

OLD, NEW AND FORGOTTEN WISDOM FOR TANK AND VESSEL LININGS

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ABSTRACT

In the last decade, against a backdrop of stringent environmental legislation, enhanced tank lining performance requirements, economic constraints, and so-called “value-engineering”, several new technologies for tank and vessel linings have been introduced into the market place.

In the context of old, new and forgotten wisdom, this paper probes critical issues that intrinsically have a significant impact on either the success, or failure, of tank and vessel lining applications.

An accelerated laboratory testing program was carried out to investigate the performance of nine epoxy linings used, or intended for use, in oil and gas production systems. Candidate epoxy coatings were either proven commercial performers, experimental in nature, or those based on new generation formulations. Thin film multi-coat systems and single coat, solvent free (plural component and single leg airless spray applied) coatings were tested in sweet and sour crude oil.

The efficacy of a proprietary cleaner intended to decontaminate abrasive blasted steel was also investigated.

INTRODUCTION

An Old Wisdom to New Wisdom Transition

Several decades ago the tank and vessel linings used in oil and gas extraction processes were often based upon low volume solids materials that typically had an upper temperature resistance of about 160°F - 180°F. The chemistries of these coatings were relatively simple, based on Bis A or epoxy phenolic epoxies co-reacted with amine and amine adduct curing agents. As a result, the life expectancy of these coatings in harsh chemical and thermal immersion environments was relatively short. For pitted tank floor applications, fiberglass or fibreglass chop strand was typically used in these coatings. Nowadays, however, more sophisticated coatings based on novolac epoxy chemistry are used and reinforcement is often achieved in high build solvent free epoxies using special pigments instead of fiberglass. These new coatings comply with API652 and enable facility owners to extend the intervals between lining inspections.

Historically, the pre-selection of coatings for use in the Western Canadian oil patch was largely based upon autoclave studies at elevated temperatures and pressures in sour conditions (5% H₂S and 5% CO₂) using a 24 hour test period (1). However, over time, it has been recognized that a test duration of 96 hours was more indicative of coating performance. Moreover, a combination approach of using autoclave studies in tandem with Electrochemical Impedance Spectroscopy (EIS) investigations has come into vogue. This has proven to be a far more useful predictor of real-world coating performance in the oil patch where EIS measurements are a useful measure of the barrier properties of the coating (2).

Curiously, some of the long lasting and field proven novolac epoxy coatings that perform well in the autoclave-EIS tests do not perform well in the Atlas Cell Test, another test used by some to indicate coating performance in immersion. The explanation lies in the unrealistically high temperature gradients used in the Atlas Cell testing regimen and chilling with water versus chilling with air (3). These findings are very much part of the new wisdom emerging from research work done in the oil patch.

At a more rudimentary level, it is well known that proper surface preparation is axiomatic to the success of a lining. Both the surface profile and cleanliness of the steel are clearly of paramount importance. Many years ago it was not uncommon for specification authorities to specify angular profiles of 1.5 to 2 mils for high build lining systems. However, recent work has shown that a deeper profile and with a high surface area is required for these linings (4, 5). The present authors contend that in the case of high build, single coat and solvent free coatings the profile depth be greater than 2.5 to 3 mils (preferably 3-4 mils) and jagged as opposed to a peen pattern (6).

As the arrow of time progresses, even if the received wisdom is old it does not mean that it will necessarily be superseded. For instance, with good reason it has been customary in the oil patch for the past twenty years to line tanks and vessels with multiple coats of solvent borne novolac epoxy coatings. Nevertheless, in the past ten years or so, some owners have elected to use a single coat of a high build epoxy coating expecting similar success to that afforded by the use of multi-coat systems.

In this regard the chemistry of linings requires careful consideration. Optimally selected solvents are required to dissolve the solid - and high molecular weight and high functionality - novolac epoxy resins. When the latter are co-reacted with high functionality curing agents, highly cross-linked and chemically resistant thin film epoxies are produced. These systems are usually multi-coat and invariably outperform many one coat high build epoxy systems that are based on their lower functionality and lower molecular weight liquid epoxy resins. Until recently the multi-coat systems have been much more user friendly for an applicator. Now, with the advent of thermally resistant high build, single coat epoxy linings that can be applied by single leg spray equipment (rather than plural spray equipment) facility owners have another option. A full discussion of the multi-coat vs. single coat topic has been given elsewhere (7-9).

Spanning three decades, a common practice in the oil patch has been to use thin film multi-coat novolac epoxies as the primary linings of choice for oil and gas production fluids. Highly cross-linked, with hard and tough films, these thin film linings - and single coat high build solvent free types - must handle ever increasing temperatures, pressures, higher H₂S and CO₂ concentrations, and immersion in many performance enhancement chemicals. The upshot has been a significant challenge for the coatings industry in terms of judicious lining selection.

The chemical resistance, thermal resistance, and resistance of linings subjected to rapid emergency depressurization are very much dependent upon the chemical structure and pigmentation of the epoxy lining. Recent studies have shown the importance of the epoxy chemical structure and not just the curing agent being of primary significance (10). In the oil patch, conditions have become more difficult for linings as the use of CO₂ for Enhanced Oil Recovery (EOR) has increased and facilities operate at higher temperatures and pressures and in more sour conditions. Certain novolac epoxies perform well in terms of “breathability” in elevated pressure environments compared to other novolac epoxies with similar curing agent chemistry. This observation highlighted the myth of generic equivalency amongst coatings with similar generic descriptions.

A new paradigm was offered recently to enhance the correlation between accelerated laboratory testing and real-life coating performance (11). In essence, the idea put forward was to pre-establish with a facility owner what constitutes a coating failure in their facility in a real-world service environment and then develop appropriate test protocols and determine the point of failure of the coating system. It cannot be overemphasized that laboratory tests are merely indicators of real-world coating performance and should not be over interpreted when a significant amount of case history information is available.

Given the importance of a successful coating application it is recommended that the specification authority audit the third party independent inspectors, preferred contractor, the crew assigned to undertake the lining work, and the application equipment.

Forgotten Wisdom

In part because of stringent VOC regulations and the lure of the economic benefits of one coat tank and vessel linings, some owners feel driven to specify single coat high build epoxy coatings that have a quicker return to service capability. The coating selected may indeed perform admirably in relevant accelerated tests and be appropriate for many tank and vessel lining applications.

However, caveat emptor – buyer beware. First, the single coat high build coatings may not be particularly applicator friendly or conducive to application in poorly designed vessels with complex geometries and difficult access. Also, it may not be realized that in a one coat application the high build epoxy coating may have insufficient chemical resistance and may not adequately wet the steel substrate for the intended service given the aforementioned chemistry of the coating.

Second, an alarming practice is where authorities working on behalf of facility owners sanction the use of an abrasive swept pre-construction primer, or holding primer, instead of correctly specifying its total removal prior to application of the lining by abrasive blasting to SSPC SP5/NACE 1 white metal standard. In this case the specter of an expensive premature coating failure looms large for an unsuspecting owner. In a nutshell, the life of the coating has been compromised. Worse, it has probably been sacrificed on the altar of cost cutting, ignorance of coatings chemistry, and not properly recognizing the implications of the harsh chemical and thermal environments of SAGD operations. Simply put, any holding primer allowed to cure for an extended period of time must be completely removed before a lining is applied for high temperature oil patch immersion service.

Another practice that sometimes gets forgotten is not to thin solvent free epoxies and instead use heat for viscosity control. If a small amount of thinner is permitted by a coatings manufacturer then any solvent reduction must not exceed the manufacturer's recommendations. Thinning solvent free epoxies depresses the glass transition temperature (T_g), can entrap solvent and lower the chemical resistance of the lining.

In the final analysis, armed with the knowledge that coating failures often cause inordinate down-time problems, huge costs to facility owners, and possible litigation, it is crucial to be mindful of old and new wisdom in the coatings industry and employ best practices in coating selection, inspection and application.

Sweet Crude, Sour Crude and Shale Oil

In the present study both sweet crude and sour crude oil samples were obtained from an upstream producer in the Alberta Oil Patch. Both crude oils were derived from the SAGD process and used as the hydrocarbon phase in the autoclave test program.

Crude oils are generally classified as sweet or sour when they respectively contain less than, or greater than 0.5% sulfur. The sweet crude used was an oil emulsion with a water content of approximately 60%. Its resistivity was 0.66 ohms at 77°F (25°C) and it had a TAN (total acid number) value of 0.94. In contrast, the sour crude sample used contained virtually no water and had a lower TAN value of 0.12. The higher the TAN value of a crude oil the higher its corrosive nature. The acidity is often associated with naphthenic acid, a by-product of oil sands production processes.

Both crude oil samples had an API (American Petroleum Institute) Gravity of approximately 21°. According to some classifications a crude oil is considered a light crude (floats on water) when its API Gravity is 31.1° and a heavy crude (sinks in water) when it is below 22.3°. For example, bitumen from Athabasca tar sands operations has an API Gravity of ca 7.7° to 9° (12).

In future work, the authors will expand the coating investigations to include a hydrocarbon phase of shale oil in the autoclave tests. In the US, shale oil is becoming better known as tight oil (13). Shale oil is very

paraffinic, has high level of aromatics, an array of heavy metals, and high sulfur content. Some raw oil shale has been shown to have sulfur contents of 3-4%. Shale oil will be interesting to study in light of the present investigations. Apart from the aforementioned constituents, unlike crude oils, shale oil contains unsaturated hydrocarbons that are formed during the pyrolysis of the kerogen of oil shale (14).

EPOXY COATINGS SELECTED FOR TEST PROGRAM

The accelerated laboratory performance of nine proprietary epoxy coatings was investigated on the basis that the coatings selected would offer a range of coating composition types with the potential to give good performance in the aggressive conditions of 300°F (149°C) in 10% H₂S, 10% CO₂/balance CH₄, and at 250 psig. Aside from two experimental coatings all candidate coatings either had an extensive track record in tanks, vessels and pipe internal applications in oil and gas service. The field proven coatings had at least previously demonstrated good high temperature immersion performance to 200°F (93°C) in 5% H₂S, 5% CO₂ and at 250 to 1000 psig, and the higher performers in some instances up to 350°F (176°C) in 5% H₂S, 5% CO₂, and at 200 psig (15,16).

Coatings A and B were the same thin film, 2 coat polycyclamine cured novolac epoxies applied to SSPC SP5/NACE 1 white metal blasted surfaces except that Coating B was so designated to reflect that it had been applied over the blasted steel where a proprietary cleaner had then been applied and removed. Coatings C and D were experimental coatings based upon novolac epoxy technology and a relatively new curing agent technology.

The thin film polycyclamine cured novolac epoxies Coatings C1 (and C2) and D1 (and D2) have been successfully applied to more than 40 million square feet of tanks, vessels and pipe spools during the past twenty five years in the Western Canadian oil and gas industry. The multi-coat Coating C1 is a solvent borne, multi-functional novolac epoxy used for immersion service where temperatures can reach 350°F (177°C). Given its three-dimensional network, carefully selected PVC (pigment volume concentration) and higher permeability, Coating C1 is also known to possess good resistance to high pressures and rapid emergency depressurization.

With a significant track record in the oil patch, Coating D1 is a solvent borne, compact, three-dimensional structure novolac epoxy with exceptional water, oil, and chemical resistance. Historically, Coating D1 is used for immersion temperatures in sour produced oil and gas up to 250°F (121°C) and at pressures up to 1000 psig.

It should be noted that Coating C2 and Coating D2 were the same as Coating C1 and Coating D1, respectively, except that the former series received an additional post cure treatment of 170°F (77°C) for three hours after an initial curing period of 7 days at ambient temperatures.

Coating E was another novolac epoxy that had not been extensively proven in the oil patch.

Invariably, Coatings A through E are usually applied by airless spray equipment. They all cure as low as 50°F (10°C).

Applied by plural spray equipment, Coatings F and G are single coat solvent free polycyclamine cured novolac epoxies with a good track record in the oil patch. Both are high build coatings and possess a somewhat lower cross-link density than either Coating C1 or Coating D1.

Coating H and Coating I are a new generation of novel polycyclamine curing agents co-reacted with novolac hybrid epoxies. While they have been formulated to some degree upon a chemistry platform of Coating G they have been largely engineered using proprietary technology (a) to be applied by single leg spray equipment, and (b) to have longer pot lives than most rapid curing, solvent free high build epoxies while still offering quick return to service. Coatings F, G, H and I all cure as low as 40°F (5°C).

TEST METHODS FOR COATING EVALUATION

Preparation of Coated Steel Panels

Carbon steel panels measuring 15.0 x 3.8 x 0.32 cm (6 x 1.5 by 0.125 inches) were abrasive blasted to SSPC SP5/NACE 1 white metal standard to obtain a sharp angular profile in the range of 2.5-4 mils. Each coating was spray applied in either shop or laboratory conditions according to the coating manufacturer's instructions.

Autoclave

The primary screening test most commonly employed by facility owners in the oil patch for tank and vessel linings is NACE TM0185 (Evaluation of Internal Plastic Coatings for Corrosion Control of Tubular Goods by Autoclave Testing). Three test runs were conducted for 96 hours in an autoclave made from Hastelloy. The test environment consisted of three phases: a gas phase mixture of 10% H₂S, 10% CO₂ and 80% CH₄, a hydrocarbon phase of either sweet crude or sour crude, and an aqueous phase of a 5% NaCl solution. The tests were conducted at 300°F (149°C) and at a total pressure of 250 psig. The test temperature had an accuracy of ±3°C.

In the present work, a more aggressive gaseous mixture was employed by the authors compared to the more typical 5% H₂S, 5% CO₂/balance CH₄ mixture. Furthermore, other conditions being equal, in lieu of the more typical hydrocarbon test phase of a 1:1 toluene/kerosene mixture, it was decided to conduct testing in both an owner's sweet crude and sour crude oil emulsions.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) was used as a diagnostic tool used to assess loss of barrier properties of Coatings A through I after they were removed from the autoclave. Essentially, the low frequency impedance (AC electrical resistance) is related to the permeability of the coating to water, organic molecules, and small gaseous molecules such as H₂S and CO₂. When a coating exhibits high impedance it indicates that it has a low permeability and no appreciable penetration of corrosives, in accord with good barrier properties and superior protection of the substrate from a corrosive environment. Conversely, a coating with low impedance implies it has a high permeability, poor barrier properties and susceptibility to under-film corrosion (16). A basic “rule of thumb” is that the barrier performance of the coating is excellent, good or marginal when log Z impedance values are of the order of 10, 8 and 6, respectively.

Visual Inspection and Adhesion

After the coating panels were removed from the autoclave they were evaluated visually for any blistering, cracking or other defects (ASTM D714). The film thickness was measured and adhesion assessed for each coating. The pre-and post-test adhesion of each coating was rated according to the key below:

Adhesion Rating Key

10	0 mm removed (cohesive failure)
9	Over 0 - 0.5 mm removed
8	Over 0 - 1.0 mm removed
7	Over 1.0 - 2.0 mm removed
6	Over 2.0 - 3.0 mm removed
5	Over 3.0 - 5.0 mm removed
4	Over 5.0 - 7.0 mm removed
3	Over 7.0 - 10.0 mm removed
2	Over 10.0 - 13.0 mm removed
1	Over 13.0 - 16.0 mm removed
0	Over 16.0 mm removed

COATINGS IN THE TEST PROGRAM

Table 1: Autoclave – EIS Test 1

Test temperature 149°C/300°F, Pressure 250 psig, 10%H₂S, 10%CO₂, 80% CH₄, *Sweet Crude*, 5% NaCl in distilled water, 96hrs

Coating	Coating Description	Number of coats	DFT range mils
A	Thin film polycyclamine cured Novolac epoxy	2	17 - 20
B	Thin film polycyclamine cured Novolac epoxy	2	10 - 14
C	Thin film polycyclamine cured Novolac epoxy	2	16 - 21
D	Thin film polycyclamine cured Novolac epoxy	2	19 - 21
E	Thin film polycyclamine cured Novolac epoxy	2	11 - 16
F	Solvent free, high build polycyclamine cured Novolac epoxy	1	21 - 29
G	Solvent free, high build polycyclamine cured Novolac epoxy	1	17 - 22
H	Solvent free, high build polycyclamine cured Novolac Hybrid epoxy	1	23 - 30

Table 2: Autoclave – EIS Test 2

Test temperature 149°C/300°F, Pressure 250 psig, 10%H₂S, 10%CO₂, 80% CH₄, *Sour Crude*, 5% NaCl in distilled water, 96hrs

Coating	Coating Description	Number of coats	DFT range mils
A	Thin film polycyclamine cured Novolac epoxy	2	15 - 16
B	Thin film polycyclamine cured Novolac epoxy	2	12 - 15
C	Thin film polycyclamine cured Novolac epoxy	2	14 - 36
D	Thin film polycyclamine cured Novolac epoxy	2	17 - 22
E	Thin film polycyclamine cured Novolac epoxy	2	7 - 12
F	Solvent free, high build polycyclamine cured Novolac epoxy	1	17 - 21
G	Solvent free, high build polycyclamine cured Novolac epoxy	1	21 - 25
H	Solvent free, high build polycyclamine cured Novolac Hybrid epoxy	1	19 - 25

Table 3: Autoclave – EIS Test 3:

Test temperature 149°C/300°F, Pressure 250 psig, 10% H_2S , 10% CO_2 , 80% CH_4 , *Sour Crude*, 5% NaCl in distilled water, 96hrs

C1, C2, D1, D2 and I were included after Tests 1 and 2

Coating	Coating Description	Number of coats	DFT range mils
A	Thin film polycyclamine cured Novolac epoxy	2	15 - 17
C	Thin film polycyclamine cured Novolac epoxy	2	15 - 23
C1	Thin film polycyclamine cured Novolac epoxy (Ambient Cured)	2	15 - 22
C2	Thin film polycyclamine cured Novolac epoxy (Ambient Cure/140°F Post-Cure)	2	12 - 18
D	Thin film polycyclamine cured Novolac epoxy	2	15 - 20
D1	Thin film polycyclamine cured Novolac epoxy (Ambient Cured)	2	13 - 21
D2	Thin film polycyclamine cured Novolac epoxy (Ambient Cured/140°F Post-Cured)	2	13 - 21
G	Solvent free, high build polycyclamine cured Novolac epoxy	1	19 - 23
H	Solvent free, high build polycyclamine cured Novolac Hybrid epoxy	1	23 - 28
I	Solvent free, high build polycyclamine cured Novolac Hybrid epoxy	1	14 - 24

TEST RESULTS

Test Program 1:

149°C/300°F, 250 psig, 10% H_2S , 10% CO_2 , 80% CH_4 , Sweet Crude, 5% NaCl, 96hrs

The results of the autoclave testing at 300°F (149°C) in sweet crude are summarized in Table 4 and Figures 1 and 2. The thin film novolac epoxies Coating A and Coating B exhibited good resistance to the test environment, with no blistering taking place. While both coatings were the same formulation, adhesion tests revealed that Coating B had better adhesion ratings in all three phases than did Coating A. Thus Coating B clearly benefited from the white metal substrate being treated with a proprietary cleaner (ostensibly designed to remove a variety of contaminants but possibly modifying the steel surface). Log Z impedance values for both coatings were similar, with fair to good values measured in regions exposed to the water phase, and excellent values recorded from the gas and hydrocarbon phases. These results indicated that good corrosion protection was maintained in both Coating A and Coating B.

Coating C was an experimental solvent borne novolac epoxy that did not perform well in test. While it did not blister, and did possess high post-test impedance values, its poor post-test adhesion might indicate that Coating C did not sufficiently wet-out the abrasive blasted steel. In comparison, the other

experimental coating, Coating D, clearly could not handle the severity of the test conditions and delaminated in all three phases.

Another thin film novolac epoxy, Coating E, blistered in the water phase with evidence of medium #4 blisters (ASTM D714). The dry film thickness of Coating E was lower than that of the other candidate coatings. Nevertheless, despite blistering in the water phase Coating E had excellent impedance values in the gas and hydrocarbon phases.

The thick film solvent free novolac epoxies Coatings G and F both blistered in the water phase. In contrast, the performance of the solvent free novolac epoxy Coating H was particularly good. Like the thin film Coating B, the thick film Coating H did not blister in the test conditions and showed good corrosion protection with high log Z impedance values.

Table 4: Post-Autoclave Analysis from Test Program 1

Panel	DFT mils (av)	Adhesion Rating				Blistering (ASTM D714)			Impedance Log Z @ 0.1 Hz			
		Pre-test	Water	HC	Gas	Water	HC	Gas	Pre-test	Water	HC	Gas
Conditions: Test temperature 149°C/300°F, pressure 250 psig Gas phase: 10% H ₂ S, 10% CO ₂ , 80% CH ₄ for 96 hrs. Hydrocarbon (HC) phase: <i>Sweet Crude</i> Water phase: 5% NaCl in distilled water												
A	18.6	10	4	4	4	None	None	None	10.76	7.21	10.32	10.80
B	12.2	10	5	8	10	None	None	None	10.59	7.25	10.19	10.82
C	16.8	10	0	0	0	None	None	None	10.77	10.50	10.23	8.36
D	19.8	6	Dd	Dd	Dd	Dd	Dd	Dd	ND	ND	ND	ND
E	13.6	10	5	7	8	M#4 ^B	None	None	10.80	ND	10.89	10.85
F	24.0	6	2	6	6	F#0, M#2 ^A	None	None	9.77	ND	11.18	11.96
G	20.3	9	2	2	4	M#0 ^A	F#0 ^A	None	11.49	ND	ND	10.84
H	25.5	7	5	6	7	None	None	None	10.31	7.27	10.65	10.67

Special note: DFTs were measured for each coating and each phase. Reported DFT average of control panels
HC = hydrocarbon; W = water Dd = disbonded ND = Not Done

^A Blisters are liquid filled and extend to substrate ^B Blisters are gas filled and extend to substrate

Figure 1: EIS of Coatings from Test Program 1

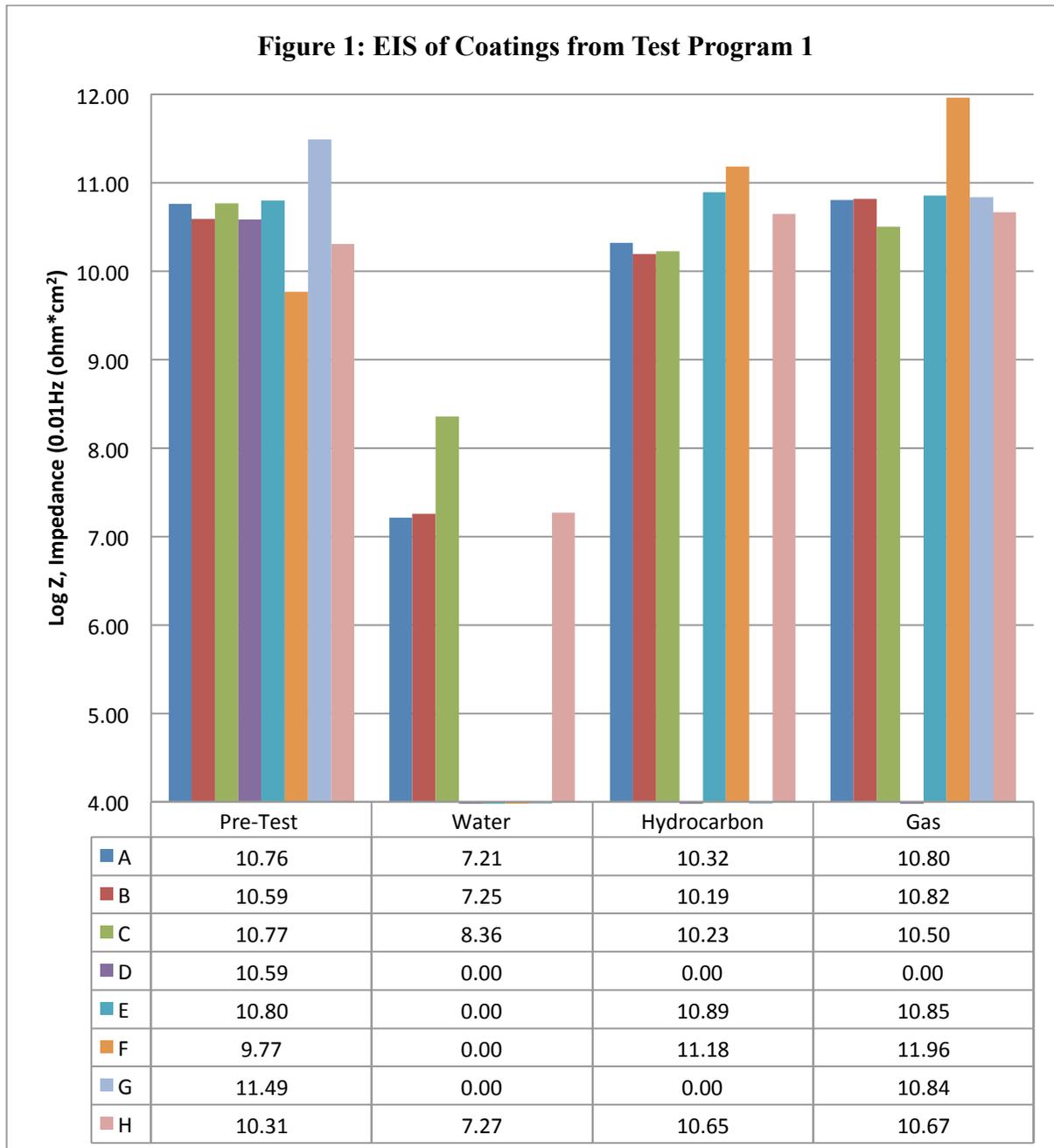


Figure 2: Post –Test Program 1 Autoclave Panels after Exposure to 300°F, 250 psig

(Sweet Crude Hydrocarbon Phase)

**Top Left to Right: A, B, C and D
Bottom Left to Right: E, F, G and H**



Test Program 2:

149°C/300°F, 250 psig, 10% H₂S, 10% CO₂, 80% CH₄, Sour Crude, 5% NaCl, 96hrs

The only difference between Test 1 and Test 2 was that the sweet crude was replaced by sour crude for the hydrocarbon phase in Test 2. The results are shown in Table 5 and Figures 3 and 4. With significant blistering evidenced in both the hydrocarbon and water phases, the performance of Coating A in sour crude was much poorer than that in sweet crude where the coating did not blister. Coating B, however, showed a similar performance in Test 2 to Test 1, with no blisters occurring, good adhesion, and good resistance to the harsh test conditions. Interestingly, the initial Log Z impedance of 10.59 for Coating B fell almost two orders of magnitude in sour crude compared to that in sweet crude. The marked decrease in impedance indicates coating deterioration in the exposure to test conditions. Notwithstanding, as in Test 1, the enhanced performance of Coating B compared to Coating A appears to be related to the influence of the proprietary cleaner treatment of the abrasive blasted surface. Aside from the absence of blistering at 300°F (149°C), the log Z impedance values > 8 showed that good corrosion protection was maintained in Coating B.

The experimental coatings C and D performed poorly under the conditions tried. Coating C blistered in the sour crude phase whereas it did not do so in the sweet crude phase. Coating D again delaminated.

Counterintuitively, Coating E did not blister in sour crude unlike its performance in sweet crude. Also, the impedance values of Coating E were as high as some of the solvent free, thick film coatings, notably for Coating F and Coating G. Although the latter coatings did not blister the post-test adhesion ratings of Coating F in all three phases was good, yet the adhesion of Coating G in the hydrocarbon and water phases was poor.

With no blistering taking place, good adhesion and log Z impedance values > 9 the corrosion protection afforded by the novolac hybrid epoxy H, was very good.

Table 5: Post-Autoclave Analysis from Test Program 2

Panel	DFT mils (av)	Adhesion Rating				Blistering (ASTM D714)			Impedance Log Z @ 0.1 Hz			
		Pre-test	Water	HC	Gas	Water	HC	Gas	Pre-test	Water	HC	Gas
Conditions: Test temperature 149°C/300°F, pressure 250 psig Gas phase: 10% H ₂ S, 10% CO ₂ , 80% CH ₄ for 96 hrs. Hydrocarbon (HC) phase: <i>Sour Crude</i> Water phase: 5% NaCl in distilled water												
A	15.5	10	4	4	5	F#2 ^B	F#2 ^A	None	10.76	ND	ND	10.56
B	13.8	10	5	5	6	None	None	None	10.59	8.39	8.39	8.59
C	16.4	10	0	0	4	F#0	F#0	None	10.77	ND	ND	11.67
D	19.4	Dd	Dd	Dd	Dd	Dd	Dd	Dd	ND	ND	ND	ND
E	10.2	10	6	5	6	None	None	None	10.80	11.12	10.43	10.98
F	19.5	10	5	5	6	None	None	None	9.77	10.15	10.32	11.40
G	22.2	10	0	0	10	None	None	None	11.49	10.87	10.93	10.93
H	21.4	7	5	5	7	None	None	None	10.31	9.92	10.14	9.38

Special note: DFTs were measured for each coating and each phase. Reported DFT average of control panels

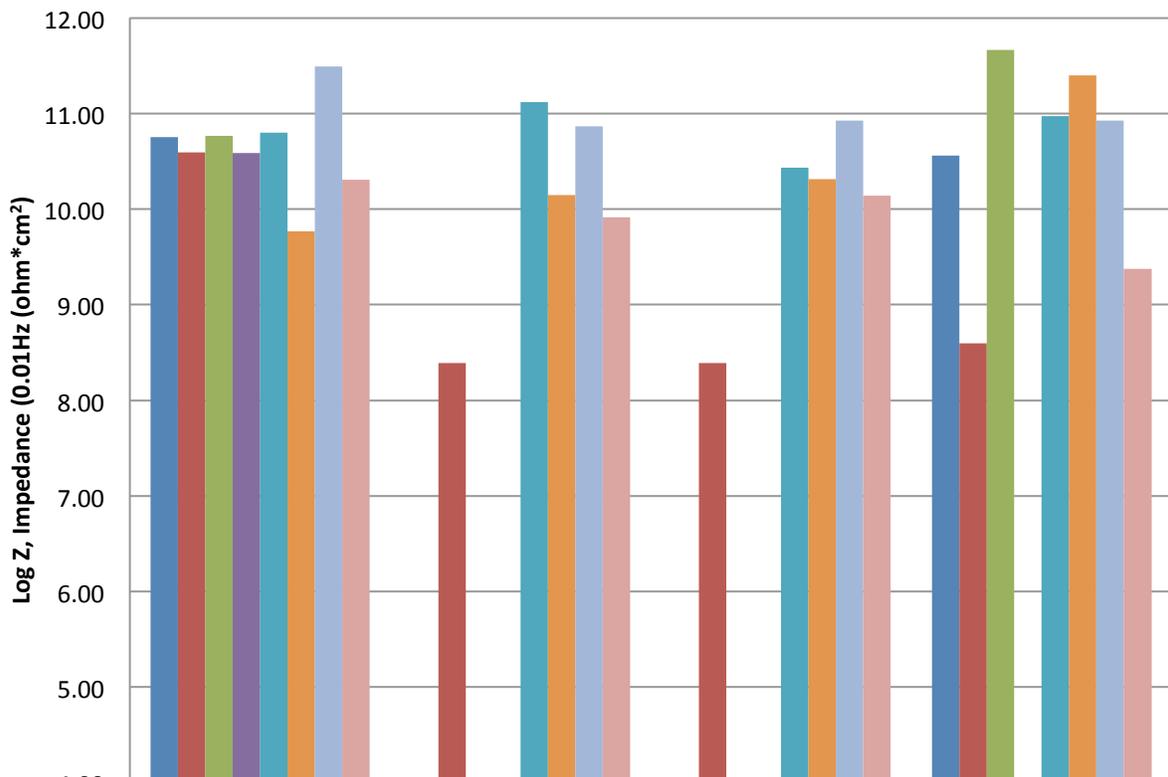
HC = hydrocarbon Dd = disbanded ND = Not Done

W = water

^A Blisters are liquid filled and extend to substrate

^B Blisters are gas filled and extend to substrate

Figure 3: EIS of Coatings from Test Program 2



	Pre-Test	Water	Hydrocarbon	Gas
A	10.76	0.00	0.00	10.56
B	10.59	8.39	8.39	8.59
C	10.77	0.00	0.00	11.67
D	10.59	0.00	0.00	0.00
E	10.80	11.12	10.43	10.98
F	9.77	10.15	10.32	11.40
G	11.49	10.87	10.93	10.93
H	10.31	9.92	10.14	9.38

Figure 4: Post –Test Program 2 Autoclave Panels after Exposure to 300°F, 250 psig

(Sour Crude Hydrocarbon Phase)

**Top Left to Right: A, B, C and D
Bottom Left to Right: E, F, G and H**



Test Program 3:

149°C/300°F, 250 psig, 10% H₂S, 10% CO₂, 80% CH₄, Sour Crude, 5% NaCl, 96hrs

Upon completion of Test 1 and Test 2, two thin films, solvent borne, novolac epoxy coatings with decades of proven track records in the oil patch were introduced into the test program, via Coatings C1 and D1. Both coatings were cured under ambient conditions for 7 days (77°F or 25°C). Separate panels of C1 and D1 were ambient cured in excess of 7 days and subsequently post-cured at 170°F (77°C) for three hours. These panels were respectively designated C2 and D2. Coating I was also introduced into the test protocol at this juncture, a thick film, solvent free novolac hybrid epoxy with novel curing agent technology. Testing in sour crude was chosen for the third and final test program. Re-runs of coatings A, C, D, G and were also of interest to the authors and these coatings were investigated again in a duplicate test of Test 2.

The results of the autoclave testing at 300°F (149°C) in sour crude are shown in Table 6 and Figures 5 and 6.

Coating A blistered as before in sour crude (Test 2). The impedance log Z of 5.68 in the gas phase was very low (cf log Z of 10.56 in Test 2) and the reason for the markedly diminished value is unclear. Further autoclave tests will be carried out in the future.

Another anomalous finding was the performance of the experimental Coating C. In the same conditions of Test 2, Coating C blistered whereas it did not blister in Test 3. As seen in Table 6 the adhesion values of Coating C were also poor. The Log Z impedance values of Coating C in the sour test conditions of Test 3 were comparable with those in sweet crude (Test 1). The finding that the experimental Coating D delaminated was consistent with the two previous tests.

As anticipated, the field proven Coatings, C1/C2 and D1/D2, performed well in the autoclave-EIS Test 3 regimen. These coatings gave the best test results of the thin film coatings. Both C1 and C2 did not blister in any phase, showed good adhesion, and had good log Z impedance values. An exception was a low impedance value of log Z 4.8 in the gas phase for C1. The latter result is considered anomalous since the impedance of C2 in the gas phase was in-line with all the other values (ca log Z of 10).

The post-cure bake for C1 to produce the C2 coating increased the adhesion for the latter in the hydrocarbon and water phases but the impedance diminished somewhat in the gas phase. Coating D1 did not blister and had good adhesion to the steel substrate. Slightly better impedance results were also obtained for Coating D1 compared to Coating C1. However, the post-cured Coating D2 cracked. This result was not surprising given that Coating D1 and D2 are not normally known to withstand oilfield process fluid temperatures in excess of 275°F (135°C) and are routinely specified for temperatures up to 250°F (121°C). Overall, these findings reflect the historically excellent oil patch performance of Coating C1 and Coating D1.

The good performance of the hybrid novolac epoxy Coating H in Test 1 and Test 2 was repeated in Test 3. Once again Coating H somewhat outperformed the traditional novolac epoxy Coating G. Neither coating blistered. Curiously, the adhesion of Coating H in Test 3 was markedly superior to its performance in Test 2. Both coatings had excellent log Z values close to 10 in all phases indicating excellent corrosion protection against oil patch process fluids.

The newly introduced coating candidate in Test 3, Coating I, outperformed all the thin film and thick film coatings. Coating I did not blister and its post-test values in all three phases was ranked best-in-test. Moreover, the pre-test and post-test adhesion ratings of Coating I were identical. It was evident that the log Z impedance values in each phase were slightly lower in the case of Coatings H, and I, compared to Coating G. However, the adhesion ratings of H and I were the best seen in any of the three autoclave tests.

Table 6: Post-Autoclave Analysis from Test Program 3

Panel	DFT mils (av)	Adhesion Rating				Blistering (ASTM D714)			Impedance Log Z @ 0.1 Hz			
		Pre-test	Water	HC	Gas	Water	HC	Gas	Pre-test	Water	HC	Gas
Conditions: Test temperature 149°C/300°F, pressure 250 psig Gas phase: 10% H ₂ S, 10% CO ₂ , 80% CH ₄ for 96 hrs. Hydrocarbon (HC) phase: <i>Sour Crude</i> Water phase: 5% NaCl in distilled water												
A	16.0	10	6	5	4	F#2	None	None	10.76	7.86	8.64	5.68
C	16.1	10	0	0	4	None	None	None	10.77	10.63	9.91	9.31
C1	17.4	10	6	5	10	None	None	None	11.13	10.62	10.67	4.80
C2	15.2	10	7	7	7	None	None	None	11.13	11.17	10.04	10.00
D	17.5	Dd	Dd	Dd	Dd	Dd	Dd	Dd	10.59	ND	ND	ND
D1	15.7	10	6	7	6	None	None	None	11.12	11.26	10.51	10.66
D2	17.0	10	6	7	6	None	None	None	11.12	10.99	11.12	10.01
G	21.5	10	2	2	10	None	None	None	11.49	10.33	10.25	10.75
H	25.1	10	10	8	10	None	None	None	10.31	9.92	10.14	9.38
I	18.2	10	10	10	10	None	None	None	10.60	10.53	9.78	9.82

Special note: DFTs were measured for each coating and each phase. Reported DFT average of control panels
HC = hydrocarbon W = water

Figure 5: EIS of Coatings from Test Program 3

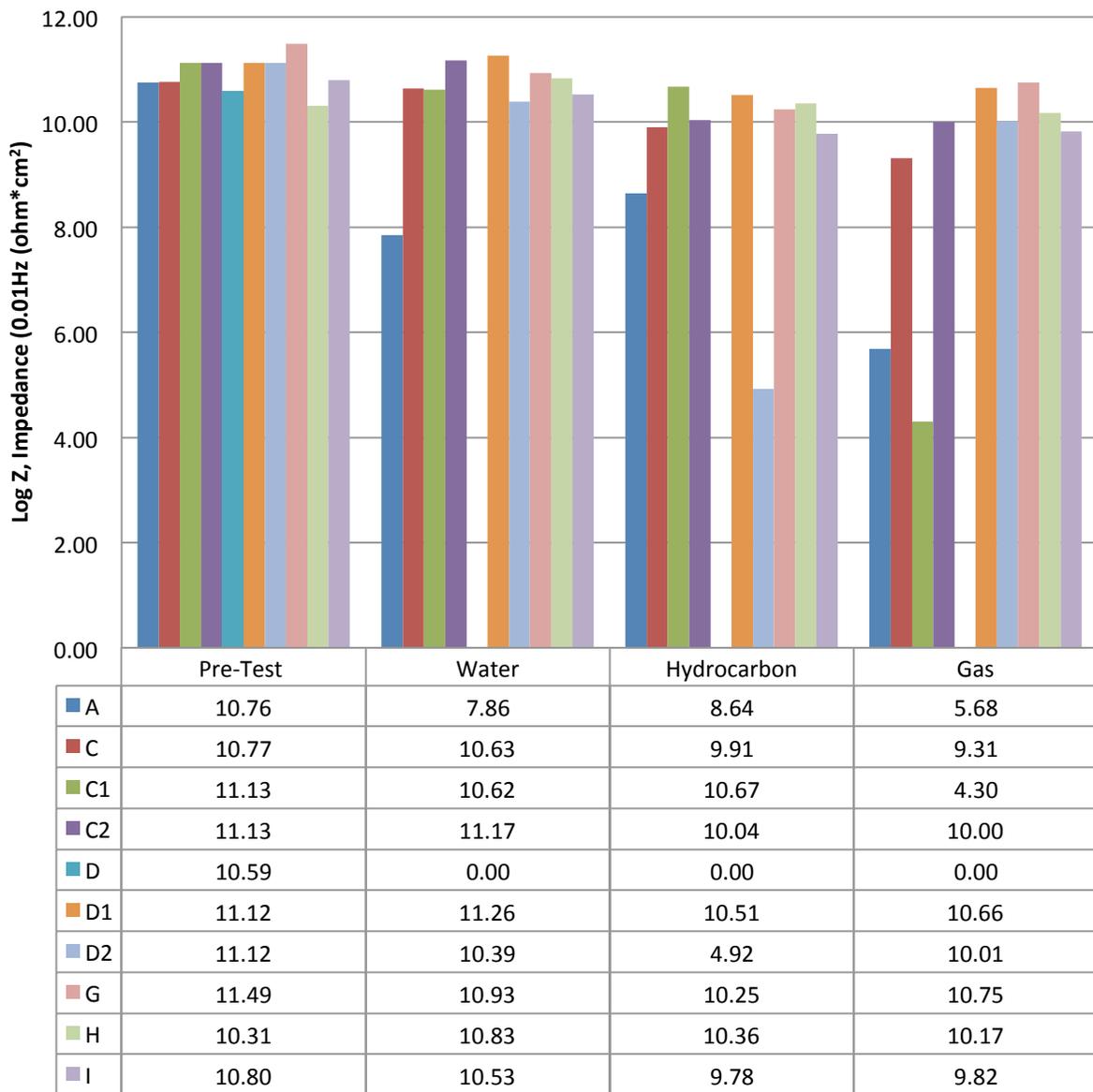
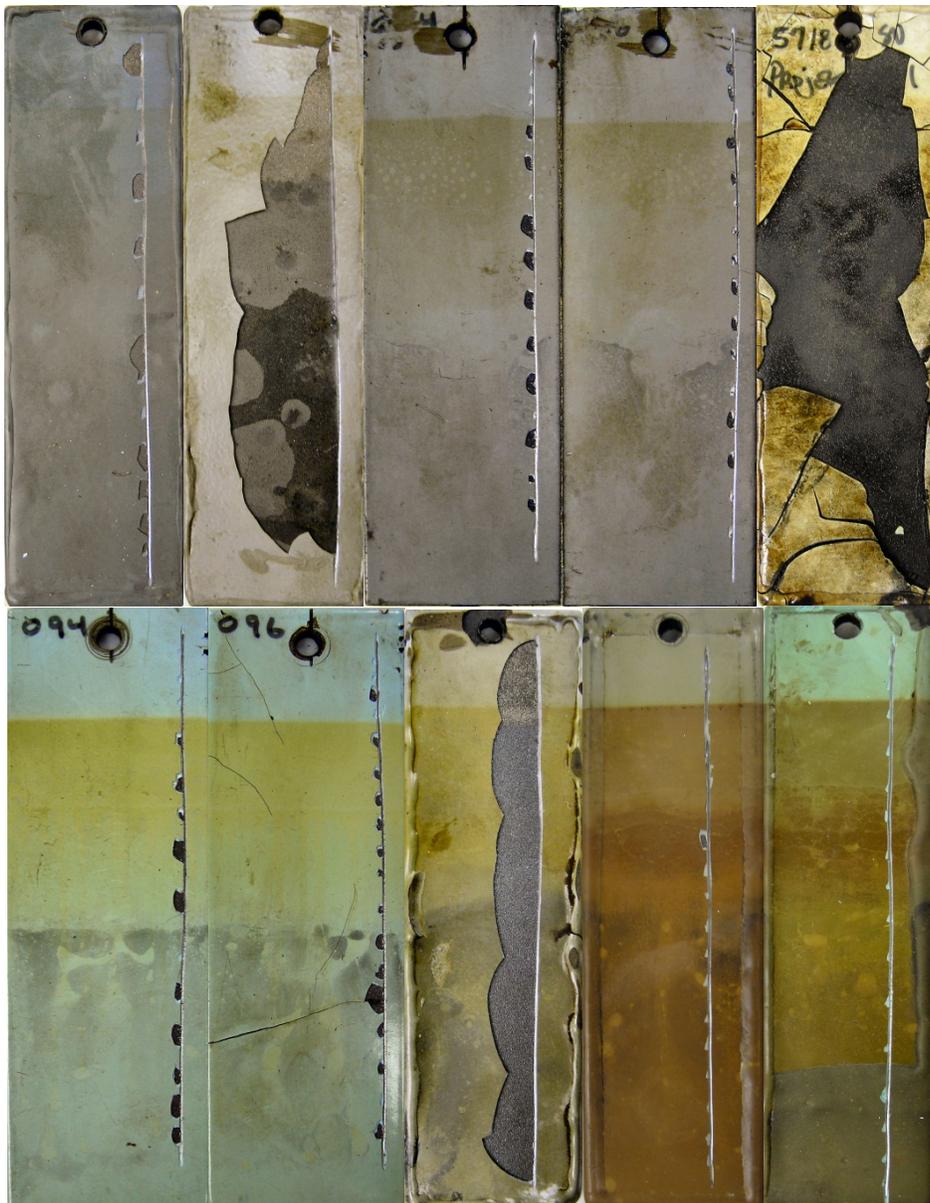


Figure 6: Post –Test Program 3 Autoclave Panels after Exposure to 300°F, 250 psig

(Sour Crude Hydrocarbon Phase)

Top Left to Right: A, C, C1, C2, and D
Bottom Left to Right: D1, D2, G, H, and I



DISCUSSION

A coating was deemed to have failed in the autoclave test if it blistered, cracked or flaked in any of the three phases. Adhesion ratings of the coating film were considered of lower importance than the presence, or absence, of film blistering. Coatings may provide sufficient adhesion and sub-film corrosion resistance even when water has been imbibed and reached the coating-polymer interface (17). All the coatings were ranked on the basis of blistering and adhesion ratings. They were also ranked upon their log Z impedance values, and level of post-test impedance reduction.

One of the primary goals in this study was to determine what thin film multi-coat epoxy coatings and thick film solvent free epoxy coatings could perform well in autoclave tests under very aggressive conditions described earlier. One of the secondary goals was to determine if an apparently unique cleaner might show merit as an adjunct treatment to abrasive blasting.

For the sake of clarity the key points are as follows.

Coatings A and B (2ct systems):

These coatings were based on polyclamine cured novolac epoxies with high functionality. They performed well in the autoclave test at 300°F (149°C) when the hydrocarbon phase was sweet crude, but did not survive when the hydrocarbon phase was sour crude. At first glance this indicates sour crude is more aggressive than sweet crude for the novolac epoxy of Coating A. In contrast, however, the same coating as Coating A, designated Coating B, actually performed well in the sour crude test environments.

This result is attributed to either (a) the carbon steel substrate having contaminants removed with a proprietary cleaner after abrasive blasting and prior to application of Coating B, or (b) the cleaner modifying the steel surface in some way and enhancing the adhesion of the coating, or a combination of both.

Hence a secondary goal in this study was accomplished whereby a specialty cleaner touted to improve the performance of immersion grade linings did appear to do so, albeit for reasons yet to be established. Interestingly, it has been the experience of the authors that certain cleaners may indeed remove hydrophilic contaminants but unfortunately leave residual films, or moieties, which prove deleterious to coating performance in immersion service. Given the encouraging results of this cleaner treatment further work will be undertaken by the authors to investigate the polymer-substrate interfacial region of other well proven (thin and high build) coatings after substrate treatment. Impedance data were good for Coatings A and B in the three tests.

Coatings C and D:

These experimental novolac epoxy coatings were formulated with a relatively new curing agent technology. Essentially, their performance was poorer compared to thin film and thick film coatings used in the oil patch. While Coating C did not blister in the autoclave test using sweet crude, and did possess high post-test impedance values, its poor post-test adhesion results suggested that it did not sufficiently wet-out the abrasive blasted steel. The performance of Coating C was inconsistent in sour crude, blistering in Test 3 but not in Test 2. This may be due to poor flow-out and heterogeneities in the film as indicated by the poor visual appearance of the coating.

Another experimental coating, Coating D, gave the worst accelerated test performance of all coatings investigated. It failed consistently, cracking and flaking in each autoclave test, and in all three phases of each test. From a formulation viewpoint, the coating was expected to perform reasonably well given that the novolac resin used possessed high functionality. However, the sobering result serves to underscore the importance of the total coating formulation as a whole.

Coatings C1 (ambient cured) and C2 (ambient and post cured):

Coating C1 was a 2 coat, field proven epoxy with a breathable, and high temperature and pressure resistant three dimensional molecular structure. The excellent performance of Coating C1 can be largely attributed to its carefully balanced pigment-to-resin ratio, the use of a high functionality novolac epoxy resin, and a modified polycycloaliphatic polyamine curing agent (10). Earlier high temperature studies conducted by the authors (350°F; 191°C; 5% H₂S and 5% CO₂) used a hydrocarbon phase of 1:1 kerosene: toluene mixture and C1 and C2 performed well. In the present study with the hydrocarbon phase switched to sour crude, C1 and C2 also performed well, albeit at a somewhat lower temperature and in higher molar concentrations of 10% H₂S and 10% CO₂.

As expected, the post-cure bake for Coating C1 (to produce the designated Coating C2) slightly increased the in-test performance of Coating C2, with the impedance and adhesion results slightly superior to those of Coating C1. The increased network density afforded by post curing Coating C2 was reflected in its increased adhesion and barrier performance.

Coatings D1 (ambient cured) and D2 (ambient and post cured):

Coating D1 had one of the highest pre-test impedances of any coating in the replicate Test 1 and Test 2 autoclave tests using sour crude as the hydrocarbon phase. Its post-test impedance in the water phase was virtually unaffected and the post-test log Z impedance values in all phases were >10.5. Surprisingly, Coating D1 performed better than expected given that its upper threshold value is normally 250°F (121°C). Notwithstanding, as anticipated the post cured version of Coating D1, namely Coating D2, cracked and flaked unlike its more flexible, and breathable Coating C2 analog.

Coating E:

This thin film coating has a highly cross-linked structure and is based on a modified aromatic amine curing agent. Medium sized blisters in the water phase were seen in the Test 1 (sweet crude) results but the coating retained excellent barrier impedance values in the gas and hydrocarbon phases. Coating E did not blister in Test 2 using sour crude.

Coatings F and G:

As shown in Tables 4 and 5 and Figures 1 and 2 the single coat, solvent free Coating F and Coating G were blister free in the sour crude test environments of Tests 2 and 3. Both coatings have a lower functionality and lower cross-link density compared to the thin film coatings series. Intriguingly, Coating F and Coating G blistered in the water phases of Test 1 using sweet crude, a media that again appears more aggressive than sour crude depending upon the chemistry of a given novolac epoxy. The post-test adhesion of the coatings was poor, especially for Coating G.

With respect to barrier performance from EIS studies the log Z impedance data remained high for both Coating G and Coating F. The latter is well known to give good performance in autoclave studies up to 250°F (121°C) in 5% H₂S and 5% CO₂. In the present work Coating F also did well in sour crude at 300°F (149°C) and with higher concentrations of H₂S (10%) and CO₂ (10%).

Coatings H and I:

The solvent free, and single coat Coating H and Coating I, were the top performers in the autoclave-EIS test program. This was as expected based on two factors. First, the novel curing agents in their formulations indicated that these coatings should not be susceptible to degradation in the autoclave tests. Second, their proprietary chemistry and the approach taken to enhance adhesion at the polymer-steel interface indicated they should perform well. Both coatings are based upon the use of 100% novolac resin content but with a somewhat lower functionality compared to the thin film novolac epoxy coatings tested in the present work. While they may not be so tightly cross-linked, neither coating blistered under any conditions tried.

The adhesion ratings of Coating H and Coating I were best-in-test as exemplified by the results in Table 6. Curiously, the adhesion of Coating H in Test 3 was markedly superior to its performance in Test 2 for reasons that remain unclear. Both coatings had excellent log Z impedance values. Of key interest to applicators, these coatings can be readily applied with single leg spray equipment. This makes their use as single coat systems in vessels with complex geometries particularly appealing.

Ranking of Coatings in Test Programs 1 to 3

For the sake of clarity, the results for the coatings in the autoclave-EIS tests have been classified according to whether the coatings are thin film or thick film. The performance has been sub divided in terms of (a) their blister resistance and adhesion ratings and (b) their log Z impedance results. The rankings are summarized in Tables 7 to 9 where NBL and BL refer to “no blistering” and “blistering”, respectively.

**Table 7
Ranking of Coatings
Test Program 1 (Sweet Crude)**

Thin Film^A	B	>	A	>	C	>	E	>	D
	NBL		NBL		NBL		NBL		DELAMINATED
Thin Film^B	C	>	B	>	A	>	E	>	D
Thick Film^A	H	>	F	=	G				
	NBL		NBL		NBL				
Thick Film^B	H	>	F	>	G				
Overall	B	=	H	>	C	>	E		

A = Results based on Blistering and Adhesion B = Results based on EIS

Table 8
Ranking of Coatings
Test Program 2 (Sour Crude)

Thin Film^A	B > C > E > A > D NBL NBL NBL BL DELAMINATED
Thin Film^B	E > B > C > A > D
Thick Film^A	F > H = G NBL NBL NBL
Thick Film^B	H > F > G
Overall	E = F > H > G

A = Results based on Blistering and Adhesion *B* = Results based on EIS

Table 9
Ranking 3 Coatings
Test Program 2 (Sour Crude)

Thin Film^A	C1 > C2 > D1 > A NBL NBL NBL BL
Thin Film^B	D1 > D2 > C2 > C > A
Thick Film^A	I > H > G NBL NBL NBL
Thick Film^B	G > I = H
Overall	I > H > D1 = C2 = C1

A = Results based on Blistering and Adhesion B = Results based on EIS

The ranking of novolac epoxy performance differed in the three autoclave tests. Some test results were also consistent while others were not. In addition, the type of crude oil used in the hydrocarbon phase of the autoclave made a difference in coating performance. For some novolac epoxies sweet crude oil was a more aggressive hydrocarbon media than sour crude oil, whereas the converse was true for other novolac epoxies. This serves to illustrate that it is the chemistry of a given coating that dictates the coatings' susceptibility to degradation in a specific type of crude oil. Further work will be undertaken to examine this phenomena in more detail. In addition, the authors intend to elucidate the influence of thin and thick film curing times on the performance of the novolac epoxies used in the present work in sweet, sour and shale oil.

CONCLUSIONS

Various thin film multi-coat epoxy novolac coatings, and thick film single coat solvent free epoxy novolac coatings, either showed good performance or failed in the aggressive autoclave test conditions (300°F (149°C) and 10% H₂S and 10% CO₂, and in a sour crude hydrocarbon phase). This illustrates that even within the generic description of epoxy novolacs the coatings have widely varying performance profiles.

Two single leg spray applied thick film 100% solids hybrid novolac epoxies, Coating H and Coating I, gave excellent results when exposed to the autoclave test conditions. The coating technology for these coatings has been successfully designed to provide enhanced adhesion at the polymer-substrate interface. The latter will be explored further in future studies.

By a slight margin the coating that performed the best after exposure to autoclave test conditions a sour crude hydrocarbon phase was Coating I a single coat high build polycyclamine cured hybrid novolac epoxy.

Overall ranking of the coatings, based on blistering, adhesion, and impedance evaluation, was as follows: Coating I > H > D1 = C2 = C1. Coatings C1 and C2 are thin film polycyclamine cured epoxy novolacs with decades of proven success in the Alberta oil patch.

Overall ranking of the coatings in sweet crude, based on blistering, adhesion, and impedance evaluations, was as follows: Coating B = H > C > E

Applied to an SSPC 5/NACE 1 white metal blasted surface (jagged profile of ca 3 to 4 mils) a proprietary cleaner and surface decontamination process markedly improved the test performance of a thin film epoxy novolac system. The cleaner may be removing contaminants or modifying the steel surface in some way that enhances the adhesion of coatings. This will also be explored in future studies with thick film and other thin film linings.

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