

Handling Extreme Environments With Novel Multi-Functional Epoxy Terminated Resins Platform Technology

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ABSTRACT

The material selection community can find the most demanding challenges for coating systems in the corrosive environments created by processes and equipment used in upstream oil and gas extraction. Elevated temperatures, high pressures, and harsh chemicals consistently wreak havoc on coating systems used in these environments. Specifically, few services rival the aggressive exposures created by fire tube heaters in process vessels. When seeking to solve the problem of coatings failures in these conditions, understanding the unique performance characteristics of novel technologies is a critical factor in the success of a coating system. Atypical performance criteria that show a solid correlation to field performance include dry and wet glass transition temperature (dry/wet T_g), critical pigment volume concentration (CPVC), heat distortion temperature (HDT), and free volume. When backtested in a laboratory using aggressive autoclave testing, these metrics, while infrequently considered, can indicate a robust performing coating system in the developmental phase of new coating technology. The investigation of a new Multi-Functional Epoxy Terminated Resin (METR) analyzing these uncommonly tested properties led to developing a new coating prototype tailored to withstand the harsh conditions of heater treater fire tubes. The results of two successful field trials of the prototype using the novel resin platform on fire tubes further validate the correlation of a robust performing coating system and the atypical performance criteria considered in the study.

Keywords: Fire tube, oil and gas upstream, autoclave, glass transition temperature, epoxy, heater treater, coatings research

INTRODUCTION

One can find some of the most aggressive and corrosive environments for coatings in the process work and equipment functions for Oil and Gas Upstream facilities. These conditions have typically been handled using traditional coating options such as vinyl esters, epoxies, or baked phenolic linings. While these products are often tailored to environments with elevated temperatures and pressures found within upstream and “downhole” oil and gas production, the inception of new drilling techniques and the discovery of new shale basins has morphed the landscape of corrosive environments in this market. Hot crude with hydrogen sulfide concentrations, hot hydrocarbons, and increasingly elevated temperatures have put a strain on owners and operators who rely on traditional coatings technology to solve these issues. Traditional coating systems are subjected to increased strain and often fail under stress. A lack of other options suitable for these harsh environments sparked the interest of a team of researchers to understand the new conditions that operators are facing in the field, and to tailor new technology to handle these circumstances. This paper aims to summarize the research process used to understand the changing conditions in Oil and Gas Upstream facilities, show the evaluation methods of new technology, understand distinctive critical performance characteristics, and present the results of the back testing new technology in both field and lab settings.

AUTOCLAVE TESTING METHODOLOGY AND EXPERIMENTATION

Evaluating the Environment and Identifying the Challenges

The first challenge presented when evaluating the novel environments to which the coatings in the industry are subjected was to determine what testing criteria would be used to assess traditional and new technology prototypes. In looking at the existing coating systems, the lack of a baseline for testing was a clear gap in understanding what the new could confront, and the old would handle. The first task was to develop a testing protocol that best simulated the environment in question. To do this, an industry-standard autoclave test as outlined by NACE Testing Method 0175 formed a baseline in testing methodology. The research team altered the variables to develop an experiment that would challenge all coating technologies. The parameters included determining a temperature, pressure, hydrocarbon blend, gas blend, and liquid element. The duration of the test was also a factor. Leveraging various knowledgeable connections in the oil and gas industry, the research team polled several owners/operators on their current testing criteria to merge the survey results into one stringent regimen for testing. The pass-fail criteria for the post-test evaluations were also crucial in determining the effectiveness of the coatings tested. After an extensive survey, the research team fused the results into a rigorous standard of autoclave testing they referred to as the Aggressive Upstream Testing in Autoclave (AUTA) method. The original parameters of the test are summarized in the following table:

Table 1
Parameters of AUTA Test

Duration	Temperature	Pressure	Gas Composition	Hydrocarbon	Liquid Phase
7 Days	300°F (149°C)	2000 PSI	100% Nitrogen	1:1 ratio of Toluene:Kerosene	Deionized Water

The autoclave testing started by testing several coatings technologies against the AUTA conditions. Those types included but were not limited to baked phenolic linings, vinyl esters, novolac epoxies, Bisphenol A epoxies, among others. The initial findings and evaluations of the products subjected to the test were not favorable to the performance of the coating. Some coating systems, such as the vinyl esters tested, exhibited a complete failure and delamination from the substrate.

The linings with more favorable results would hold up well to the gas and hydrocarbon phase, but nearly all failed in the deionized water phase. Apart from the visual post-test evaluations of the panels, which would quickly determine the viability of the lining or coating after being subjected to the autoclave, other post-test evaluations were performed based on the feedback from the owners and operators initially polled. The additional post-test criteria were:

- Visual inspection of blistering, softening, cracking, and delamination
- ASTM D4541 – Pull Off Adhesion (Evaluated on separate panels both pre-and post-test)
- ASTM G106-89 – Electrochemical Impedance Spectroscopy

These inspection methods were performed only after a passing result of the panels was shown after the AUTA testing. Table 2 shows the generic types of products tested and their corresponding failure modes:

Table 2
AUTA Testing of Various Coating Technologies

Duration	Temperature	Pressure	Gas Mixture	Hydrocarbon	Liquid Phase	Performance Notes	Pass/Fail
<i>Novolac Epoxy</i>							
7 days	300°F	2000 PSI	100% N ₂	1:1 by volume toluene:kerosene	DI water	• 40-60 mils DFT • Blistering	Fail
<i>Bisphenol F Epoxy</i>							
7 days	300°F	2000 PSI	100% N ₂	1:1 by volume toluene:kerosene	DI water	• Water phase blistering • 40-60 mils DFT	Fail
<i>Ceramic Filled Epoxy</i>							
7 days	300°F	2000 PSI	100% N ₂	1:1 by volume toluene:kerosene	DI water	• 25-30 mils DFT (single coat) • #6 medium dense blisters in water phase	Fail
<i>Novolac Epoxy #2</i>							
7 days	300°F	2000 PSI	100% N ₂	1:1 by volume toluene:kerosene	DI Water	• Blistering in all three phases	Fail
<i>Polycyclamine Epoxy</i>							
7 days	300°F	2000 PSI	100% N ₂	1:1 by volume toluene:kerosene	DI water	• 34-44 mils DFT • Blistered all phases and delaminated in water phase	Fail
<i>Polycyclamine Epoxy #2</i>							
7 days	300°F	2000 PSI	100% N ₂	1:1 by volume toluene:kerosene	DI water	• 21-26 mils DFT • Blistered all phases	Fail
<i>Solvent-Free Epoxy – Hand Applied</i>							
7 days	300°F	2000 PSI	100% N ₂	1:1 by volume toluene:kerosene	DI Water	• Tested multiple panels. 1 panel did delaminate in the water phase between coats, but the 1st coat was intact and no sign of failure.	Pass
<i>Flake filled, Solvent-Based Novolac Epoxy</i>							
7 days	300°F	2000 PSI	100% N ₂	1:1 by volume toluene:kerosene	DI water	• 15-20 mils DFT in one coat • No post exposure testing performed, visually unaffected other than discoloration	Pass

Despite the long list of failures reported in this study, there were still some promising results reported by two of the product types that passed the initial testing. The second phase of testing involved the introduction of a hydrogen sulfide (commonly referred to as H₂S) component to more accurately mimic the environment of an upstream oil and gas process and create an even more aggressive exposure condition. In this test facilitated by a third-party testing laboratory, the two passing coating systems were subjected to the Autoclave parameters described in Table 3, which became Phase 2 to the AUTA testing methodology:

Table 3
Parameters of AUTA Phase 2 Testing

Duration	Temperature	Pressure	Gas Mixture	Hydrocarbon	Liquid Phase
7 Days	325°F (149°C)	2000 PSI	90% CH ₄ , 5% H ₂ S, & 5% CO ₂	1:1 ratio of Toluene:Kerosene	Tap Water

The results of this next phase of Autoclave testing revealed the following results:

Table 4
AUTA Phase 2 Testing of Two Coating Types

Duration	Temperature	Pressure	Gas Mixture	Hydrocarbon	Liquid Phase	Performance Notes	Pass/Fail
<i>Solvent Free Epoxy – Hand Applied</i>							
7 days	325°F	2000 PSI	90% CH ₄ , 5% H ₂ S, & 5% CO ₂	1:1 by volume toluene:kerosene	Tap Water	Partial pass- Did not blister but had adhesion loss to steel in all phases and weak parallel scribe adhesion all phases	Partial Pass
<i>Flake Filled, Solvent-Based Novolac Epoxy</i>							
7 days	300°F	2000 PSI	90% CH ₄ , 5% H ₂ S, & 5% CO ₂	1:1 by volume toluene:kerosene	Tap water	15-20 mils DFT - Pull-off testing - Adhesive failure to substrate post-exposure - Rust in water phase but no blistering or delamination.	Marginal (Poor EIS)

While the original AUTA results were promising, the coatings re-tested in a similar environment with a hydrogen sulfide component and a slightly different gas mixture proved marginally effective against the upstream environments in question.

Based on the reported results and the limited clear options that could survive in the aggressive environments identified by the owner/operator conditions survey results, it was apparent that more robust technology was needed. Not only would investigation of new technology be essential to solving the problem of the aggressive upstream environment, but an understanding of the critical elements of the coating's physical properties would be vital in determining the efficacy of the coatings and linings moving forward.

MULTI-FUNCTIONAL EPOXY TERMINATED RESIN (METR) EXPERIMENTATION

Understanding the Performance of New Technology

Finding a suitable resin base to adapt to these highly corrosive environments occurred almost by happenstance for the research team. A product with a resin base used outside common protective coating industries was being evaluated for alternate use in other markets from a separate research project. After noticing several promising applications and performance characteristics, further exploration of the new resin type, a Multi-Functional Epoxy Terminated Resin (METR), began to reveal many unique capabilities that had the potential to solve the challenges presented to the team.