.5% NaCl suspensions

	PPA	8-HQ	2-MBT
Inhibitors	0.1	0.1	0.1
Particles	0.3	0.25	0.2

RESULTS & DISCUSSION

Encapsulation

For this work, PPA, 8-HQ and 2-MBT encapsulated in polymeric microparticles were used based on the synthesis process described in the referenced patent[20] and previous papers.[21-24] Figure 1 shows a representative microparticle SEM image and a photo of the microparticles as free-flowing powders. Producing encapsulated inhibitors as powders allows for simple, safe handling and facile incorporation into existing coatings systems.
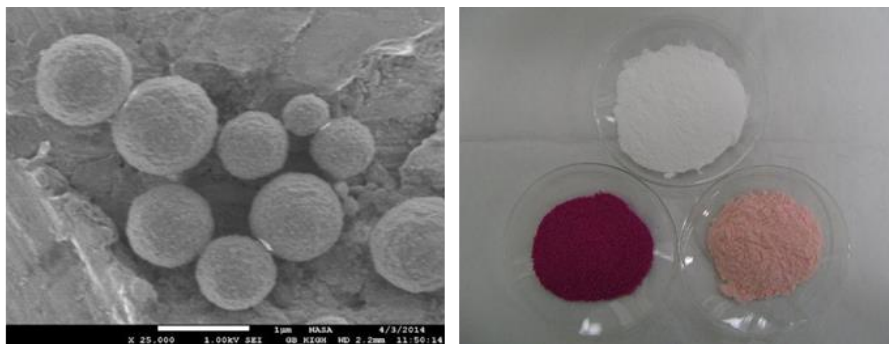
Figure 1: Images of microparticles in SEM (left) and as free-flowing powders (right)

In this paper, when referring to solutions containing an inhibitor or particle, it will be labeled as the name of the inhibitor followed by Inh for the pure inhibitor and Part for the particles, e.g. 8-HQ Inh or 2-MBT Part.

Inhibitor Content and Release Behavior

The total inhibitor content of the 2-MBT Part was determined. Particles with inhibitor concentrations ranging from 16 to 60 wt% were synthesized. The cumulative release of 2-MBT from three generations of organic particles in 0.01 M KOH is shown Figure 2.

The 2-MBT particles have a low initial release (<6% after 1 hour), followed by a slow but consistent release over time. In successive iterations of the microparticle formulae, it was possible to not only double the inhibitor payload but also to significantly increase the amount of released material and the period of time over which it is released. The third generation of these microparticles, where the inhibitor content was consistently found to be 55 ±2 wt% and which was used for all testing, released half of their payload after exposure to base solution for 18 weeks.
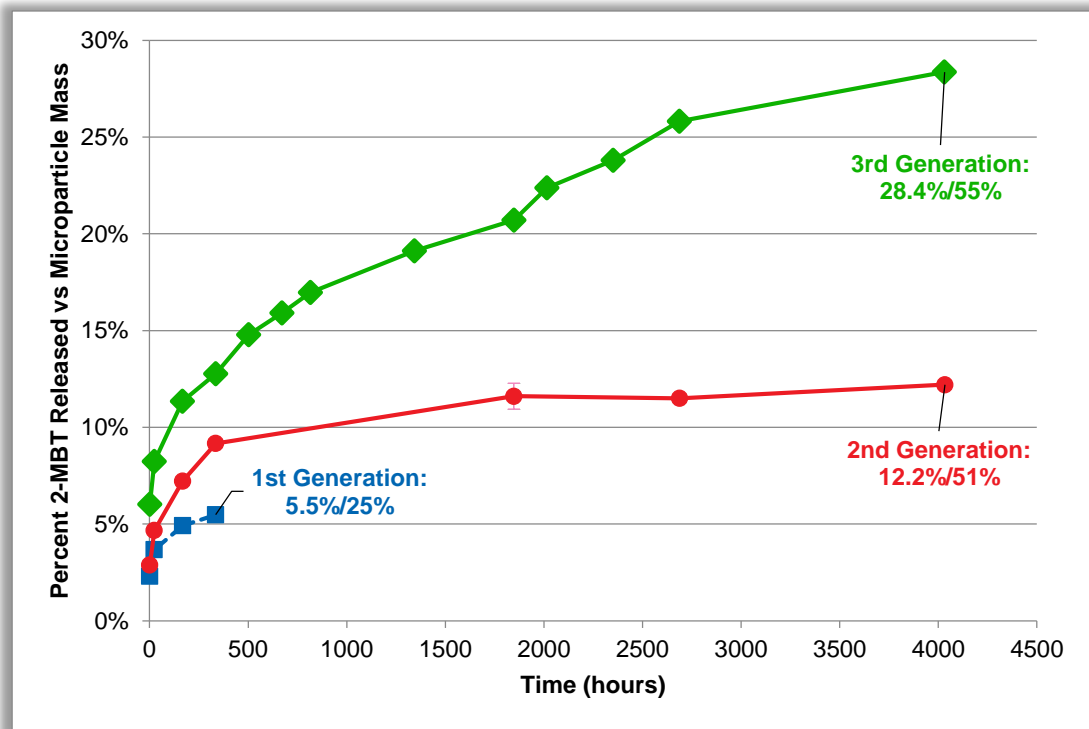
Figure 2: Cumulative release of inhibitor from organic 2-MBT particles
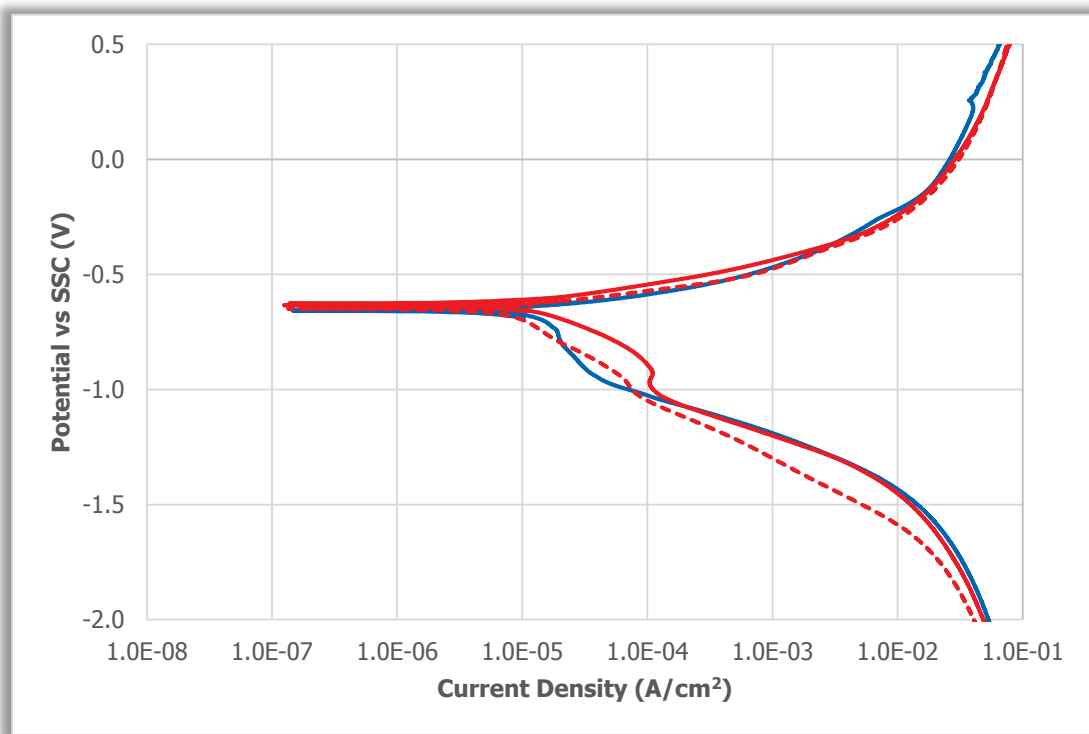
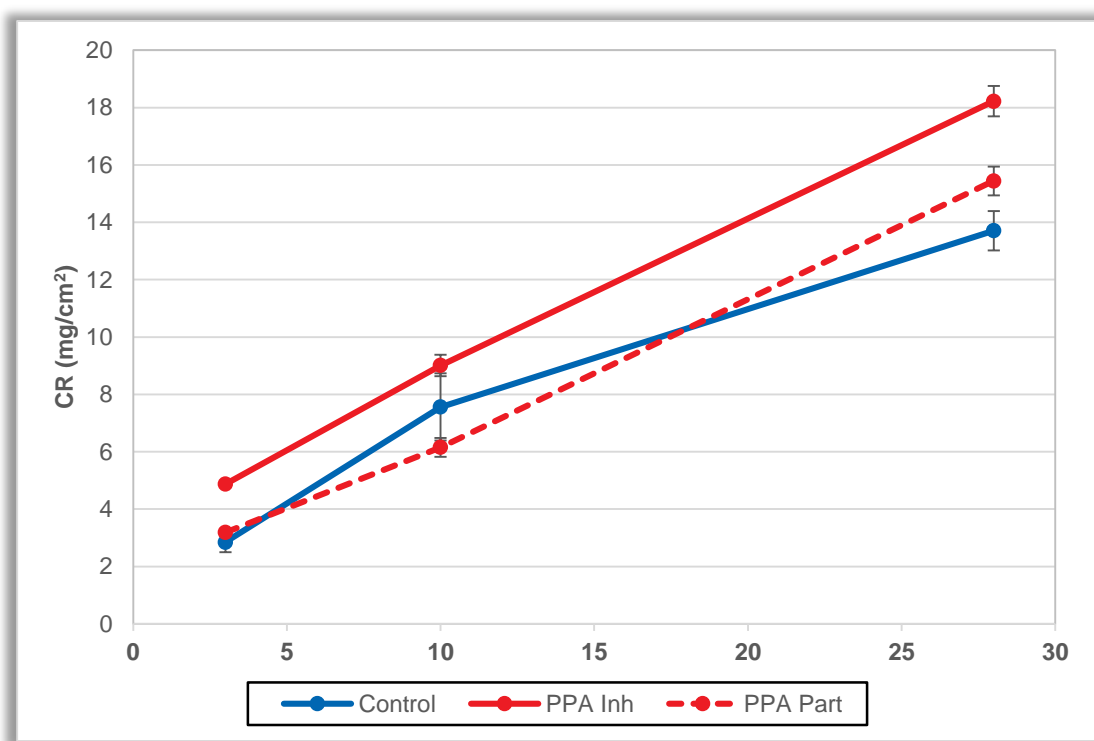## Accelerated Corrosion Testing: PPA

Figure 3: Polarization curves of carbon steel in the presence of PPA inhibitor (solid red), PPA particle (dashed red) and the Control (solid blue)

The polarization curves of PPA Inh, PPA Part and the Control sample are plotted in Figure 3. Neither PPA Inh nor PPA Part show significant changes in the corrosion potential or anodic polarization, which are indicative of corrosion inhibition. A slight shift in the cathodic polarization curve for PPA Inh between 10^{-5} and 10^{-4} A/cm^2 suggests that the inhibitor is affecting certain cathodic reactions. The precise origin of this effect could be determined by further electrochemical measurements, e.g. by excluding oxygen.

Similar behavior is observed in the mass loss experimental results. Figure 4 shows the corrosion rate (CR) in terms of carbon steel mass loss (mg/cm^2) of PPA Inh and PPA Part measured during the mass loss experiments. The pure inhibitor and particles exhibit the same or even higher mass loss than the control sample. This is despite the fact that this inhibitor exhibited some of the best corrosion protection behavior, based on the appearance of the corrosion test panels. Figure 5 shows the Control and PPA Inh panels after they were removed from solution and cleaned with water after 10 days of immersion. Whereas the Control panels show significant discoloration due to corrosion, a gray film of PPA adhered to the surface of the PPA Inh panels gives the impression of a well-protected metal (a similar film is observed for PPA Part after 3 days). Though PPA bonds well with iron, it is most effective when used as pretreatment,[25] especially in combination with other protective agents.[26-30] In the conditions where exposure to PPA and corrosion are occurring at the same time, despite its appearance, the PPA film on the metal does not significantly protect the panels.
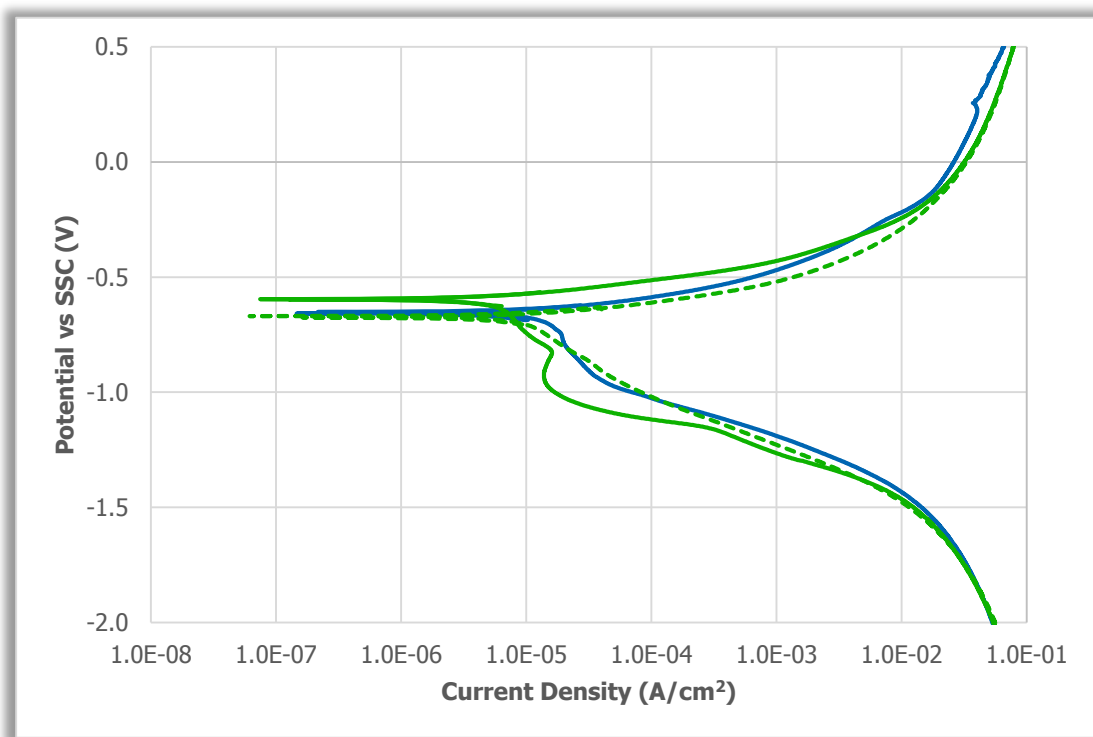

Figure 4: Corrosion rate of carbon steel in the presence of PPA Inh, PPA Part and Control as a function of immersion time

Figure 5: Front and back of Steel panels after immersion in 3.5% NaCl for 10 days Left: Front and back of Control; Right: Front and back of PPA inhibitor
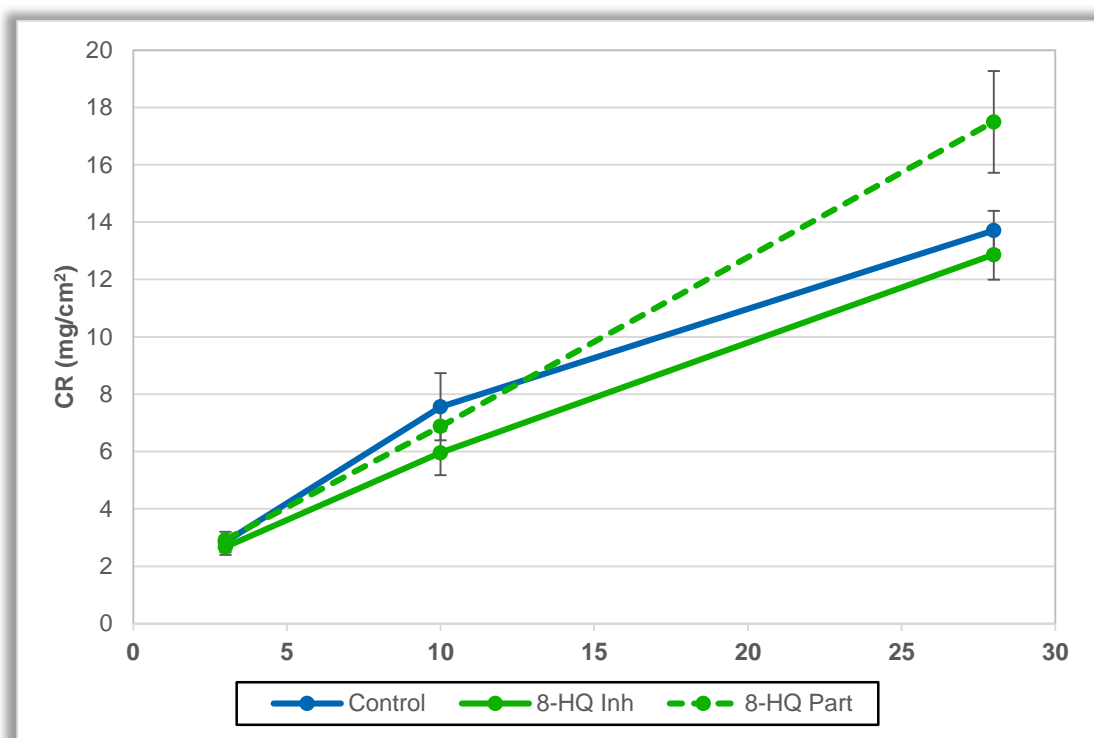
Accelerated Corrosion Testing: 8-HQ

Figure 6: Polarization curves of carbon steel in the presence of 8-HQ inhibitor (solid green), particle (dashed green) and the Control (solid blue)

The polarization curves of 8-HQ Inh, 8-HQ Part and the Control sample are plotted in Figure 6. The presence of 8-HQ Inh causes a shift in the corrosion potential to more positive (passive) potential values, and a decrease in the corrosion current density. This data shows that 8-HQ inhibits both the anodic and cathodic corrosion reactions. Similar behavior has been observed

for 8-HQ on other metals in different electrolytes, and the inhibition is attributed to the complexation with metal ions, absorption onto the metal surface, and film formation.[31-33]

The corrosion inhibition observed in the electrochemical measurements for 8-HQ Inh is not observed in the mass loss test data (Figure 7). 8-HQ Inh exhibits the same corrosion rate as the Control sample over the four week immersion period. This suggests that while 8-HQ is able to inhibit corrosion over short periods of time, as seen in the electrochemical studies, the corrosion of steel in the aggressive NaCl solution is likely too high for the 8-HQ inhibitor to make any notable impact on inhibiting the metal during longer immersion.

The inhibitor-filled particles showed no significant difference in corrosion behavior when compared to the Control and actually exhibited an increase in the corrosion rate after 28 days of immersion. This data suggests that the release properties of the particles are not adequate to provide corrosion protection within the test conditions.


Figure 7: Corrosion rate of carbon steel in the presence of 8-HQ Inh, 8-HQ Part and Control as a function of immersion time

Accelerated Corrosion Testing: 2-MBT

The polarization curves of carbon steel in the presence of 2-MBT inhibitor, 2-MBT particles, and the Control sample are plotted in Figure 8. The presence of 2-MBT provides significant protection to the metal, acting as a mixed type inhibitor by absorbing onto the metal surface and slowing both the anodic and cathodic reactions.[34-36] The corrosion potential is shifted over 130 mV to more positive potentials accompanied by a decrease in the corrosion current by nearly one order of magnitude, indicating that significant inhibition is occurring due to the presence of 2-MBT.
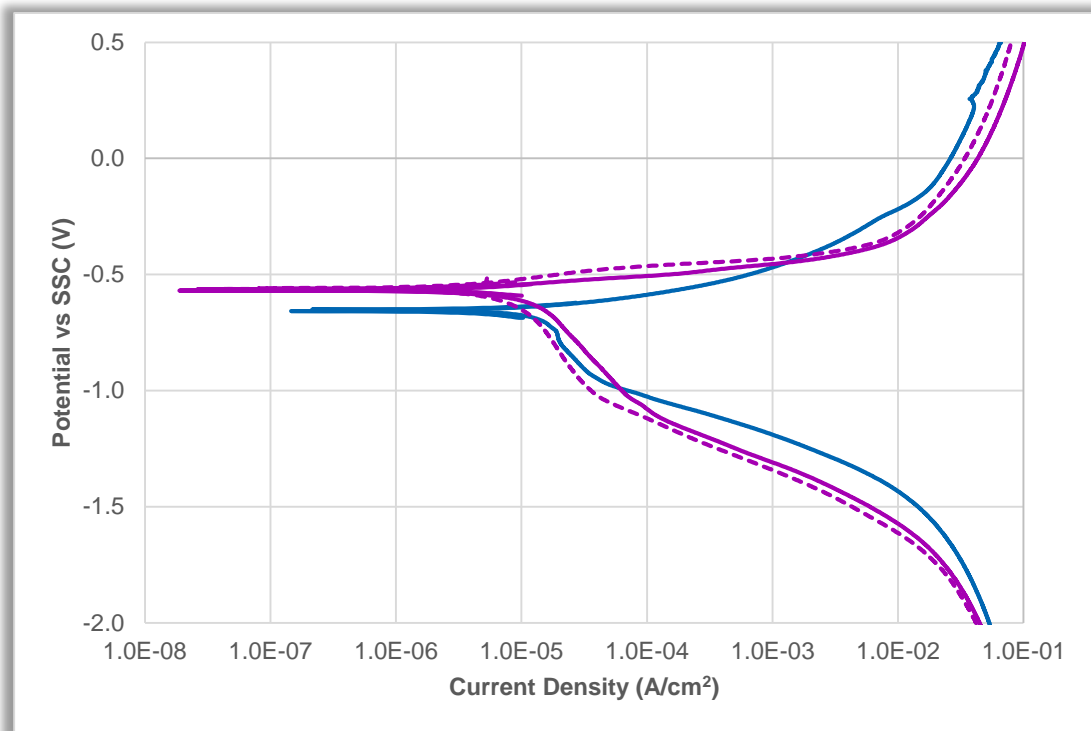
Figure 8: Polarization curves of carbon steel in the presence of 2-MBT inhibitor (solid purple), 2-MBT particle (dashed purple) and the Control (solid blue)

However, in the mass loss test method 2-MBT Inh (Figure 9) exhibits the same and after 28 days actually a worse corrosion rate than the Control. This suggests that 2-MBT, similar to the results obtained for 8-HQ, is able to inhibit corrosion in an immersion environment for short periods of time. However, at longer immersion times, the corrosion of steel in the highly corrosive salt solution exceeds the inhibitive strength of pure 2-MBT.

In the polarization curve measurements, 2-MBT Part shows near identical behavior to the pure inhibitor (Figure 8). A shift to more positive potentials, mixed-type inhibition and a decrease in the corrosion current, which are all signs of inhibition. However, in contrast to 2-MBT Inh, the 2-MBT particles perform significantly better than the Control over the whole 28 days of mass loss immersion, reducing the corrosion rate by up to nearly 40%.

There are a few of reasons for the higher performance of the 2-MBT particles over the pure inhibitor. 2-MBT is nearly insoluble in neutral and acidic media. Though the low concentrations of 2-MBT are sufficient to provide inhibition for small electrochemical samples, for larger panels and longer immersions periods, the corrosion of steel is too great for 2-MBT to provide significant protection. In contrast, the 2-MBT particles can deliver higher amounts of inhibitor to the metal. As shown earlier for the release studies (see Figure 2), at elevated pH, as present at active corrosion sites, the 2-MBT particles are able to quickly release small but significant amounts of their payload to inhibit initial corrosion. Furthermore, the microparticles that are settled onto the steel can continue to release inhibitor providing continuous long term corrosion protection. This demonstrates that the 2-MBT particles are, as designed, delivering inhibitor to the metal when needed to inhibit corrosion.
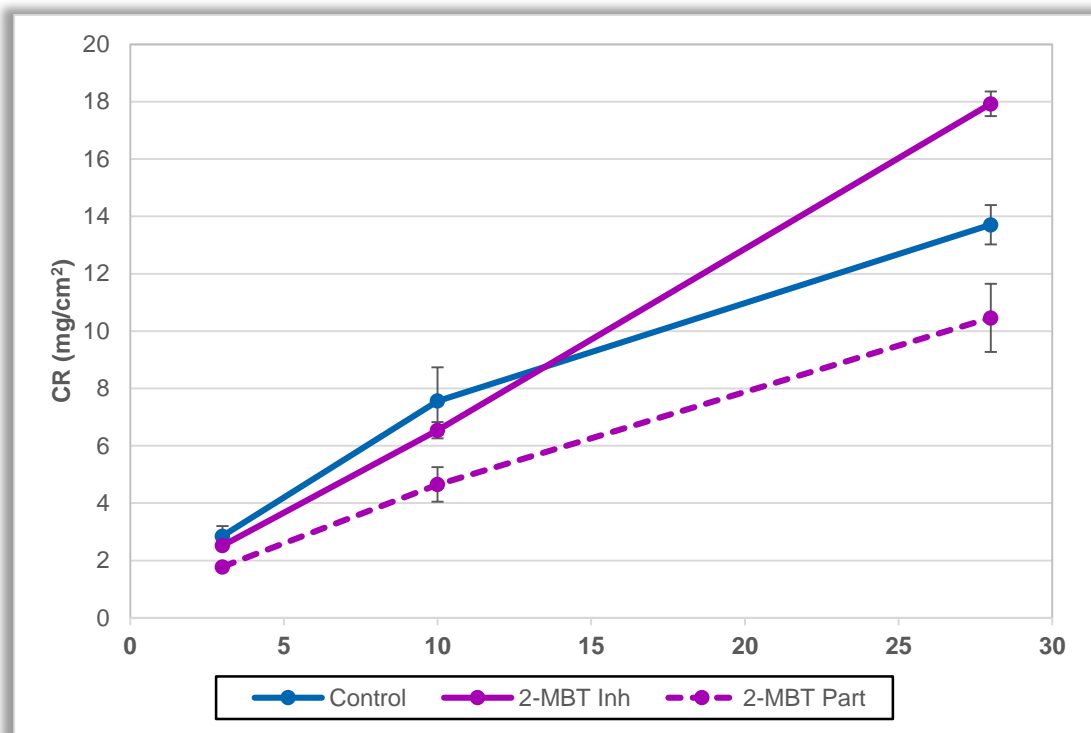
Figure 9: Corrosion rate of carbon steel in the presence of 2-MBT Inh, 2-MBT Part and Control as a function of immersion time

CONCLUSION

Three inhibitors were encapsulated into corrosion sensing microparticles. The total inhibitor content of 2-MBT in organic microparticles could be modified over a wide range of concentrations (16-60 wt%). The release of inhibition in 0.01 M KOH solution was studied. All formulations showed a fast release of small amounts of inhibitor within an hour followed by a consistent release over longer periods of time. The formula was optimized to yield microparticles with a reproducible loading of 55 wt%±2wt% that were capable of releasing inhibitor for a period of immersion in a base solution of up to 18 weeks.

Accelerated electrochemical and mass loss testing of all three inhibitors, both in their pure and encapsulated forms, was performed on carbon steel. Though it provided the steel with a homogeneous gray film, PPA was not able to reduce the corrosion rate in the mass loss testing and showed no significant inhibitive effects in polarization curves. 8-HQ Inh showed significant corrosion inhibition in the electrochemical testing but, in longer-term mass loss experiments, it proved to be ineffective. 8-HQ particles showed no differences to the Control samples in either tests. Similarly, 2-MBT inhibitor performed well during electrochemical testing, however, over the four weeks of immersion to measure mass loss, it was not able to provide significant corrosion protection, due to its low solubility. On the other hand, the 2-MBT particles not only showed the same electrochemical behavior as the pure inhibitor, but also provided significant corrosion protection to carbon steel over the whole 28 days of salt solution immersion. As designed, 2-MBT particles are able to deliver inhibitor directly and consistently to active corrosion sites, providing short- and long-term protection in immersion conditions and making the particles potential candidates for additives for corrosion resistant smart coating.

ACKNOWLEDGEMENTS

References

x

[1] George F. Hays. (2010) [Online]. http://events.nace.org/euro/corrodia/Fall_2010/wco.asp

[2] Sahar Amiri, "Preparation of supramolecular corrosion-inhibiting nanocontainers for self-protective hybrid nanocomposite coatings," *Journal of Polymer Research*, vol. 21, p. 566, 2014.

[3] Daria V. Andreeva, "Layer-by-Layer Polyelectrolyte/Inhibitor Nanostructures for Metal Corrosion Protection," *ACS Applied Materials & Interfaces*, vol. 2, no. 7, pp. 1954-1962, 2010.

[4] Daria V. Andreeva, "Self-Healing Anticorrosion Coatings Based on pH-Sensitive Polyelectrolyte/Inhibitor Sandwichlike Nanostructures," *Advanced Materials*, vol. 20, pp. 2789-2794, 2008.

[5] Alexei A. Antipov, "Carbonate microparticles for hollow polyelectrolyte capsules fabrication," *Colloids and Surfaces A- Physicochemical and Engineering Aspects*, no. 224, pp. 175-183, 2003.

[6] Dimitriya Borisova, "Influence of Embedded Nanocontainers on the Efficiency of Active Anticorrosive Coatings for Aluminum Alloys Part II: Influence of Nanocontainer Position," *ACS Applied Materials & Interfaces*, vol. 5, pp. 80-87, 2013.

[7] Dimitriya Borisova, "Influence of Embedded Nanocontainers on the Efficiency of Active Anticorrosive Coatings for Aluminum Alloys Part I: Influence of Nanocontainer Concentration," *ACS Applied Materials & Interfaces*, vol. 4, pp. 2931-2939, 2012.

[8] Arunchandran Chenan, "Hollow mesoporous zirconia nanocontainers for storing and controlled releasing of corrosion inhibitors," *Ceramics International*, no. 40, pp. 10457-10463, 2014.

[9] Yuhua Dong, "Protective behaviors of 2-mercaptobenzothiazole intercalated Zn–Al-layered double hydroxide coating," *Journal of Coatings Technology and Research*, 2014.

[10] M.F. Montemor, "Functional and smart coatings for corrosion protection: A review of recent advances," *Surface & Coatings Technology*, vol. 258, pp. 17-37, 2014.

[11] John Sinko, "Challenges of chromate inhibitor pigments replacement in organic coatings," *Progress in Organic Coatings*, vol. 42, pp. 267–282, 2001.

[12] Elshad Abdullayev, Ronald Price, Dmitry Shchukin, and Yuri Lvov, "Halloysite Tubes as Nanocontainers for Anticorrosion Coating with Benzotriazole," *ACS Applied Materials & Interfaces*, vol. 1, no. 7, pp. 1437-1443, 2009.

[13] Daria V. Andreeva, "Layer-by-Layer approaches for formation of smart self-healing materials," *Polymer Chemistry*, 2013.

[14] S.R. Taylor, "Identification and Characterization of Nonchromate Corrosion Inhibitor Synergies Using High-Throughput Methods," *Corrosion*, vol. 64, no. 3, 2008.

[15] Dmitry G. Shchukin, "Active Anticorrosion Coatings with Halloysite Nanocontainers," *Journal of Physical Chemistry C*, vol. 112, pp. 958-964, 2008.

[16] I.A. Kartsonakis, "Multifunctional epoxy coatings combining a mixture of traps and inhibitor loaded nanocontainers for corrosion protection of AA2024-T3," *Corrosion Science*, vol. 85, pp. 147-159, 2014.

[17] Martin F. Haase, "Development of Nanoparticle Stabilized Polymer Nanocontainers with High Content of the Encapsulated Active Agent and Their Application in Water-Borne Anticorrosive Coatings," *Advanced Materials*, vol. 24, pp. 2429-2435, 2012.

[18] R.L Jr. Cook, "Pigment-Derived Inhibitors for Aluminum Alloy 2024-T3," *Corrosion*, vol. 56, no. 3, 2000.

[19] Ravindra G. Puri, "Recent developments in smart coatings for corrosion protection," *Paintindia*, 2012.

[20] S.V. Lamaka, "High effective organic corrosion inhibitors for 2024 aluminium alloy," *Electrochimica Acta*, vol. 52, pp. 7231–7247, 2007.

[21] Ganesha Achary, "The corrosion inhibition of mild steel by 3-formyl-8-hydroxy quinoline in hydrochloric acid medium," *Materials Chemistry and Physics*, vol. 107, pp. 44-50, 2008.

[22] G.P. Cicileo, "Inhibitory Action Of 8-Hydroxyquinoline On The Copper Corrosion Process," *Corrosion Science*, vol. 40, no. 11, 1998.

[23] N. Etteyeb, "Protection of reinforcement steel corrosion by phenyl phosphonic acid pre-treatment PART I: Tests in solutions simulating the electrolyte in the pores of fresh concrete," *Cement & Concrete Composites*, vol. 55, pp. 241-249, 2015.

[24] C. F. Glover, "In-Coating Phenyl Phosphonic Acid as an Etch-Primer Corrosion Inhibitor System for Hot Dip Galvanized Steel," *Journal of the Electrochemical Society*, vol. 162, no. 9, pp. C433-C441, 2015.

[25] Jose E. Pereira da Silva, "Polyaniline acrylic coatings for corrosion inhibition: the role played by counter-ions," *Corrosion Science*, vol. 47, pp. 811-822, 2005.

[26] J.E. Pereira da Silva, "Polyaniline/poly(methylmethacrylate) blends for corrosion protection: The effect of passivating dopants on different metals," *Progress in Organic Coatings*, vol. 58, no. 1, pp. 33-39, 2007.

[27] Susai Rajendrana, "Synergistic and antagonistic effects existing among polyacrylamide, phenyl phosphonate and Zn2+ on the inhibition of corrosion of mild steel in a neutral aqueous environment," *Electrochimica Acta*, vol. 44, no. 2-3, pp. 533-537, 1998.

[28] S. Rajendran, "Corrosion inhibition by phenyl phosphonate and Zn2+," *Anti-Corrosion Methods and Materials*, vol. 45, no. 3, pp. 158-161, 1998.

[29] Xiaofeng Liang, "Corrosion Inhibition of 2-Mercaptobenzothiazole for Carbon Steel in Sulfuric Acid Solution," *Advanced Materials Research*, vol. 557-559, pp. 92-95, 2012.

[30] Yuanyuan Feng, "Characterization of iron surface modified by 2-mercaptobenzothiazole self-assembled monolayers," *Applied Surface Science*, vol. 253, pp. 2812-2819, 2006.

[31] Goudarzi Narges, "Investigation on 2-mercaptobenzothiazole behavior as corrosion inhibitor for 316-stainless steel in acidic media," *Anti-Corrosion Methods and Materials,* vol. 61, no. 1, pp. 20-26, 2014.

[32] W. Li, "pH-sensitive microparticles with matrix-dispersed active agent," US patent 8859288, 2013.

[33] J.W. Buhrow, "Microencapsulation Technology for Corrosion Miti-gation by Smart Coatings," in *DoD Corrosion Conference 2011*, Palm Springs, U.S.A., 2011.

[34] W. Li, "Microencapsulation of Corrosion Indicators for Smart Coatings," in *DoD Corrosion Conference 2011*, Palm Springs, U.S.A., 2011.

[35] W. Li, "Synthesis of Elongated Microcapsules," in *3rd International Conference on Self-Healing Materials*, Bath, UK, 2011.

[36] S.T. Jolley, "Microencapsulation of Self-Healing Agents for Corrosion Control Coatings," in *3rd International Conference on Self-Healing Materials*, Bath, UK, 2011.

x