Y-12

OAK RIDGE Y-12 PLANT

MARTIN MARIETTA

A PERFORMANCE EVALUATION OF COATING SYSTEMS FOR LONG TERM AQUEOUS IMMERSION SERVICE

S. J. Pawel

Materials Engineering Department
Development Division

November 8, 1994

Article to be submitted to:
Materials Performance

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY
UCN-13672 (2 10-90)

Prepared by the
Oak Ridge Y-12 Plant
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DT

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

**A PERFORMANCE EVALUATION OF COATING SYSTEMS
FOR LONG TERM AQUEOUS IMMERSION SERVICE**

S. J. Pawel

**Materials Engineering Department
Development Division
Oak Ridge Y-12 Plant***

November 8, 1994

**Article to be submitted to:
Materials Performance**

MASTER

***Managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy
under contract DE-AC05-84OR21400.**

**A Performance Evaluation of Coating Systems for
Long Term Aqueous Immersion Service**

S. J. Pawel

Materials Engineering Department

**Development Division, Oak Ridge Y-12 Plant*; P.O. Box 2009,
Oak Ridge, TN 37831-8096**

Abstract

The static immersion of coated steel panels in various media representative of chemical and waste processes around the Oak Ridge Y-12 Plant was terminated after 16 months exposure for evaluation of coating performance and comparison with observations collected following 1, 6, and 11 months exposure. In each environment, a wide range of coating performance was observed, including some coatings unsuitable for use in the test environment (despite the high recommendation of the vendor). Further, coating performance as a function of time suggests a test duration of at least several months is required to fully assess candidate coating performance for specific applications. The performance of many coatings, particularly in the most alkaline environment, was adversely affected by the imposition of supplemental cathodic protection on the coated test panels.

*Managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy under contract DE-AC05-84OR21400.

Introduction

The Oak Ridge Y-12 Plant* operates a number of large aboveground steel tanks that are protected on the process side by various inorganic coating systems (with supplemental cathodic protection in many cases). During a recent investigation of internal coating failure at a particular waste processing tank facility, many shortcomings associated with the failed coating - including its general suitability for service and potential application errors - were noted. Further, due to the need to act quickly, the selection of a repair/replacement coating system was performed without benefit of long-term exposure tests to collect performance data for candidate materials. This experience highlighted several weaknesses in the material selection process for coatings and lining materials, including

- lack of expertise/experience in coating selection and testing;
- reliance on vendor-generated literature, performance data, and salesmanship for coating selection; and
- no program in place to address future technical requirements for coatings and linings.

The large capital and maintenance costs for chemical/waste handling and containment requires ever greater care in materials selection to provide maximum service life and cost efficiency. Therefore, a program to evaluate candidate products for performance in specific environments - free of vendor bias and salesmanship in the decision making - is of paramount importance. As a result, a test program was initiated to evaluate "high performance" coating materials in a variety of service conditions representative of those experienced around the Oak Ridge Y-12 Plant. Although direct comparison of coating performance is possible with data collected during this effort, the primary purpose was not to compare coatings but to assess reliability of material selection based on vendor-generated information and the utility of cathodic protection as a supplementary corrosion protection for coated carbon steel tanks. This document summarizes some of the important observations over the total 16 month exposure.

Experimental Approach

Environments. Three environments were selected for this immersion test study. These environments were chosen primarily on the basis of being chemically representative of the range of environments likely to be encountered around the facility. The specific waste solution selected for study is presently processed on site in 100,000 gallon coated steel tanks. The specific test solutions chosen include:

1) alkaline bath: sufficient reagent grade sodium hydroxide was added to demineralized water to establish a pH of 12.75; sufficient reagent grade sodium chloride was added to generate about 600 ppm chloride ions to increase conductivity; ambient temperature with no specific aeration or agitation.

2) acid bath: sufficient reagent grade hydrochloric acid added to demineralized water to establish a pH of 2.0; ambient temperature with no specific aeration or agitation.

3) biodenitrification bath: waste process solution taken from a tank farm on site; major components include high concentrations of chlorides, sulfates, alkali metals, and active microbes, and some suspended solids; bulk pH near 9.5; periodic aeration with associated agitation; primarily ambient temperature service with possible excursions to near 38°C (100°F).

Large troughs fabricated from type 316L stainless steel were used to contain each solution. Each trough contained near 100 liters of solution and was fitted with a lid (not air-tight, also 316L stainless steel) to minimize evaporation and return vapor condensate to the tank.

Test Panels. Coating companies were solicited for interest in participation based primarily on national reputation and/or Plant experience with products offered by the company. Each company was informed of the specific test environments, sent an appropriate number of type 1020 steel panels (all from the same master lot), and asked to return coated panels ready for long term immersion testing in each environment. Mild steel panels with dimensions 203 mm x 102 mm x 3.2 mm thick were used, with surface preparation and coating performed by the respective vendors.

In total, 22 different coating systems were submitted (at least 17 bound for each environment) representing 11 different companies. The coating systems included amine, polyamide, and novolac epoxies, vinyl esters, polyurethanes, polyesters, phenolics, and a few "other" varieties. Some contained glass flake fillers and/or used primers and some included neither feature. The coating systems ranged in total thickness from about 0.3 mm to almost 1.5 mm. Each simply represented the respective vendor's choice for resistance to the described environment.

Upon receipt of the returned panels, initial measurements (coating thickness, metallography of cross section, adhesion strength) were collected for the unexposed condition for each coating system. Subsequently, an "X" scratch (to simulate a coating flaw or application damage) was made covering most of one face of each panel destined for immersion testing. The scratch, covering the lower 150 mm of each specimen, was cut with a 0.6 mm carbide wafering saw to a depth that the substrate metal was just exposed at the bottom of the groove. Panels were hung in the troughs such that the "X" was fully immersed leaving about 50 mm of the panel exposed above the solution line.

In all, four identical panels representing each coating system were exposed in each solution. One panel representing each system was strapped to a sacrificial anode to provide cathodic protection (CP) to the panel in an attempt to determine the long term influence of this variable in each environment.

Test Strategy. During the first six months, panels in each test were examined on a weekly basis to determine the earliest onset of color changes, wrinkling, blistering, and other changes. Solution level, pH, and performance of the CP systems were also checked on these intervals. At longer test times, these checks were performed less frequently. At 1, 6, 11, and 16 months cumulative exposure, more invasive (and destructive) evaluations were performed, including evaluations for extent of chipping

and undercut at the "X" scratch and pull-off adhesion tests [ASTM D4541] on the side of the panel opposite the "X" scratch.

Also, for the alkaline bath, attempts were made to accelerate testing and evaluation of coatings by using an "Atlas cell" concept [NACE TM0174]. The panels exposed in this test were from the same group of panels submitted for immersion testing but no "X" scratch was included on these panels.

To permit a crude comparison of performance, an evaluation scheme was created to "score" each system based on various criteria. The scheme (with maximum number of points in parentheses) included evaluation of degree of discoloration (5 pts), swelling (5 pts), toughness and flexibility retention (5 pts), chipping and undercut (10 pts), blistering (15 pts), adhesion and adhesion retention (15 pts), and environmental friendliness (a relative measure of volatile organic content [VOC], with low VOC deemed good, 5 pts). Thus, a maximum total of 60 performance points were available in this scheme.

Results and Discussion

Alkaline Bath. Among the 17 coatings exposed for 16 months, there was a typical gaussian-type distribution of performance. The median performance score was 40 and ten systems were rated 40 +/- 4 pts. At the high end of performance, four systems scored 49 or greater points and at the low end, three scored 31 or fewer points. Several important trends in the data are evident.

For example, there is no pattern regarding performance as a function of the type of coating. Among the best four best systems, there are four different types of coatings: a novolac epoxy, an amine epoxy, a vinyl ester, and an "other," respectively. Similarly, the three lowest scores include two amine epoxies and a polyurethane. Further, it is not clear that coating thickness is necessarily a strong indicator of performance (although the top three coatings are all at least 1 mm thick) because some of the poor performers are greater than 0.75 mm thick. Each of the top four was a 2-topcoat system and two contained glass flake fillers in the topcoats.

In addition, relative adhesion appears to be a "discriminating" factor in that all of the top performers (each of the top seven, but no others) have a "double-digit" rating in this category. This is potentially significant for a variety of reasons, including the fact that evaluation of adhesion can be performed in the field on a qualitative basis where the other factors may include some degree of subjectivity or judgement on the part of the evaluator.

Adhesion data as a function of time appears in Figure 1 for representative coating systems exposed in the alkaline bath. [Data points represent the average of at least six tests per coating system - two tests on each of three panels exposed without CP.] These data represent several important trends. For example, the adhesion strength of many systems decreases rapidly over the initial six months of exposure. Following this time, the decrease in adhesion strength is much slower and represents an "equilibrium" process controlled primarily by the permeation resistance of the coating and the initial

quality of the steel/coating bond. Often, the position of the adhesion failure (result of the pull-off test) changes with time. For example, the novolac epoxy system depicted in Fig. 1 exhibited a "mixed" failure (variable pull-off position from substrate to very shallow topcoat) in the virgin condition and after one month, but entirely substrate failure at six months and longer. After the 16 month exposure, the substrate also appeared wet and somewhat corroded. It appears that for this particular system, the coating has become nothing more than a rigid but permeable "bag" providing only marginal protection for the substrate steel. Other coatings with very low adhesion (particularly those for which adhesion is decreasing sharply as a function of time) may have a similar problem at longer exposure times.

For the initial six weeks exposure, sacrificial zinc anodes were used for CP and potential at the steel exposed at the "X" varied from -0.80 v vs a saturated calomel electrode (SCE) to about -0.4 v as exposure time increased. Adherent corrosion products on the zinc (and a relatively rapid corrosion rate) caused the decrease in CP voltage and necessitated a change to magnesium anodes. These resulted in a constant potential at the "X" of -1.05 v vs SCE for the remainder of the evaluation. Five coating systems revealed blisters on only the panels protected by a CP system (with the other panels showing no blistering at all). In addition, three other systems revealed significant decreases in adhesion strength for the CP panel compared to those without CP but no blistering was detected on these three systems. Although there were some short initiation times for blistering (in general or due to CP), about three months were typically required for blisters that formed as a result of CP.

It is perhaps significant that all of the adhesion data were collected on the face of the panel opposite the face bearing the large "X" scratch. The intention of the "X" scratch was to simulate a realistic flaw or process damage to the coating that might accelerate failure tendency. The absolute significance of the "X" scratch in this regard is difficult to assess, but almost 100% of the blistering observed on panels with no cathodic protection was found on the side of the panel bearing the "X" scratch. In many cases, the blisters obviously intersected the "X" but in others, solution penetration under/along the "X" appears to have contributed to coating failure at least slightly removed from the "X." Clearly, the role of the "X" in accelerating potential problems is significant.

Another attempt to accelerate coating reactions and performance estimates utilized an "Atlas cell" concept to maintain a temperature gradient across the coating. This effect is also called the "cold wall" effect and works on the following principle. In many examples of coating service, a process fluid is contained inside a coated tank. Under many conditions, it is possible for the process fluid to be at a higher temperature than the tank wall. Under these conditions, there is a thermal driving force for water - perhaps carrying other constituents - to collect/condense in the coldest region (in this case, the interface between coating and substrate). Depending on a variety of other conditions, this can be a very corrosive condition for the substrate the coating is intended to protect.

In the present case, coated panels were placed across the ends of cylindrical glass vessels via four bolts equi-spaced around the glass circumference. Neoprene o-rings,

Fig. 1. Adhesion strength as a function of exposure time for representative coatings in the alkaline bath.

squeezed between the panels and glass by the bolts, sealed the solution inside each vessel. An immersion heater was used to slightly heat the alkaline solution (near 40°C). The entire assembly was then placed in a large water bath circulating demineralized water at near ambient temperature (about 28°C at "equilibrium"). Heat transfer from the process solution to the water bath was much more efficient than anticipated and maintenance of a temperature gradient larger than about 10°C proved unrealistic for this arrangement. Tests were conducted on panels (no "X" scratch, no cathodic protection) for three weeks under this thermal gradient. Substantial decreases in adhesion - roughly consistent with decreases expected after six months of static exposure - were observed for 9 of 14 systems so tested. However, with only one exception, no blisters or other changes in properties were detected for any of these coatings. It appears that this method of accelerating compatibility tests may have merit and warrant further effort.

The data collected for the alkaline bath exposure seem to indicate that (for standard immersion at ambient temperature) a lengthy period - greater than one month - is required to fully evaluate a group of coatings. For example, adhesion strength for many systems decreases sharply between 1 and 6 months total exposure. Blisters first formed on three systems after six weeks of exposure (these were above the solution line in one case) and dramatically spread for another system. Generically, about three months were required for blisters to develop on the panels bearing cathodic protection, and over the 16 month exposure period, at least eight of the coating systems were

adversely affected by the application of CP. An evaluation period less than one month in duration would have missed all of these changes.

Acid Bath. Compared to the results from the alkaline bath, there is less distinction (closer spacing of scores) in performance between the various coatings exposed in the acid bath. The median score was 48, and nine coating systems had a score for acid of 48-52 for this environment. However, six coatings earned a score of 38 or less. Although there were several coating systems exposed in the acid bath that were not part of the alkaline exposure, many coatings were exposed to both environments; four of the top five systems are the same in each environment. Again, the superior coating systems generally have the highest adhesion strengths. Adhesion strength decreases similar to those observed in the alkaline bath (Fig. 1) were observed for coating systems exposed in the acid bath.

Comparison of data in for acid and alkaline bath exposure reveals that blistering is generally a much more serious concern in the alkaline environment than the acid environment. Ten systems in the alkaline environment received less than the maximum score for blistering resistance while only four systems received less than the maximum in the acid bath. Perhaps, the absence of cathodic protection after the initial eight weeks was a significant contribution to this result.

Biodenitrification Bath. The average score among the 17 coating systems exposed in this environment was 41 (median of 43) and ten coatings scored within +/- 4 points of this rating. Top performers (4) ranged from 49 to 56 points and poor performers (3) from 11 to 34 points. There are no obvious trends that reveal a commonality in performance among the high scores. Like the other exposure environments, a variety of coating types and thicknesses are found among the top (and bottom) performers. Perhaps adhesion strength was the largest single factor indicating good performance, but some of the poorest performers also earned a relatively high score in this area. General decreases in adhesion strength as a function of time similar to those shown in Fig. 1 were observed for coatings in the biodenitrification bath.

The utility of cathodic protection is particularly uncertain in this environment. At least five systems (otherwise high performers) showed increased blistering or substantial decreases in adhesion strength as a result of the cathodic protection. During the first six months, zinc was used for sacrificial anodes in this solution. Initially (about 1 month), these provided a potential at the "X" of near -1.0 v vs SCE but over the next several weeks/months, the potential at the "X" began to increase and slowly approached -0.5 v vs SCE. Observations of a "slime-like" deposit were noted on the "X" scratches during the period in which the potential was changing as indicated. At the end of the six month interval, the panels were removed from the murky solution to reveal that all panels attached to the CP anode were covered with this reaction product but that the exposed steel on panels without the CP were essentially clean and free of this deposit (see Fig. 2). This deposit displayed a crusty outer layer with a soft, gelatinous internal fluid (actually, goop is a better term) that was primarily black/deep green. The steel underneath the deposits had clearly corroded (steel was etched), but relatively little pitting or other signs of accelerated corrosion were detected. Apparently, the CP potential provided by the zinc was conducive to formation of this product and that the

Fig. 2. Panels exposed in the bionitrification bath for six months; panel A was attached to the zinc anode and exhibits extensive accumulation of a "slime" deposit while panel B (same coating system) was not attached to the anode and exhibits very little "slime" deposit along the "X" scratch.

deposit represents a high resistance that shields the underlying metal from the full effect of the CP potential. Subsequent replacement of the zinc with magnesium anodes (potential of -1.2 v vs SCE at "X") coincided with a periodic replacement of much of the test solution (to simulate the actual process). No further slime accumulation was detected and therefore it is uncertain if this effect was related to particular solution chemistry or anode potential or both. The slime-like deposit was not analytically identified, but circumstantial evidence from beaker-sized tests on bare steel (substantial decrease in sulfate content of solution and sulfur deposits on affected steel) suggests a sulfate-reducing bacteria phenomenon.

Conclusions

Perhaps the most significant conclusion of this study is that, despite aggressive marketing, high recommendations, and printed literature suggesting compatibility from the respective vendors, several coating systems (about 25%) were found to be essentially incompatible with their test environments. Further, the vendors prepared the steel panels supplied by the author, so any question regarding component mixing, application, or surface finish as it affects performance rests with the vendor of the particular product. This highlights the need for hands-on testing rather than reliance on vendor salesmanship for material selection.

The duration of testing required to fully evaluate coatings for long term immersion duty is significant. Immersion panels with only an "X" scratch on one face to accelerate coating degradation require at least several months continuous immersion to reveal substantial blistering and decreases in adhesion for some systems (with or without cathodic protection). Clearly, however, the "X" scratch does accelerate coating degradation. Encouraging data was developed suggesting that the Atlas cell concept for the cold wall effect may accelerate adhesion decreases (compress six months of ambient immersion into about one month under thermal gradient) but more work is required to refine this type of accelerated test for qualification of coatings.

The top performers in each environment tended to represent a variety of different coating types (eg amine epoxy, novolac epoxy, vinyl ester) although most tended to be two coats, relatively thick, and have glass fillers. Further, the top performers in each environment had some common members, indicating a superior product among the many tested.

The performance of many coating systems, particularly in the solutions of relatively high pH, was adversely affected by imposed cathodic protection. In some cases this was manifested by sharp decreases in adhesion or the development of significant blistering compared to identical panels without cathodic protection. In most cases, several months of exposure were required to reveal this tendency, which means that standard laboratory tests (typically only a few days or weeks) would miss this potential problem.

Acknowledgements

The author expresses appreciation to many individuals for their contributions to this effort. J. F. Newsome, C. A. Henderson, and W. C. Pullen helped prepare the panels for adhesion testing. R. F. Simandl participated in many discussions and reviewed the manuscript. P. F. Bolden helped prepare the manuscript. The financial support of the Y-12 Waste Management Division is gratefully acknowledged.

Distribution:

✓ A. K. Lee/DOE - OSTI, 9731, MS-8175 (2)
W. G. Northcutt, Jr./A. M. Ammons
S. J. Pawel
Y-12 Central Files - RC