



COATING FAILURE ANALYSIS

Editor: Jon R. Cavallo, PE



CorrCompilations: Coating Failure Analysis

Editor: Jon Cavallo, PE



NACE International
The Worldwide Corrosion Authority

©2017 by NACE International
All Rights Reserved
Printed in the United States of America

ISBN: 978-1-57590-343-9

Reproduction of the contents in whole or part or transfer into electronic or photographic storage without permission of the copyright owner is strictly forbidden.

Neither NACE International, its officers, directors, nor members thereof accept any responsibility for the use of the methods and materials discussed herein. No authorization is implied concerning the use of patented or copyrighted material. The information is advisory only and the use of the materials and methods is solely at the risk of the user.

NACE International
The Worldwide Corrosion Authority
15835 Park Ten Place
Houston, TX 77084
nace.org

Contents

About the Author

Introduction

A Protocol for Performance of Coating Failure Analyses

SECTION 1: GENERAL APPROACHES TO COATING FAILURE ANALYSIS

Introduction

How Not to Perform a Failure Analysis

Coating Failures in Plants and Industrial Environments

Coating Failure: Mechanical Flaw or Human Fault?

A Coating Supplier's Perspective

Coating Failures—A Coating Supplier's Perspective—Part 1

Coating Failures—A Coating Supplier's Perspective—Part 2

SECTION 2: PIPELINE COATINGS

Introduction

Pipeline Coating Failure – Not Always What You Think It Is

External Polymeric Pipeline Coating Failure Modes

Failure Analysis of Three Layer Polypropylene Pipeline Coatings

Report of a Coating Failure on a 16-Inch Oil Pipeline Under Wet CO₂ Service

Mitigating Coating Failures in Trenchless Pipeline Construction

Eliminating Coating Failures—A Case Study for Achieving Long-Term Cost Savings in the Oil Field

SECTION 3: LININGS

Introduction

Investigation and Analysis of Lining Failure

Premature Coating Failure of a Tank Lining System

Analysis of Failed Rubber Linings – A Failure Analysis Methodology

SECTION 4: OFFSHORE AND MARINE

Introduction

Early Coating Failures on Offshore Platforms

Case Studies on Failures for Waterborne Coatings in Shipbuilding

Review of Coating Failure Incidents on the Norwegian Continental Shelf since the Introduction of NORSOK M-501

SECTION 5: LABORATORY ANALYSIS

Introduction

Infrared Spectroscopy as a Failure Analysis Tool for Coatings

Analysis of Digital Images During the Assessment of the Results of the Pull-Off Adhesion Tests During the Coating Evaluation of the Fernando Espinosa Bridge

Degradation Study of Polymer Coating: Improvement in Coating Weatherability Testing and Coating Failure Prediction

About the Author

Jon R. Cavallo, PE, FASTM is a Registered Professional Engineer in three states and holds a Bachelor of Science Degree in Engineering Technology from Northeastern Engineering in Boston, Massachusetts. Mr. Cavallo is a Certified Nuclear Coatings Engineer of the National Board of Registration for Nuclear Safety Related Coating Engineers and Specialists, a Senior Nuclear Coatings Specialist of Board of Registration of Nuclear Coatings Specialists (BIRNCS) and a NACE International CIP Level 3 Inspector with Nuclear Facilities Endorsement.

Mr. Cavallo was elected President of the Maine Society of Professional Engineers for 2008–2009. He was elected President of the Board of International Registration for Nuclear Coatings Specialists (BIRNCS) in 2009. In 2010, Mr. Cavallo received the ASTM Award of Merit and is an ASTM Fellow. He also served as Chairman of the Industry Coating Phenomena Identification and Ranking Table (PIRT) Panel reviewing the work of Savannah River Technical Center on the USNRC Containment Coatings Research Project (Generic Safety Issue—191).

Mr. Cavallo was appointed by Dr. James M. Turner, Acting Director of the National Institute of Standards and Technology (NIST), to the 2008 Board of Examiners for the Malcolm Baldrige National Quality Award.

During his over 40 years of work in the coatings and corrosion mitigation field, he has gained a reputation as a world-renowned expert. His recent work has included assignments in USA, Canada, Slovenia, India, Peoples' Republic of China, Japan, and South Korea.

Introduction

Many books, articles and other materials have been published over the years, related to various aspects of protective coating failure analysis. Some have been general and non-technical in nature, some have been industry-specific, and some have been highly technical laboratory-focused studies.

In all cases, it is important for coating failure analysis to be performed in an orderly and consistent manner to produce meaningful results. If a comprehensive coating failure analysis protocol is not followed, important facts and data related to the failure may be missed or dismissed as unimportant. This compendium has been prepared to provide a roadmap to be followed by investigators in the future.

The compendium includes a comprehensive approach to protective coating failure analysis that can be universally used to perform coating failure analysis in many technical categories. This step-by-step approach, entitled “A Protocol for Performance of Coating Failure Analysis,” has been prepared by the author to capture and pass on the methodology that he has developed over the years to successfully execute coating failure analysis projects.

The compendium also contains technical papers concerning coating failure analysis prepared by authors working in various industries that include industrial protective coatings.

A Protocol for Performance of Coating Failure Analyses

Jon R. Cavallo, PE, FASTM

Objective

To provide a structured protocol for performance of coating failure analysis that can be used in many industrial applications.

Preliminary Requirement—Determine if it is a Failure or Not?

First, it must be determined whether or not a failure has actually occurred.

All paints and coatings deteriorate naturally over time. If the observed deterioration occurred predictably, and within the anticipated (and warranted, if applicable) time frame, “failure” as defined in most coating contracts did not occur.

To call a failure a failure, the performance requirements for the paint or coating system must be defined before application (life duration and maximum limits for defects).

Coating Failure Analysis Steps

Once it is determined that a coating failure has occurred, investigation must be conducted in an organized method. The investigator must be sure to perform ALL of the steps in the failure analysis protocol. Never skip a step in the protocol and assume “That could never happen!” because, in fact, it might have happened!

Step 1—Define Failure

The key to this step is to succinctly characterize the failure morphology of the coating system.

1. The failure must be correctly and accurately described
2. The description of the failure must be described clearly (use ASTM Standards, photos, etc.).

Step 2 – Interviews and Records Examination

To understand a coating failure, it is necessary to review all available records and, if possible, interview personnel who were originally involved with the selection and application of the coating system.

Interviews are particularly important in cases where written documentation of coating work may not exist.

Information that should be assembled includes:

1. Contemporaneous product data sheets for coating materials,
2. Coating work records,
3. Nonconformance reports,
4. Start and end dates of coating work,
5. Temperature, humidity, and weather data, and,
6. Information from coating manufacturers concerning coating material formulation changes made since the coating was applied.

Step 3—Specification Review

Review the job coating application specifications for the coating system involved.

Important! Review documentation contemporaneous with actual coating work! Coating application specifications change over time.

Step 4—Field Observations

Perform a close-up examination of the coating failure site(s). First, carefully analyze the failure site's environment and identify any effect on failure. Then, perform nondestructive and destructive examinations of the failed and intact coating system as appropriate.

Subsequent laboratory examinations of the failed coatings may be required, so be prepared to take samples.

Step 5—Laboratory Examinations

If you determine that laboratory tests are necessary to support the coating failure analysis effort, the following are tests that can be performed by knowledgeable coatings laboratories to contribute to the failure analysis effort.

1. Optical and Digital Microscopy
 - 30X—200X works well in most cases
 - Can be used to determine the number of coats making up a system and the relative thicknesses of each coat

- Often contaminants are visible (such as mill scale, dirt, overspray, salts)
- Small cracks, voids, inclusions, etc. can be observed

2. Gas Chromatography (GC)

- Used to examine relatively volatile materials, such as solvents
- Often used to identify improper or contaminated thinners and solvents
- The GC instrument is an oven containing a special column
- More volatile compounds pass through the column more rapidly than less volatile compounds

3. Ion Chromatography

- Primary use in paint/coating failure analysis is to identify salts that may have led to failure
- The instrument uses ion-exchange resins to identify the presence of ionic contaminants such as chloride, sulfate, and phosphate

4. Differential Scanning Calorimetry (DSC)

- Used to thermally analyze paint/coating samples
- Little or no sample preparation is required
- Instrument is basically an oven—heated sample properties are compared to sample at ambient temperature
- Provides information concerning the sample's degree of cure and/or cross-link density

5. Physical Properties Test Methods

- Adhesion
- Flexibility and Impact Resistance
- Solvent Resistance
- Weathering Resistance
- Chemical Resistance
- Freeze-Thaw
- Application Variations and Tolerances

Step 6 – Examination of the Actual Coatings Involved

This step is usually performed in two distinct parts:

1. Review available data sheets and batch tickets supplied by the coating manufacturer.
2. Review results of chemical analysis and physical testing of the failed coating with chemical analysis and physical testing of properly formulated, mixed, and applied coating (from manufacturer batch retain samples). See Step 5, above, for physical tests that can be performed.

Step 7—Literature Survey

Review available technical literature to determine whether the failure being analyzed had been

observed previously at the facility involved or at other facilities.

Step 8—The Hypothesized Failure Mechanism

If possible, identify the failure mechanism(s) involved. If not possible, postulate a failure mechanism(s) based on the results of Steps 1 through 7.

In both cases, vet your hypothesis—use an independent third-party if required.

Step 9—Reconstruction and Testing

If possible and necessary, prepare “bench batch(es)” using the formulation(s) of the actual coatings batch(es) involved in the failure and recreate the failure to validate the failure hypothesis. This step is not always possible, usually because all variables connected with the failure are not known.

COMPILATION OF TECHNICAL PAPERS RELATED TO COATING FAILURE ANALYSIS

These papers have been prepared by a number of authors and address various aspects of coating failure analysis and coating failures in various industries.

section 1

General Approaches To Coating Failure Analysis

Introduction

The papers in this section provide general information related to performing coating failure analysis.

“How Not to Perform a Failure Analysis” – Nixon and Shilling

“Coating Failures in Plants and Industrial Environments” – Ashiru and Al-Sonidah

“Coating Failure: Mechanical Flaw or Human Fault?” – Augustyński and Królikowska

“A Coating Supplier’s Perspective” – Spotten

“Coating Failures—A Coating Supplier’s Perspective—Part 1” – Spotten

“Coating Failures—A Coating Supplier’s Perspective—Part 2” – Spotten

HOW NOT TO PERFORM A FAILURE ANALYSIS

Randy Nixon
Mark Schilling
Corrosion Probe, Inc.

ABSTRACT

Too often, coating failure analysts ignore the evidence in front of them and obsess with hi-tech analytical analysis simply because it is available to them, or perhaps because that is what they themselves are in the business of doing. This tendency to rely on hi-tech test data to find a conclusion that supports a biased point of view is the wrong way to approach failure analyses, but it can impress and even dazzle. Frequently, this overuse of analytical methods complicates logical and accurate failure analysis work. This paper discusses a classic example where the facts surrounding the failure of a lining system were ignored and undue reliance was placed on laboratory analysis. This “blind faith” in analytical data without a sound causal theory caused the failure analysts to disregard or overlook the obvious.

Keywords: isocyanate, polyol, polyurethane, carbon dioxide, hydrolysis

INTRODUCTION

Over the past few years, the authors of this paper have been involved in several coating failure analysis projects in which our final assessment was at complete odds with the findings of other analysts. It is not uncommon to disagree on details. There is almost always some uncertainty. But profound differences of opinion should be uncommon when everyone is reviewing the same evidence. In one particular case, it was our conclusion that the mode of lining system failure as well as all circumstantial evidence in project documentation clearly supported one failure mechanism. Yet other analysts believed that the causes of the failure were probably several and in one aspect, something completely new that no one seemed to have heard of before. These analysts put forth their theory as to one of the primary causes of failure, freely admitting that they could find nothing in an extensive literature search to support their opinion. We simply could not comprehend how they reached their conclusions. There was too much focus on chemical analysis, seemingly without purpose other than to simply get data. In addition, the facts were obscured and seemingly driven more by what their client wanted to hear rather than what the evidence really indicated. This paper reviews that case history

and illustrates how not to conduct an independent, third party, coating failure analysis.

DISCUSSION

The Failure

In February of 2006, we were retained to investigate the cause of the delamination failure of a flexible PVC sheet lining in three anaerobic digesters and a Digested Sludge Storage Tank (DSST) at a large wastewater treatment plant. The lining system consisted of a thin, modified epoxy primer applied directly to concrete followed by a 120 mil (3mm) thick layer of a spray-applied, polyurethane mastic coating with a 30 mil (0.76 mm) thick layer of PVC sheet adhered to the urethane layer via a proprietary chemical surface activator.

The liners were installed between 1997 and 1998 as part of a secondary treatment plant upgrade project. The vessels were placed in service in early 2000. After approximately 18 months in service, the liners had failed in Tanks #1 and #2. The liners in Tank #3 and the DSST failed subsequently. The mode of failure was loss of adhesion between the PVC sheet and the urethane and also between the urethane and the epoxy primer on the concrete. Prior to our investigation, another failure analysis outfit (referred to hereafter as ACME Labs) conducted an independent failure investigation. They represented the facility owner. We were retained by the design engineer. This paper will carefully examine the two independent failure analyses.

The Facts

Here is what the evidence showed:

- (1) The lining failed primarily between the polyurethane and the epoxy primer. The PVC sheet lining also showed some delamination.
- (2) Samples of the failed polyurethane coating had a foamed appearance on the underside, the surface in contact with the epoxy primer, in all cases except where it had been applied between PVC sheets at overlapped seams in the lining. The foamy material was fairly brittle. It had little flexibility. It looked like polyurethane foam thermal insulation. It had expanded well beyond its original target thickness of approximately 120 mils. The polyurethane coating at the seams, where it had been applied between two PVC sheets, remained flexible and was not full of tiny air voids.
- (3) Whenever the polyurethane coating had been in contact with the epoxy primed concrete, it showed some degree of foaming.
- (4) The tanks were heated and ventilated during the lining application shifts, but not at night when work ceased for the day.
- (5) Surface moisture tests were taken at various times prior to primer application and the relative humidity in the tanks was checked during application of the polyurethane mastic and the PVC sheet.

(6) Review of the inspection reports from the job revealed numerous references to gassing problems, bubbling problems, and difficulty with gas under the PVC sheets during installation. Here are a few examples:

10-2-98 – “The PVC Lay-up crew is still getting air entrapment.” “The walls are gassing out and causing a lot of gas bubbles.” “Since the material was still soft, I informed them to put a pinhole puncture into the bubble, flatten out all air bubbles, etc.”

9-17-98 – “There were some of the bubbles sporadically throughout yesterday’s work. There also was some gassing of the material creating air bubbles.”

9-18-98 – Section 3 environmental conditions-points out that it rained and there was a leak into the work area. No moisture tests were performed prior to priming on this shift.

9-2-98 – This report notes that water present on some material containers and air flow not sufficient.

10-5-98 – “Water is leaking through the manway openings.” “Contractor will cover holes.” Next day

10-6-98 – “There is gassing going on under the sheets that were installed earlier. There’s nothing they can do about them.” Such report information makes it clear that there were gassing problems.

(7) Numerous photographs taken by the inspector during the installation work showed frequent and large bubbles beneath the PVC sheets.

(8) Samples of the failed lining system taken from one of the tanks showed the foamed texture of the polyurethane coating where it had been in contact with the concrete.

After visual examination of coating samples, ACME labs did seemingly all they could. They performed a wide variety of hi-tech analytical techniques including elemental analysis, scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy, thermal analysis, and Fourier transform infra-red spectroscopy (FTIR).

Inspection showed the surface preparation of the concrete was adequate in terms of degree of cleanliness and roughness. Chemical analysis of the condensate collected in the tanks confirmed that the wastewater condensate contained no contaminants that would be expected to be harmful to the liner system except the water. Chemical analysis of the polyurethane mastic material confirmed that the two components were well mixed and in the correct ratio when applied. Degradation of the polyurethane mastic material was initiated from the epoxy primed concrete and progressed outward from there. The PVC sheet cover for the lining system behaved as an effective diffusion barrier against the substances that promoted degradation of the urethane coating. Therefore, water was thought to be permeating from below, through the concrete into the urethane coating.

Laboratory analysis of the urethane coating samples suggested that the degradation of the urethane coating occurred by reversion to low molecular weight compounds. This was explained as a post-cure hydrolysis reaction caused by exposure to temperature and moisture. The increasing porosity of the polyurethane mastic material allowed for increased water absorption which increased the mechanical load (the weight) that the liner could support. The increased weight and reduced

properties of the urethane coating caused adhesive and cohesive failure of the lining from the epoxy primed concrete substrate. The deterioration mechanism was said to be accelerated by the elevated operating temperature of the tanks (55°C or 131°F) and moisture permeating into the urethane coating from the concrete roofs and walls of the tanks.

The ACME Labs report raised the possibility that “moisture present in the substrate at the time of application of the urethane may have inhibited the curing reaction, resulting in undercure, an excess of polyols, bubbling due to carbon dioxide generation, poor film integrity and low adhesion.” This reference was taken from the Handbook of Polymer Degradation by S. H. Hamid, M.B. Amin, and A.G. Maada, page 515. The report went on to rule this out because “this would have been detected during inspection and created difficulties during the subsequent installation of the PVC sheet. There are no indications that these symptoms existed during the liner application.”

ACME Labs reported that they had conducted an extensive literature search in an attempt to support their post-cure hydrolysis conclusion with references. They admitted in their report that they could not find any such references. They must have been on to something new.

The Author’s Initial Failure Analysis

The primary cause of failure was most likely a chemical reaction of the isocyanate component of the polyurethane mastic material with water during coating application. The isocyanate component of the polyurethane mastic material is reactive with water. The reaction with water allows polymerization but it produces a urea linkage in the polymer instead of a urethane linkage. More importantly, carbon dioxide gas is kicked-out as a by-product. That changes the physical properties of the material during solidification from the liquid. One milliliter of water may react with isocyanate to form more than one liter of carbon dioxide gas under typical conditions, and so a little water can cause a lot of gassing. The chemistry is well understood. We have seen this gassing problem many times and one can find ready reference to it in the coatings literature.

Moisture during application was a known threat for gassing on this particular project. The inspection records indicated that gassing was evident during and soon after installation of the polyurethane mastic. The source of the moisture was most likely condensation on the epoxy primer but there was also the possibility of moisture having been present in the polyol component of the coating. The polyol resin component of the polyurethane mastic is hygroscopic. It will readily absorb moisture from relative humidity. The inspection records documented ponded water on containers. The polyol resin component can absorb and hold a significant amount of water with no discernible impact on the properties (e.g., viscosity, consistency) of the polyol component. It simply holds the water until the two components of the polyurethane are mixed together, at which time the water molecules may find and react with the isocyanate component to form carbon dioxide gas.

We quickly came to the conclusion that water during coating application was the root problem because the review of project documents including photographs, and examination of coating samples, were all consistent with a common and well understood problem. There was no need for further study. Application of the polyurethane over condensed moisture on a surface provides for gassing at that surface, in this case the interface between the epoxy primer and the polyurethane. Some of the carbon dioxide gas may move as bubbles and escape through the polyurethane to the atmosphere

while the material is still sufficiently liquid. In some cases, pinholes will be left in the top surface. In that case the carbon dioxide gas managed to escape but the coating was no longer sufficiently liquid to be self-healing. Some gas bubbles will never make it to the surface. The coating solidifies fairly quickly and gas bubbles get locked in to produce internal voids as with Swiss cheese. Most importantly, when water of condensation is present on the substrate that is where the gassing initiates.

Weighing the Evidence

That is how the expert opinions diverged from the same evidence. The physical evidence seemed obvious to us. The reaction of isocyanates and water gives off carbon dioxide gas as a by-product. The inspection records noted gassing during and soon after coating application. Application of the polyurethane over condensed moisture on a surface provides a foaming in the polyurethane at that surface. That is expected to minimize physical contact of the polyurethane to the epoxy primer. Adhesion is compromised from the get-go. It was a built-in condition as the polyurethane material was solidifying. Once the polyurethane is cured and solid, the isocyanate is no longer present. It has been reacted to make polymer.

ACME Labs seemingly ignored the inspection records that noted gassing during liner installation. They took up an initial position that the polyurethane mastic material had been properly applied and cured and that it was initially in full contact with and had good adhesion to the epoxy primer. They argued from that position that later on, while in service, the polyurethane material was chemically degraded by a chemical reaction with water. That chemical reaction resulted in the foaming and observed porosity, originating from the substrate and extending up into the bulk thickness of the polyurethane.

That chemical reaction was referred to as a post-cure hydrolysis. It was not explained in any detail. The term “post-cure” was used as a reminder that the material was properly cured and then chemically attacked at some later time. Hydrolysis is a broad term that refers to a reaction with water. Many organic polymers contain linkages that are susceptible to hydrolysis. The most familiar example to the coating industry is saponification, an alkaline catalyzed hydrolysis of ester linkages found in oil and alkyd based paints. Acid catalyzed hydrolysis reactions are also possible. Some polymers can be attacked by water at pH 7, if the water is hot enough. In any case, the problem is chain scission. Large polymer molecules are literally chopped to little bits. ACME Labs argued that their analysis suggested that the degradation of the urethane coating occurred by *reversion* to low molecular weight compounds. They may or may not have actually found any evidence for that (to be discussed later on) but hydrolysis of the solid material would occur as fairly uniform surface attack. The low molecular weight compounds would be liquids, primarily carboxylic acids. Whether or not they had any good evidence for the expected low molecular weight compounds was debatable. But more importantly, their post-cure hydrolysis theory could not explain the observed morphology. The solid polyurethane material could not be chemically attacked in this manner and be made to foam.

Convincing the Attorneys

Whenever there are dueling narratives, competent attorneys don't want to *believe*; they want to be convinced. To affirm our opinions regarding the cause of the liner failures, laboratory mock-ups of the lining products were conducted. The purpose of the mock-ups were as follows: