TNEMEC

SUBJECT

A Novel Approach for Evaluating Protective Coatings Performance in Wastewater Environments

GENERAL

THE WASTEWATER MARKET PRODUCT INITIATIVE

In 1999, Tnemec Company embarked on a new wastewater product initiative to develop superior coatings for the barrier protection of concrete and metallic substrates exposed to elevated hydrogen sulfide gas conditions in wastewater collection and treatment structures. The impetus for this R&D program was the awareness that products used successfully in the past were no longer performing as well under severe wastewater conditions. In particular, coal tar epoxy (CTE) and standard thin-film epoxy products, the longtime workhorse products of the wastewater industry, were prematurely failing. This awareness drove Tnemec to carefully assess the associated coating failure mechanisms and the process changes responsible for more severe exposure conditions. This assessment effort, including investigation of coating failures and consultation with experts in wastewater corrosion, yielded the following:

A. Most premature coating failures were associated with blistering combined with substrate chemical attack or corrosion.

B. Exposure conditions in the headspaces of wastewater structures have become more severe. Specifically, hydrogen sulfide gas (H_2S) concentrations have increased in the aerated vapor phase of sewer pipes, tanks, manhole chambers, and other wastewater structures. This increase, in turn, has resulted in greater sulfuric acid (H_2SO_4) generation by sulfur oxidizing bacteria that colonize in the headspaces. The result is higher acid gas concentrations (CO_2, H_2S) and ultimately, increased concentrations of sulfuric acid developing up wards of 7%. A pH of 0.5 has also been measured on surfaces exposed to severe H_2S environments >50 ppm.

   As the concentration of these chemicals increased, the performance of the old workhorse coating tech nologies (i.e., CTE's, thin-film polyamide, polyamidoamine and amine epoxies) became unacceptable; their life expectancy reduced from several years to only a few months.

   As a response, coating manufacturers and specifiers began recommending Novolac epoxies for these aggressive wastewater areas. Despite their excellent chemical resistance, these epoxy technologies also exhibited signs of premature failure by extreme cracking. The anticipated service life of these products was also reduced from several years to a few months.

Although sulfuric acid concentrations increased, it was not of sufficient concentrations to cause the blis tering and cracking failures observed in several of the traditional polyamide-, amine-, and Novolac-cured, thin-film epoxy formulations. The blistering mode of failure attracted Tnemec's interest in the higher H_2S gas concentrations known to be present. It is common knowledge that gas and liquid molecules travel through coating films on a microscopic level. It became Tnemec's belief that the coatings were no longer resistant to the permeation of the increased levels of H_2S gas.

C. The causes of the more aggressive wastewater headspace environments are many and include the following:

- **Pretreatment Regulations**

The Clean Water Act of 1980 required that all industrial contributions to municipal wastewater systems implement pre-treatment for pH control and heavy metals removal prior to discharging their wastewater to municipal treatment systems. However, the removal of heavy metals such as mercury, lead, chromium, etc., caused H_2S production to rise because previously the heavy metals were toxic to the Sulfate Reducing Bacteria (SRB) responsible for dissolved H_2S gen eration. With the toxins gone, the SRB's became much healthier increasing H_2S production.

- **Regionalizing of Wastewater Treatment**

Since the late 1980's, the trend in wastewater treatment has been to build larger, regional wastewater treatment plants rather than constructing smaller, more local plants. Economy of scale reduces the cost of plant construction. How ever, the advent of larger, regional facilities has necessitated the need for transporting wastewater over longer distances. Because hydrogen sulfide is produced within the anaerobic slime layers that form on sewer pipes and related surfaces, the more surface area in the collection system, the greater the hydrogen sulfide production. These longer transport distances for wastewater increase wastewater septicity and the dissolved H_2S concentrations. When the wastewater becomes turbulent, the dissolved H_2S is stripped out of solution as gaseous H_2S. This process is further increased when the topography prevents gravity flow over the longer transport distances. Under such conditions, the wastewater must be pumped. Pumping of wastewater through force mains means the pipes run full. As such, the slime layer responsible for anaerobic sulfide production forms on the entire circumference of the piping. This further increases the dissolved H_2S concentration in the wastewater, which later becomes gaseous, leading to the more severe conditions for the coatings described above. Furthermore, the pump stations required for the force mains generally increase the H_2S production as they create turbulent wastewater flow and their wet wells often increase wastewater detention time.

- **Odor Control Containment**

Because the public finds wastewater related odors offensive and because these odors have become stronger due to higher sulfide production, wastewater headworks, clarifiers, grit removal tanks, and other structures are now typically covered. The corrosive gases that once escaped into the atmosphere are now contained in the headspaces. The gases are trapped by these covered structures and are then drawn away by fans to be filtered or scrubbed to control the odors. By not allowing H_2S gas to escape into the atmosphere, odor control containment has greatly increased the severity of exposure in these covered headspaces. The result is higher H_2S gas and H_2SO_4 liquid concentrations to which coating systems and concrete substrates are now exposed.

Most importantly, Tnemec Company recognized that new coating formulations having greater permeation resistance needed to be developed.

PRODUCTS DEVELOPED

Based on these lessons learned, Tnemec Company determined that a group of complimentary coating products with very low permeability properties is necessary to address the newer, more severe wastewater exposure conditions. Formulation of these products focused on developing superior H_2SO_4 resistance, H_2S gas and liquid permeation resistance, and good working characteristics. Hundreds of candidate formulations were screened over a two-year period. Once the best candidate formulas were established, Tnemec Company and its consultants set out to develop a testing method specifically designed to replicate and accelerate wastewater headspace conditions. A product initiative was established to develop the following products:

1. A trowel-applied, 1/8" thick, moisture-tolerant, modified-amine epoxy mortar lining for concrete substrates for retrofit and new construction. This product has become Series 434 Perma-Shield H_2S.

2. A spray applied, 50-125 mils, moisture-tolerant, fiber-reinforced modified-amine epoxy coating used as a liner for high-build applications for retrofit and new construction concrete substrates. This product has become Series 436 Perma-Shield FR.

3. A spray applied, 30-40 mils, moisture-tolerant, modified-amine epoxy coating used as a glaze coat for the Series 434 mortar, or as a stand-alone coating for metallic substrates, or as a liner used at 40-80 mils for new or retrofit concrete con struction. This epoxy product became Series 435 Perma-Glaze.

4. A spray applied, 5-9 mils per coat, two-coat moisture-cured polyurethane coating system used for concrete, miscellaneous metals and piping where thicker barrier protection is not needed, but rapid-return-to service is desired. This product be came Series 446 Perma-Shield MCU

Tnemec also investigated competitive high-build epoxy and polyurethane liners that failed in severe wastewater conditions despite being marketed for such exposures. Tnemec found that failures of these types of systems were attributed to the formation of pinholes or blowholes due predominately from improperly addressing the corroded concrete substrate prior to application of the system. Many other coating manufacturers promote their high-build resinous systems direct to concrete and neglect to restore the degraded surface. Moreover, independent laboratory testing confirms that mortar or filler extended systems used to restore or resurface the substrate have dramatic improvements over the neat resin high-build liners when exposed to accelerated sulfide corrosion conditions.

Tnemec's investigation also found that some manufacturers recommend Portland-based cementitious resurfacers to repair the concrete prior to the application of high-build liners. However, it is Tnemec's experience that these resurfacer types are rarely applied correctly. Specifically, these materials generally have a minimum thickness requirement, usually ½", which must be obtained in order for the cement matrix to form properly. Additionally, Portland-based resurfacers must be wet- or membrane-cured for a minimum 7 days in accordance with ACI 308 to maintain sufficient moisture within the mortar. Another drawback with Portland-based resurfacers is that they form a weak laitance layer at the surface because of troweling and migration of bleed water. This weak layer must be removed per SSPC-SP13/NACE 6 to ensure long-term success with a high-build liner.

Recognizing that these requirements are rarely followed by contractors in the field, Tnemec set out to develop an epoxy modified cementitious material with product attributes commensurate with common contractor placement and curing practices.

5. A spray-applied, trowel-finished, waterborne epoxy cementitious filler/surfacer for concrete substrates to be used for resurfacing prior to application of the Tnemec Perma-Shield products. The benefit of the epoxy modification allows the resurfacer to be applied down to 1/16" in thickness and eliminates the laitance layer formation as well as the need for wet- or membrane-curing. This product became Series 218 MortarClad.

DEVELOPMENT OF A WASTEWATER H_2S ENVIRONMENTAL CHAMBER

The main objective for the testing program developed by Tnemec for the wastewater market was to establish a quantifiable method to evaluate the performance of coating systems with regard to permeation resistance to H_2S, H_2SO_4, and other associated wastewater gases and liquids. Once established, the evaluation method would be used to conduct comparative performance evaluation of Tnemec coating formulations against competitive products and to drive future improvements in Tnemec product technology. The testing program is founded on a testing chamber (see Figure 1) permitting the simulation and acceleration of the conditions characteristic of severe wastewater collection and treatment systems. These parameters needed to include:

- Controllable concentrations of hydrogen sulfide gas.

- Intermittent immersion exposure to H_2SO_4, H_2S (aq), and sodium chloride at varying concentrations and time in im mersion cycles. (The sodium chloride exposure is needed to replicate wastewater in coastal areas where seawater infil tration occurs in the collection system).

- Elevated Temperature: There is a general rule in organic chemistry that for every 18°F (10°C) increases in tempera ture, the reaction rate doubles. The average temperature of wastewater is between 50°-70°F (geographically depen dent). The chamber temperature of 150°F (65°C) was established to induce a reaction rate 4-5 times actual wastewater to simulate an accelerated condition.

- Immersion Cycle: Test panels immersed in $H_2SO_4/H_2S/NaCl$ aqueous solution for 15 minutes, 3 times per working day, Monday through Friday.

- Total Test Time: 28 days of exposure with 60 immersion cycles

Figure 1

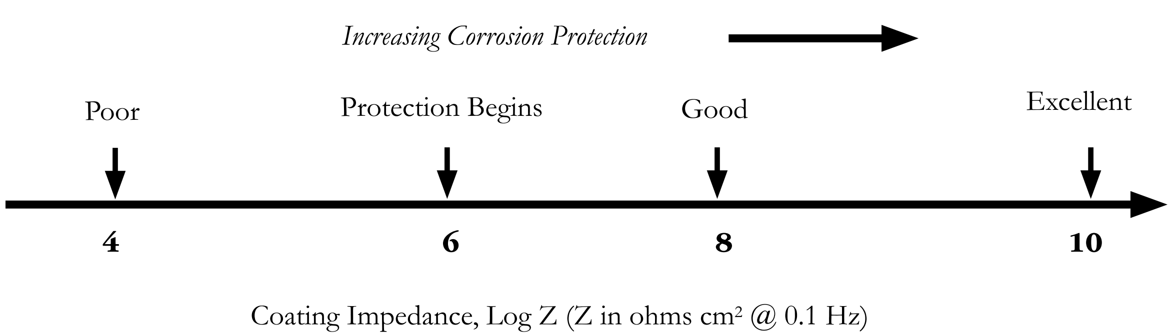
ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Polymeric coatings act as a barrier separating the substrate from the corrosive service environment. A key attribute in the performance of the protective coating is, therefore, a low permeability to salt, water, gases, and other corrosive species in the service environment. EIS is a technique well suited for evaluating coating permeability or barrier properties based on electrical resistance of the coating (referred to as impedance). The impedance of the coating is related to the nature of the polymer, its density, film thickness and its fillers. EIS has been widely used in the laboratory and field for determining coating performance and obtaining quantitative information on coating deterioration.

The impedance of a coating is observed to decrease as a function of time of exposure to a corrosive environment. The decrease in impedance is observed to be related to the loss of barrier properties and deterioration of the coating under the specific environment. The quantitative data referred to as a Log Z value at 0.1 Hz (specific current) is tabulated and used as the basis of comparison between coatings, monitoring the change as a function of exposure time to the environment.

Anticipated performance of a coating based on the Log Z is shown below. The summary presented in Figure 2 is derived from a large body of literature of laboratory and fieldwork.

Figure 2
Corrosion Protection of Organic Coatings



The measurement of the performance of the coating in the simulated wastewater environment was based on the barrier properties of permeability, blistering, adhesion, and visual inspection. Electrochemical Impedance Spectroscopy (EIS) was used to evaluate the permeability resistance of the coatings as related to barrier properties.

EIS readings were taken before the coating was exposed to the test; intermediate readings were also monitored at 10 and 20 days and at the completion of the test duration. The four readings were crucial to determine if the polymer was attacked or breached during the test. Any polymer degradation would be easily detected by a decrease in the measured impedance.

Remember that the higher and more stable the impedance over time, the better the long-term permeability resistance and, therefore better long term coating performance. A high initial impedance followed by a fast decrease in impedance with exposure time means fast degradation of the coating's barrier properties.

SEVERE WASTEWATER SIMULATION TESTING OBJECTIVES

The testing was focused on five objectives:

1. To optimize the conditions of the chamber to best replicate real world exposure in an accelerated fashion.

2. To understand why some Tnemec formulations fail to perform in wastewater headspaces.

3. To compare performance of the Tnemec Perma-Shield systems to the leading competitive products.

4. To assess the performance of coating systems over concrete substrates, the most prevalent surface to be coated in wastewater environments. EIS cannot be performed on concrete. However, tensile adhesion and microscopic visual observation (cross-section after the test) can be evaluated.

5. Special modifications were also made to the chamber to evaluate the physical properties of free films.

Optimization of S.W.A.T. Chamber Conditions

The role of the chamber was to simulate and accelerate a test method to evaluate coating performance in wastewater headspace conditions. Chemical selection was based on some of the corrosive species found in all wastewater streams: H_2S, NaCl and H_2SO_4. Tnemec also decided that temperature and H_2S would be the two parameters that would vary during the optimization. The test would also be kept at the same length of time, 28 days, and the same products would be analyzed.

Initial Wastewater Autoclave Testing Parameters

	Test #1	Test #2	Test #3
H_2S	150 ppm	10,000 ppm	500 ppm
Temperature	95˚F (35˚C)	150˚F (65˚C)	150˚F (65˚C)
H_2SO_4	10%	10%	10%
NaCl	4000 ppm	4000 ppm	4000 ppm

PRODUCTS TESTED

Some of the products evaluated in three initial tests included Series 434, Series 435, Plasite 5371, Sauereisen 210T, Series 46H, Series 66, Series 104, and Series 406. Table 1 summarizes the results.

Table 1
Comparative Impedance Values for Coatings

Test #1 (160* ppm H_2S)								
EIS Impedance	434	434/435	5371	210T	66	406	104	46H
Baseline	10.7	11.3	11.3	11.4	10.2	11.2	9.5	10.8
10 days	9.5	10.3	10.2	11.2	9.3	11.2	9.5	9.6
20 days	9.1	9.6	9.6	11.1	5.2	11.2	9.5	9.1
28 days	9.1	9.5	9.5	10.9	4.9	11.2	9.4	8.6

Test #2 (10,000 ppm H_2S)								
EIS Impedance	434	434/435	5371	210T	66	406	104	46H
Baseline	10.7	11.3	11.3	11.4	10.2	11.2	9.5	10.8
10 days	9.3	9.7	9.3	9.1	5.3	11.1	6.7	6.0
20 days	9.1	9.8	8.8	7.7	3.4	11.1	4.9	4.4
28 days	9.6	9.9	8.1	7.3	Fail	11.2	Fail	Fail

Test #3 (536* ppm H_2S)								
EIS Impedance	434	434/435	5371	210T	66	406	104	46H
Baseline	10.7	11.3	11.3	11.4	10.2	11.2	9.5	10.8
10 days	8.5	8.8	9.3	7.8	5.2	11.3	5.6	7.5
20 days	9.0	9.8	9.1	7.7	4.9	11.3	4.9	Fail
28 days	9.1	9.8	8.0	7.2	Fail	11.3	4.3	--

* The actual H_2S concentrations were measured and reflected for Test #1-3.

From these results, Tnemec concluded that 150 ppm of H_2S was not high enough to differentiate and cause failure of standard coatings used in severe wastewater headspace environments in an accelerated manner. H_2S gas concentrations of 10,000 ppm and 500 ppm gave very similar results and demonstrated much more information regarding the mode of failure of the coatings tested for a 28-day period. Based upon these consistencies, Tnemec determined that 500 ppm H_2S is of adequate volume to test the permeation performance of organic coatings and have established it as the standard level.

Tnemec can also conclude from the results that the chamber can correlate with actual field failures in a wastewater environment. The failure of the older Tnemec coating formulations used in severe wastewater environments correlated closely with real life experience. Series 66, 104 and 46H failed early in the test by severe blistering and showed very low impedance values. As a matter of information, the coatings did not fail due to sulfuric acid related attack associated with insufficient chemical resistance. Also, impedance dropped rapidly within 10 days of exposure. The resulting impedance was below the protection level shown in Figure 2. This blistering failure has also been observed for these products in field applications after 12-16 months of exposure where H_2S gas concentrations were measured between 50 and 100 ppm in headspaces. This confirms the poor permeation resistance of these products. Several other products were also tested at the established 500 ppm H_2S quantity.

MANUFACTURER	PRODUCT	GENERIC COATING TYPE	DRY FILM THICKNESS (MILS)	TESTED
Tnemec	Series 46H	Coal Tar Epoxy Polyamide	33	To simulate premature failures encountered in the field.
Tnemec	Series 61	Cycloaliphatic Amine Epoxy thin-film	15	To simulate premature failures encountered in the field.
Tnemec	Series N69	Polyamidoamine Epoxy	13	To simulate premature failures encountered in the field.
Tnemec	Series 104	Cycloaliphatic Amine Epoxy thin-film	20	To simulate premature failures encountered in the field.
Tnemec	Series 120	Vinyl ester	33	To evaluate impedance (perm resistance) relative to Tnemec Perma-Shield products.
Tnemec	Series 164	Modified Polyamine Epoxy thin-film	22	To simulate premature failures encountered in the field.
Tnemec	Series 262	High-build Tar-extended Polyurethane	41	To compare performance to other products tested.
Tnemec	Series 282	Novolac Epoxy	22	To compare performance to other products tested (major competitive product).
Tnemec	Series 400	Polyurea Elastomer	50	To compare performance to other products tested.
Tnemec	Series 406	Hybrid Polyurethane Elastomer	36	To compare performance to other products tested.

MANUFACTURER	PRODUCT	GENERIC COATING TYPE	DRY FILM THICKNESS (MILS)	TESTED
Tnemec	Series 434	1/8" Modified Amine Epoxy Mortar	120	To compare performance to other products tested.
Tnemec	Series 434/435	1/8" Modified Amine Epoxy Mortar with Amine Epoxy Glaze Coat	139	To compare performance to other products tested.
Tnemec	Series 435/435	Modified Amine Epoxy	27	To compare performance to other products tested.
Tnemec	Series 446/446	Moisture-cure Polyurethane with Clean Tar	10	To compare performance to other products tested.
Plasite	Plasite 5371	1/8" Modified Amine Epoxy Mortar	120	To compare performance to other products tested (major competitive product).
Sauereisen	Sewergard 210T	1/8" Modified Amine Epoxy Mortar	117	To compare performance to other products tested (major competitive product).
Sauereisen	Sewergard 210S	Fiber-reinforced Amine Cured Epoxy	117	To compare performance to other products tested (major competitive product).
Sauereisen	Sewergard 210RS	Amine Cured Epoxy Mortar - rotary spray	101	To compare performance to other products tested (major competitive product).
Sherwin-Williams	1214 Cor-Cote CR	Novolac epoxy	87	To compare performance.
Sherwin-Williams	1215 Cor-Cote HCR	Novolac epoxy	61	To compare performance to other products tested (major competitive product).
Sherwin-Williams	Corothane 1 Coal Tar MCU	Moisture-cure polyurethane w/tar	20	To compare to Series 446.
Sherwin-Williams	Cor-Cote SC	Amine Cured Epoxy	32	To compare to Series 435.
Induron	Protecto 401	Tar extended Novolac Epoxy	41	To compare performance to other products tested.
Induron	Ruff Stuff 2100	Coal Tar Epoxy Polyamine	19	To compare to Series 435, 446.
Raven	400S	Amine Cured Epoxy	50	To compare to Series 435.
Raven	405	Amine Cured Epoxy	109	To compare to Series 435.
Raven	AquataPox A6	Amine Cured Epoxy	60	To compare to Series 435.
BLP Mobile Paint	MO Tar	Coal Tar	19	To compare to Series 46H and 446.
Wasser	Wasser MC Tar	Moisture-cure Polyurethane with Clean Tar	11	To compare to Series 446.

<u>Coal-Tar Epoxy:</u>

- Series 46H (Tnemec) displayed good initial EIS impedance but dropped rapidly within 10 days exposure, developing severe blisters. The blistering continued and burst at 20 days, yielding 0.0 impedance. The results were similar to the panel exposed in Test #2—10,000 ppm H_2S - except that the blisters did not perforate until 28 days. (This product is identified in published literature as "Alternative C".)

- MO Tar (BLP Mobile Paint) provided good initial EIS impedance but failed within 10 days exposure. Severe blister ing developed and some separation between coats also observed. The blisters cracked and yielded 0.0 after only 10 days.

- Ruff Stuff 2100 (Induron) also had good initial EIS impedance but developed extensive blisters within 10 days expo sure. The blisters filled with liquid and broke yielding a 0.0 result after 10 days.

Coal-Tar Epoxy Products (Tested at 500 ppm H_2S)			
EIS Impedance	Series 46H	2100	MO Tar
Baseline	10.9	10.7	10.9
10 days	7.5	Fail	Fail
20 days	Fail	--	--
28 days	--	--	--

The poor impedance exhibited by the coal-tar epoxies confirms that these materials are not resistant to the gas permeation found in severe wastewater environments. This finding is consistent with actual field exposures that failed in only a few months under such conditions.

Thin Film Epoxy:

- Series 66 (Tnemec) failed early in the test by severe blistering and showed very low impedance values. In addition, impedance dropped rapidly within 10 days of exposure. The resulting impedance was well below the protection level shown in Figure 2, and finally failed at 28 days.

- Series N69 (Tnemec) failed early in the test by severe blistering and showed very low impedance values.

- Series 104 (Tnemec) failed early in the test by severe blistering and showed very low impedance values. This blistering failure has been observed in Series 104 in field applications at 50-100 ppm H_2S after 12-16 months in service. (This product is identified in published literature as "Alternative B".)

Thin-Film Epoxy Products (Tested at 500 ppm H_2S)			
EIS Impedance	Series 66	Series N69	Series N104
Baseline	10.2	9.8	9.5
10 days	5.2	6.3	5.6
20 days	4.9	5.6	4.9
28 days	Fail	Fail	4.3

The poor impedance values for the thin-film epoxy materials correlates to poor permeation resistance of these products in severe wastewater environments. This observation is consistent with actual field failures of these coating types.

Novolac Epoxy:

- Series 275 (Tnemec) high-build, fiber-reinforced Novolac epoxy displayed excellent impedance of 11.0. However, the impedance quickly diminished and measured 6.4 at 28 days. This product only retained 58% of the initial imped ance. Despite formulated for high-build chemical resistance, this product is not suitable for the corrosivity of a wastewater environment.

- Series 282 (Tnemec) thin-film Novolac epoxy had good initial impedance, but delaminated and cracked in a very short period. This product exhibits otherwise excellent resistance. However, this product is not suitable for elevated H_2S environments. This cracking is consistent with our field observations of this type of coating exposed to severe wastewater environments.

- Cor-Cote 1214 CR (Sherwin Williams) showed impedance values lower than many other products tested and the impedance dropped significantly during the 28-day test exposure. The final impedance was measured at 7.2, for only a 65% retained impedance value.

- Cor-Cote 1215 HCR (Sherwin Williams) delaminated and cracked in the test chamber after 20 days of testing and its impedance dropped to 6.5 after 10 days. No impedance could be measured after the cracking and delamination oc-curred. This failure-mode is consistent with coating failures encountered in the field.

Novolac Epoxy Products (Tested at 500 ppm H_2S)				
EIS Impedance	Series 275	Series 282	1214 CR	1215 HCR
Baseline	11	10.1	11.1	10.9
10 days	8.0	Fail	7.8	6.5
20 days	6.9	--	7.6	Fail
28 days	6.4	--	7.2	--

This evaluation of Novolac epoxies demonstrates that these types of epoxy systems, which are well known for their high chemical resistance, are failing rapidly by stress cracking and delamination. By failing so quickly, it confirms the importance of the permeability resistance of the coating to H_2S in a wastewater headspace environment, rather than relying solely on higher chemical resistance to sulfuric acid.

<u>High-build Epoxy Mortar:</u>

- Series 434 (Tnemec) epoxy mortar had a good initial impedance of 10.7. The mortar maintained impedance of 9.1 after 28 days of exposure, or a retained impedance value of 85%, Additionally, the mortar exhibited excellent adhe sion to the steel panel with no blistering or cracking observed.

- The 434/435 (Tnemec) trowel-applied epoxy mortar with epoxy glaze demonstrated excellent initial impedance of 11.3. The mortar/glaze system maintained impedance of 9.8 after 28 days of exposure, or retained impedance value of 87%. The panel showed no signs of blistering, cracking, or delamination.

- Plasite 5371 trowel-applied epoxy mortar had excellent initial impedance of 11.3. However, the mortar displayed a rapid drop in impedance over the course of the 28 days to 8.0, with only a retained impedance of 71%. This indicates that over time, this mortar looses it protective qualities.

- Sauereisen 210T trowel-applied epoxy mortar had excellent initial impedance of 11.4. However, the mortar displayed a rapid drop in impedance over the course of the 28 days down to 7.2, with only a retained impedance of 63%. This indicates that over time, this mortar also looses it protective qualities. (This product is identified in published literature as "Alternative A".)

- Sauereisen 210RS rotary-spray epoxy mortar had excellent initial impedance of 11.3, comparable to the sister 210T epoxy mortar. However, the spray mortar significantly dropped impedance to 6.9 with only a 61% retained imped ance. This product performed the poorest of the epoxy mortar systems, and its low retained impedance is an indica tion that it looses it protective qualities to protect the substrate from sulfide corrosion.

High-Build Epoxy Mortar Products (Tested at 500 ppm H_2S)					
EIS Impedance	Series 434	Series 434/435	5371	210T	210RS
Baseline	10.7	11.3	11.3	11.4	11.3
10 days	8.5	8.8	9.3	7.8	8.5
20 days	9.0	9.8	9.1	7.7	7.9
28 days	9.1	9.8	8.0	7.2	6.9

<u>High-build Epoxy (resin):</u>

- Series 435 (Tnemec) high-build, modified amine epoxy coating formulated specifically for severe wastewater displayed a good initial impedance of 10.2. The impedance dropped initially, but rebounded to 10.3 after 28 days exposure. This increase in impedance is due to a reaction with a proprietary ingredient with the corrosive environment, effec tively sealing the surface. This product retained 100% of the initial impedance, demonstrating its superior perfor mance in severe wastewater environments.

- Series 436 (Tnemec) fiber-reinforced, high-build, modified amine epoxy coating formulated specifically for severe wastewater displayed a good initial impedance of 10.4. This value is consistent with the sister product, 435. Likewise, the impedance dropped during the initial testing, but rebounded to a final impedance of 10.2. This rebound in imped ance is due to a reaction with a proprietary formula ingredient with the corrosive environment, effectively sealing the surface. This product retained 98% of the initial impedance, demonstrating its superior performance in severe waste water environments.

- Series 270 (Tnemec) fiber-reinforced, high-build, amine epoxy coating exhibited excellent initial impedance of 11.5 However, the impedance steadily dropped during the testing, ultimately failing at 28 days. Despite being a fiber-reinforced amine-cured epoxy, this coating did not withstand the corrosive nature of a severe wastewater environment.

- Sauereisen 210S fiber-reinforced, high-build, amine epoxy coating displayed excellent initial impedance of 11.5. However, the impedance dropped rapidly at 10 days, and continued to downward to 7.3 at 28 days, with only 63% retained impedance. This indicates that over time this fiber-reinforced high-build epoxy looses it protective qualities, making it a poor candidate for long-term protection.

- Raven 400S ultra-high-build, amine epoxy demonstrated good initial impedance of 10.8. The impedance dropped sharply during the first 10 days to 8.9, and then leveled to a final impedance of 8.4 after 28 days. This product re tained 82% of the initial impedance.

- Raven 405 ultra-high-build, amine epoxy demonstrated excellent initial impedance of 11.5. The impedance steadily declined to a final impedance of 9.8, with 85% retained impedance.

- Raven A6 high-build modified amine epoxy displayed an excellent impedance of 11.4. The impedance steadily de clined to a final value of 7.9 at 28 days and a retained impedance of 69%. This steady decline in impedance verifies a loss of permeation resistance, and ultimately correlates to a loss long-term performance under sever wastewater conditions.

- Protecto 401(Induron) had good initial impedance of 11.2. However, the permeation resistance dropped considerably to a 28 day impedance of 5.7, below the minimum level required for corrosion protection. The panel had strong vis ible cracking over its entire surface.

- Cor-Cote SC (Sherwin-Williams) high-build, epoxy coating exhibited a good initial impedance of 10.1. However, the coating suffered severe blistering and massive impedance loss during the first 10 days. The blistering perpetuated until they broke at 20 days. These results indicate that this coating has low permeation resistance and will not perform in severe wastewater environments despite being marketed for these areas.

High-Build Epoxy Products (Tested at 500 ppm H_2S)									
EIS Impedance	Series 435	Series 436	Series 270	210S	400S	405	A6	401	Cor-Cote SC
Baseline	10.2	10.4	11.5	11.5	10.8	11.5	11.4	11.2	10.1
10 days	9.9	9.7	9.3	8.1	8.9	10.9	9.3	8.8	4.8
20 days	10.1	10.0	6.4	7.6	8.8	10.1	8.3	7.0	Fail
28 days	10.3	10.2	Fail	7.3	8.4	9.8	7.9	5.7	--

High-build Polyurethanes, Polyurethane Hybrids, & Polyureas:

- Series 262 (Tnemec) high-build, elastomeric polyurethane demonstrated excellent initial impedance of 11.5. The impedance remained steady at this level to reach a final impedance of 11.5. Although the impedance values remained stable, the adhesion to the steel panel was determined to be poor. Additionally, the surface was observed to contain many surface divot type failures over the course of the testing.

- Series 400 (Tnemec) high-build, polyurea elastomer displayed excellent initial impedance of 10.7. The final imped ance was measured at 10.2, for a retained impedance of 95%. However, the coating was noted as having poor adhe sion to the steel panel.

- Series 406 (Tnemec) is a quickset polyurethane-hybrid that displayed excellent initial impedance of 11.2. The imped ance remained steady throughout the testing and resulted in a final 28 day value of 11.3. Although the impedance val ues remained stable, the adhesion to the panel was determined to be marginal. Additionally, small foaming (surface inclusions) were observed in the coating. Upon removal of the coating down to the bare steel the surfaces revealed darkened areas under such inclusions.

- Polybrid 705 high-build, quickset, polyurethane hybrid demonstrated excellent initial impedance value of 11.4. The impedance remained level throughout the testing to result in a 11.3 final impedance. However, coating was noted to exhibit poor adhesion to the substrate and a few areas of underfilm corrosion were noted on the panel.

- Zebron high-build, quickset, polyurethane hybrid provided excellent initial impedance value of 11.7. The impedance remained steady throughout testing, resulting in a 11.6 after 28 days. However, coating was noted to exhibit poor adhesion to the substrate.

Despite these materials demonstrating good initial and retained impedance levels, these coating types categorically exhibited marginal adhesion to the substrate despite using the recommended primers. It is Tnemec's conclusion that the physical properties of these materials are affected by the severe wastewater simulation conditions, ultimately affecting the adhesion to the substrate. Further physical testing was performed on these materials to evaluate physical changes as outlined later in this document.

High-Build Polyurethanes, Polyurethane Hybrids, Polyureas (Tested at 500 ppm H_2S)					
EIS Impedance	Series 262	Series 400	Series 406	705	Zebron
Baseline	11.5	10.7	11.2	11.4	11.7
10 days	11.5	10.4	11.3	11.3	11.6
20 days	11.5	10.2	11.3	11.3	11.6
28 days	11.5	10.2	11.3	11.3	11.6

Moisture Cured Urethane:

- Series 446 (Tnemec) hydrophobic, aromatic moisture-cured polyurethane demonstrated good initial impedance of 10.2, and a final impedance of 10.1. This coating retained 99% of the initial impedance value.

- Corothane 1 Coal Tar (Sherwin-Williams) moisture-cured urethane demonstrated poor initial impedance of 7.9. The impedance continued to drop steadily to a final 28 days value of 7.3. Although this product retained 92% of the initial impedance, the values were low in comparison to the Series 446, correlating to a lesser performing coating system. This low impedance values for this product likely correlate to low corrosion protection to the sub strate in field conditions.

- The MC Tar (Wasser) displayed a marginal initial impedance of 9.1. The impedance continued to drop steadily to a final 28 days value of 7.4. Although this product retained 81% of the initial impedance, the impedance values were low in comparison to the Series 446, correlating to a lesser performing coating system

Moisture-Cured Urethane Products (Tested at 500 ppm H_2S)			
EIS Impedance	Series 446	Corothane 1	MC Tar
Baseline	10.2	7.9	9.1
10 days	10.2	7.7	8.6
20 days	10.1	7.5	8.7
28 days	10.1	7.3	7.4

As can be seen, most thin film coatings fail in high H_2S environments. Series 446 maintains very high and stable impedance for the 28-day test exposure. These results support the use of Series 446 Perma-Shield MCU for thin-film applications to intricate steel and other miscellaneous metals that otherwise would be impossible to coat with a high-build epoxy liner.

Vinyl Ester:

- Series 120 (Tnemec) had excellent initial impedance of 11.1. The impedance steadily declined throughout the 28 day testing to 10.0, resulting in a 91% retained impedance. The coating demonstrated excellent adhesion to the substrate. Additionally, no blistering, or cracking was observed in the film

Vinyl Ester (Tested at 500 ppm H_2S)	
EIS Impedance	Series 120
Baseline	11.1
10 days	10.3
20 days	10.5
28 days	10.0

The result confirms Tnemec's field success with this system for use in severe wastewater environments under high H_2S gas exposure. However, the use of Series 120 is difficult in wastewater due to moisture sensitivity, safety concerns with a styrene monomer in confined spaces, and lower temperature cure restrictions.

Coated Concrete Coupon Testing

The coatings were also applied to 2.5 inch x 4 inch concrete cylinders and tested under the 500 ppm H_2S conditions as established in Test #3. Evaluation of the concrete coupons included adhesion, blistering, foaming (surface inclusions), and color change.

EVALUATION RESULTS SUMMARIZED

Series 434, Series 434/435, Sauereisen 210T, and Plasite 5371 showed no blistering, excellent adhesion to the concrete, and some color change which penetrated the surface of the coatings. All three systems experienced dark spotting from the exposure to the H_2SO_4 droplets in the test cabinet.

Microscopic examination of cross sections showed that discoloration penetrated the 434 and 434/435 to the extent of 5 to 10 mils and 3 to 5 mils respectively. Discoloration was more intense under the dark spots. The Plasite 5371 and Sauereisen 210T showed discoloration (bleaching) to a depth of 50 mils.

Figure #3
Series 434

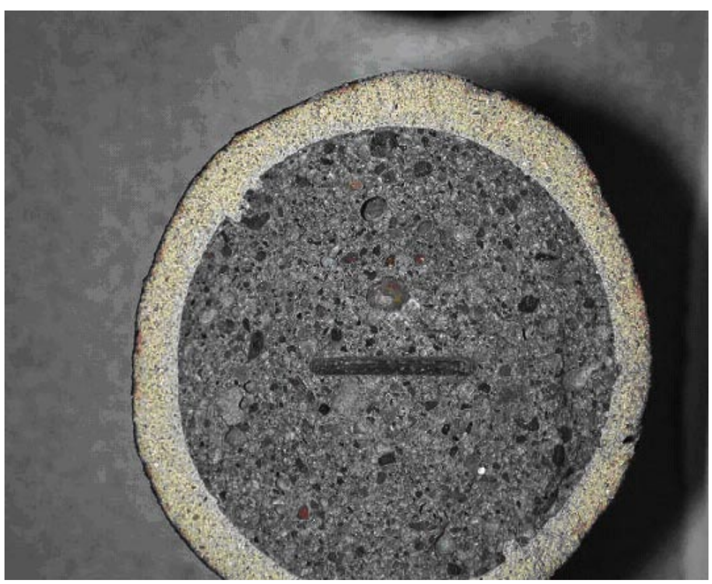


Figure #4
Series 434/435

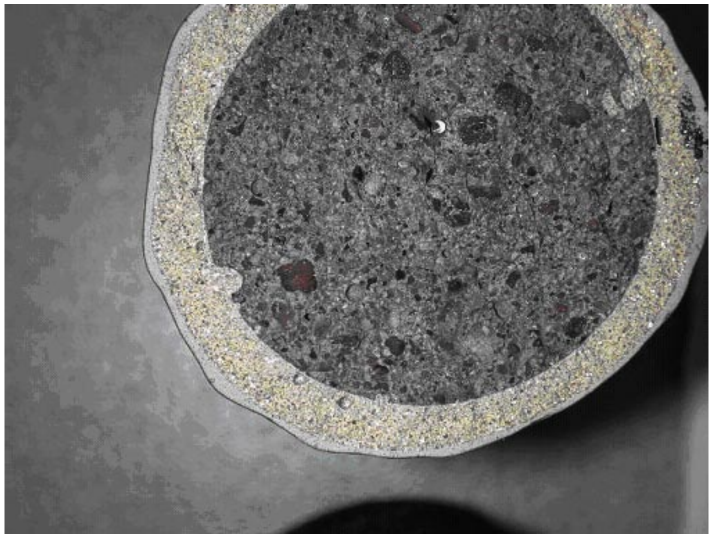


Figure #5
Sauereisen 210

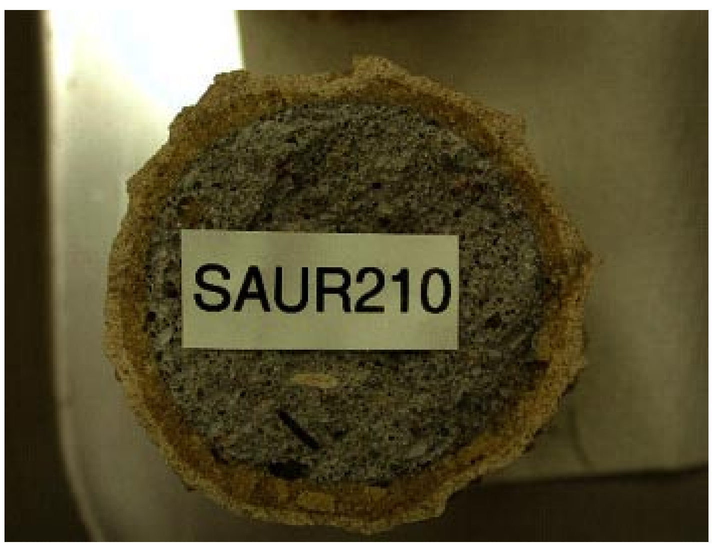
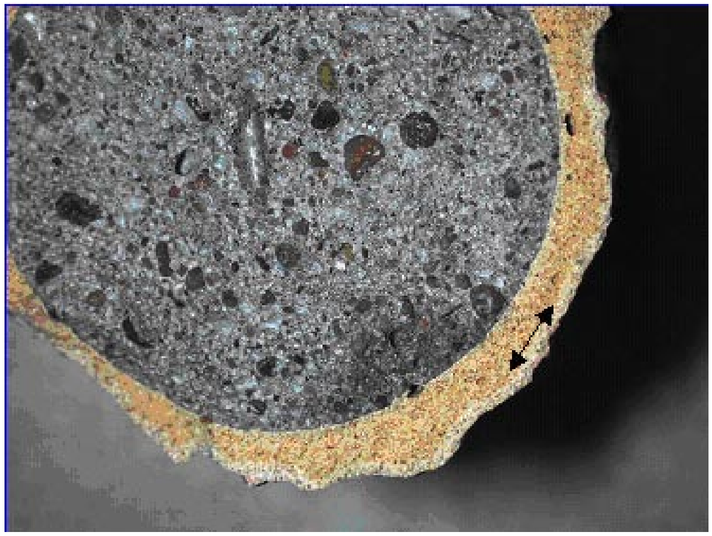


Figure #6
Plasite 5371



*The white layer (with the arrow) shows the penetration depth (50 mils) in the Plasite 5371.

Better resistance to H_2S from 434 and 434/435 can be expected when compared to Sauereisen 210T and Plasite 5371 from these observations.

Figure #7 shows the concrete core coated with Series 46H that has been severely attacked after 28 days of exposure in the chamber. This confirms the poor EIS number previously obtained for the Series 46H on the steel coupon and also duplicates the real life mode of failure of this coating.

Figure #7
Series 46H

Physical Properties Testing

Free films of Series 262, Series 400 and Series 406 were also tested to compare changes in physical properties before and after the 28 days of exposure to S.W.A.T. Coating system 66/262 did not blister, but discolored slightly and developed a roughened surface after 28 days of exposure. Examination showed a distribution of small pockmarks over the surface, indicating a chemically eroded condition. Adhesion was good, but the topcoat was somewhat gummy although still fairly tough.

For the polyurethane systems, free films were also analyzed to compare physical properties before and after cabinet exposure. The data is reported in Table 3, Table 4 and Table 5 shown below.

Table 3
Summary of ASTM D624-98 Tear Resistance

Sample I.D.	Peak Load/Thickness (psi) Control	Peak Load/Thickness (psi) Autoclaved	Percent Difference
Series 262 - Black	184	208	13.0%
Series 400 - White	669	458	-31.5%
Series 406 - Beige	502	491	-2.2%

Table 4
Summary of ASTM D638-98 Tensile Break Strength Properties

Sample I.D.	Break Strength (psi) Control	Break Strength (psi) Autoclaved	Percent Difference
Series 262 - Black	730	618	-15.3%
Series 400 - White	3672	1643	-55.3%
Series 406 - Beige	3475	3529	-6.2%

Table 5
Summary of ASTM D638-98 Elongation

Sample I.D.	Break Strain (%) Control	Break Strain (%) Autoclaved	Percent Difference
Series 262 - Black	430.05 $\pm$ 20.20	392.49 $\pm$ 12.81	-10.60%
Series 400 - White	361.92 $\pm$ 10.47	248.41 $\pm$ 27.66	-31.36%
Series 406 - Beige	430.05 $\pm$ 20.20	28.25 $\pm$ 6.88	-6.98%

From these summaries, it is evident that Series 400 has an unacceptable loss of its physical properties when exposed to the simulated exposure conditions, resulting in poor long-term adhesion to the substrate. It is Tnemec Company's conclusion that Series 400 and any type of polyurea should not be used in high H_2S environments due to the significant reduction in physical properties. A similar conclusion can be made for an elastomeric polyurethane material, such as Series 262. These two products should not be specified when high concentrations of H_2S gas will be expected. Conversely, Series 406 retained acceptable physical properties when exposed 28 days and will likely maintain sufficient physical properties so as to not affect adhesion to the substrate. However, a myriad of fastset polyurethane-hybrids are commercially available, and evaluations should be conducted to determine if the necessary physical performance requirements are achieved prior to specifying the products for severe wastewater environments.

Moreover, when considering the specification or use of polyurethane systems in a wastewater environment, it is essential to pay attention to the H_2S level, and to determine whether it is municipal or industrial wastewater. Industrial wastewater can contain solvents and other chemicals that polyurethane coatings (Series 406) will not resist. Before any recommendation can be made, always have a good understanding of the type of wastewater exposures to which the coatings will be exposed.

CONCLUSION

In comparison to the testing conducted on coating systems over steel coupons, the concrete analysis results were very similar under the same wastewater simulation conditions. The Series 434 and 434/435 showed less permeation (discoloration) than Sauereisen 210T and Plasite 5371, which is consistent with the EIS impedance values reported earlier in this document. Series 406 showed very good permeation resistance with very shallow discoloration. The Series 66/262 samples discolored slightly, but experienced chemical erosion of the topcoat surface. Also, the topcoat's integrity appeared to be changed by the exposure, which was confirmed by the free film testing.

Tnemec Company believes it is credible, based on all the testing work performed, to write specifications using the EIS results from the chamber as qualifying criteria. In the future, product performance criteria should be written as follows:

- H_2S chamber testing: Coating exposed for 28 days at 150° (65°C) to 500 ppm H_2S, 4000 ppm NaCl, and 10% H_2SO_4.

- Initial Impedance before testing should be a minimum of 10 and be over 9.0 after 28 days of exposure to S.W.A.T. No loss of adhesion or blistering should be observed.

Resume of Results

Coating	Impedance (Initial)	Impedance (28 days S.W.A.T. Exposure
Series 434	10.7	9.1
Series 434/435	11.3	9.5
Series 435	10.2	10.3
Series 436	10.4	10.2
Series 446	10.2	10.1
Series 406	11.2	11.3

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