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MATERIALS PERFORMANCE

CORROSION PREVENTION AND CONTROL WORLDWIDE

EVALUATION OF IMPRESSED CURRENT CATHODICALLY PROTECTED TANK BOTTOMS

Detecting Corrosion Inhibitor Migration Depth in Topically Treated Concrete

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Innovative and Environmentally Friendly Technologies for Corrosion Control

Vapor phase corrosion inhibitors (VCIs) and migrating corrosion inhibitors (MCIs) have been used for many years to protect structures, equipment, and the environment from the adverse effects of corrosion. These technologies offer a variety of benefits, including easy, economical application and earth-friendly qualities. This special supplement to *Materials Performance* magazine describes several projects where VCIs and MCIs have been effectively used, including applications for extending the life of machinery, protecting steel-reinforced concrete structures, using recyclable film to prevent corrosion on stored or transported equipment, and controlling corrosion on tank bottoms. Whether asset preservation is a matter of product containment or keeping structures safe and intact, environmentally friendly VCIs and MCIs are proven to control corrosion in a multitude of applications.

Vapor Phase Inhibitors in Functional Fluids

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The addition of corrosion inhibitors to lubricating compounds prolongs the service life of machinery during its working application and in storage. Criteria for selecting corrosion inhibitors for the equipment during transportation, storage, and mothballing are based on their level of corrosion protection for all metal elements while being compatible with polymers (e.g., hoses and seals) and installed lubricants. According to the application requirements, the tests for such products include evaluation of their performance in environmental chambers, including humidity and salt fog, evaluation of vapor corrosion inhibition, immersion, and other corrosion tests. In operating equipment, corrosion inhibitors added to lubricating fluids should not negatively affect their lubricity, oil-water separation, and other properties important for such fluids. In addition to corrosion tests, evaluation of the fluid with added corrosion inhibitor includes testing of the essential properties listed in the fluid specifications. This article presents the formulating approaches and evaluation of the performance of corrosion-inhibiting additives in functional fluids. The testing program is based on widely adopted standards.

In a widely cited cost of corrosion study[1] the direct cost of corrosion in the United States was estimated to equal $276 billion in 1998, approximately 3.1% of the country's Gross Domestic Product.

The indirect cost of corrosion is esti- mated to be at least equal to the direct cost. Examination of the data in 2013 indicates that total corrosion costs in the United States exceed $1 trillion annually.

Internal surfaces of equipment corrode during all segments of their life: operation, intermediate operation, and storage. The reasons and the intensity of corrosion vary. Usually functional liquids don't cause corrosion. Corrosion occurs because of the contaminants in functional liquids, such as the presence of moisture, salts, acidity, and other corrosive species. In the majority of cases, corrosion can be prevented, delayed, or reduced by using corrosion inhibitors.

The requirements of corrosion inhibitors for functional fluids are different for equipment lay-up vs. equipment in use. Corrosion protection of machinery during mothballing can be achieved by using special rust preventatives or adding corrosion inhibitors to working lubricating oils. For such application the most important properties of the rust preventative are the level of corrosion prevention; compatibility with all metals, plastics, and polymers used in the system; and sometimes removability.

In operation mode, the corrosion inhibitor additionally should not negatively affect the specified properties of lubricants. This requirement can be satisfied by using special formulas, limiting the dose rate, or using the inhibitor in combination with the additives, which can compensate for the negative effects of the rust preventative. Examples of successful applications of corrosion inhibitors in engine oils and fuels are described in publications.[2-3] The advantage of such products is that they can be high-performance lubricants, while at the same time possessing the ability to prevent corrosion in both storage and operation. This eliminates the necessity of changing the lubricant if equipment needs to be laid-up, returned back to operation, or used intermittently.

This article presents the examples of incorporating corrosion inhibitors in hydraulic fluids, both glycol/water-based and oil-based.

Experimental Procedures

Corrosion Inhibitor for Glycol/ Water-Based Hydraulic Fluid

Two vapor corrosion inhibiting additives (VCI-1 and VCI-1L) to glycol/water-based hydraulic fluid were formulated and evaluated. The main ingredients of these additives are a blend of amine salts of saturated iso-carboxylic and aromatic acids.

Among evaluated extreme pressure (EP) additives were several types of phosphate esters and polyalkylene glycol-based products. VCI-1L consisted of 96% VCI-1 and 4% of a compatible high-performance EP lubricant. Two suitable EP lubricants were found in screening tests. Either can be used in formula VCI-1L when EP performance is required as a part of the package. When VCI-1L is made with EP additive 1, it is identified as VCI-1L1; when made with EP additive 2, it is identified as VCI-1L2. Results and descriptions identified only as VCI-1L apply to both formulations.

Table 1 shows results of the additive analysis conducted by an independent laboratory using scanning electron microscopy (SEM)-energy dispersive spectroscopy (EDS). Table 2 shows the properties of VCI-1 and VCI-1L. These products are intended to be used in subsea equipment. Besides high performance in corrosion inhibition and lubricity, their impact on the sea environment had to be evaluated.

The components of the formulated additive were tested according to the North Sea (United Kingdom, Norway, Denmark, and The Netherlands) regulations to satisfy the criteria:

- Biodegradability: >60% in 28 days
- Marine toxicity: Effective concentration 50% (EC50)/lethal concentration 50% (LC50) >10 mg/L to North Sea species
- Bioaccumulation: Log octanol/water partition coefficient <3

Performance Tests

Performance testing for VCI-1 and VCI-1L included the following tests.

Compatibility with Seawater Test

This test was performed as follows: Hydraulic fluid samples with added 10% artificial seawater were subjected to cycling for 16 h at 80 °C and 8 h at 7 °C. Samples were subjected to seven cycles and then inspected visually for any changes.

IP 287 Cast Iron Chip Corrosion Test[4]

This test was performed as follows: The dilution of samples of hydraulic fluids with 10% and 25% of artificial seawater were prepared. Cast iron chips were placed on filter paper and wetted with a sample of hydraulic fluid. The area of paper stained with corrosion was recorded after 2 h.

Vapor Corrosion Inhibition Test

This was evaluated according to ASTM D5534,[5] "Standard Test Method for Vapor-Phase Rust-Preventing Characteristics of Hydraulic Fluids." This test method evaluates the ability of hydraulic fluids to prevent the rusting of steel in the vapor phase over the hydraulic fluid and water. A sample of the fluid was placed into the testing beaker. The beaker was heated to the temperature of 60 °C and then sealed with the lid, with an attached carbon steel (CS) plug (coupon) inside. The plug was evaluated for the presence of rust after 6 h of testing.

Multi-Metal Vapor Corrosion Test

This test was performed on UNS G10180 CS (SAE 1018) and copper. In this

test, hydraulic fluid with the added corrosion inhibitor was heated to 60 °C in a wide neck conical flask. The metal panel was placed over the mouth to stand for 15 min. After that, the panel was visually inspected for the presence of corrosion.

Anti-Wear Properties Test

Anti-wear properties of the corrosion inhibitor formulation were tested (only VCI-1L2) using a Falex[†] lubricant tester with 2 V-block made from UNS G11370 (AISI 1137) steel and brass pin.[6] The target torque and anti-wear properties of the final fluid were as follows:

- 15 lb·in (1.69 N*m) at a load of 500 lb (227 kg) for 1 min
- < 20 lb·in (2.26 N*m) at load of 500 lb (227 kg) for 30 min
- Wear teeth = 5 or less

Corrosion Inhibitor for Mineral/Synthetic Oil-Based Hydraulic Fluids (VCI-2)

A vapor corrosion inhibiting additive for oil-based hydraulic fluids formula is an

[†]Trade name.

oil-soluble blend of calcium sulfonate and amino-carboxylates in synthetic oil. Its physical-chemical properties are shown in Table 3.

The VCI additive was tested in hydraulic oil with physical-chemical characteristics conforming to ISO Grade 32. Testing procedures of ISO 32 hydraulic oil with and without VCI-2 included the following procedures:

- Water Separability (ASTM D1401[7]). This test method evaluates the ability of fluids to separate from water. Equal volumes of fluid and deionized water were mixed and placed in a graduated cylinder. The method evaluates the separated volume of fluid and water at the recommended temperature after several time intervals after mixing. Volumes are reported as oil/water/emulsion.
- Copper Strip Corrosion (ASTM D130[8]). This test evaluates the relative degree of fluid corrosivity to copper. A copper

TABLE 1. ADDITIVE ANALYSIS		
Element	EP Additive 1 (wt%)	EP Additive 2 (wt%)
Ash	0.007	2.27
Oxygen	54.26	53.71
Sodium	1.96	–
Aluminum	—	1.16
Silicon	38.47	9.34
Phosphorus	4.69	31.01
Potassium	0.62	1.28
Zinc	—	3.48

TABLE 2. PHYSICAL-CHEMICAL PROPERTIES OF VCI-1 AND VCI-1L		
Test	VCI-1	VCI-1L
Appearance	Clear yellowish to amber liquid	Clear yellowish to amber liquid
pH	9-8 (1% in water)	7.5-8.5 (1% in water)
Density	8.5-8.7 lb/gal (1.03-1.06 kg/L)	8.6-8.8 lb/gal (1.03-1.06 kg/L)
Non-Volatile Content	50-60%	60-70%

TABLE 3. PHYSICAL-CHEMICAL PROPERTIES OF VCI-2	
Appearance	Brown viscous liquid
Density	0.91-0.96 kg/L
Non-Volatile Content	91-97%

TABLE 4. CORROSION INHIBITION EVALUATION OF VCI-1 AND VCI-1L

Test Performed		Results
IP 287	Liquid corrosion test on neat fluid	No corrosion
	With 10% of seawater	No corrosion
	With 25% of seawater	No corrosion
Vapor Phase Corrosion Test		Pass
Compatibility with Seawater (10 % by Volume)		Clear fluid
Stability at	Room Temperature	Clear stable
	70 °C	Clear stable
	–20 °C	Clear stable
Multi-metal vapor corrosion		Pass

TABLE 5. LUBRICITY LEVEL OF GLYCOL/WATER-BASED FLUID WITH 10% VCI-1L2

Load (lb) at (min)	Torque Values (lb·in)	Load (kg) at (min)	Torque Values (N·m)
100 (1)	6.3	45.4 (1)	0.71
200 (1)	10.7	90.7 (1)	1.21
300 (1)	13.3	136 (1)	1.50
400 (1)	17.8	181 (1)	2.01
500 (1)	21.3	227 (1)	2.41
500 (30)	18.2	227 (30)	2.06
Other Lubricity Results			
Number of Teeth	6		
% Weight Loss of Pin	0.058%		

TABLE 6. SEPARABILITY TEST RESULTS

Sample	20 min	25 min	30 min	35 min	Description of Results (tested at 54 °C)
ISO 32 Hydraulic Oil (Control)	17-40-23	26-40-14	36-40-4	40-40-0	Complete separation of oil and water occurred after 35 min.
ISO 32 Hydraulic Oil + 2% VCI-2	35-39-6	40-40-0	—	—	Complete separation of oil and water occurred after 25 min.

TABLE 7. ISO 32 HYDRAULIC OIL CHARACTERISTICS

Test	Test Method	Results for ISO 32 Hydraulic Oil (Control)	Results for ISO 32 Hydraulic Oil + 2 % VCI-2
Copper Strip Corrosion Test, 3 h at 100 °C	ASTM D130	1a	1a
Pour Point	ASTM D97	–18 °C	–18 °C
Viscosity at 40 °C	ASTM D2196	26 cps (0.026 Pa*s)	25 cps (0.025 Pa*s)
Viscosity at 100 °C	ASTM D2196	6 cps (0.006 Pa*s)	6 cps (0.006 Pa*s)
Rust Prevention Test (tested at 60 °C for 4 h)	ASTM D665 (Procedures A & B)	Pass	Pass
Acid Number	ASTM D974	0.2 mg KOH/g	0.4 mg KOH/g

strip is immersed in a sealed container with fluid, which was placed in the oven (set at 100 °C) for 3 h. Classification of the corrosiveness was made by comparing the appearance of the strip with the ASTM Copper Strip Corrosion classification standards.

- Pour Point per ASTM D97.[9]
- The rust preventing characteristics (ASTM D665[10] or IP 135, Procedure B in the presence of salt water) test method covers the evaluation of the ability of an inhibited fluid to prevent the rusting of ferrous parts. A rotating testing rod made from CS was inserted into the fluid. Artificial seawater was added to the fluid in the ratio of 30 mL of seawater to 300 mL of fluid. The test was performed at 120 °F (48.9 °C) for 4 h. Afterward, the test rod was inspected for the presence of corrosion.
- Acid/base number by color indicating titration (ASTM D974).[11]
- Viscosity at 40 °C and 100 °C per ASTM D2196.[12]
- Accelerated corrosion testing (ASTM D1748 [13])evaluates the rust-preventive properties of fluid under conditions of high humidity. Panels made from UNS G10100 CS (SAE 1010) were coated with hydraulic fluid and left in a vertical position for 2 h at room temperature. The panels were placed in a humidity cabinet and inspected for the presence of corrosion on a regular basis.

Results

VCI-1 and VCI-1L Test Results

The corrosion inhibition performance of VCI-1 and VCI-1L is presented in Table 4. The results show that the formulations provide effective corrosion protection while maintaining phase stability of the hydraulic fluid.

Table 5 shows the lubricity results obtained with VCI-1L2. The results are close to the target values, and within an acceptable range for typical customers.

VCI-2 Test Results

Table 6 shows the results of ASTM D1401, "Water Separability Test." Water separation is actually improved by the addition of VCI-2.

Table 7 shows the results of the hydraulic oil characterization tests. The results for the formulation containing VCI-2 are very close to those of the base hydraulic oil. Both samples passed the rust prevention test. However, as is seen in Figure 1, the sample with VCI-2 shows improved corrosion prevention under more aggressive conditions.

Conclusions

This work confirms that functional fluids can be satisfactorily formulated with VCI-1 and VCI-2. The final formulations provide improved corrosion resistance for glycol/water- or oil-based hydraulic fluids, while conforming to required performance specifications.

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5. ASTM D5534, "Standard Test Method for Vapor-Phase Rust-Preventing Characteristics of Hydraulic Fluids" (West Conshohocken, PA: ASTM).

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8. ASTM D130, "Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strips Tarnish Test" (West Conshohocken, PA: ASTM).

9. ASTM D97, "Standard Test Method for Pour Point of Petroleum Products" (West Conshohocken, PA: ASTM).

10. ASTM D665, "Test Method for Rust Preventing Characteristics of Inhibited Mineral Oils in the Presence of Water" (West Conshohocken, PA: ASTM).

11. ASTM D974, "Test Method for Acid and Base Numbers by Color Indicator Titration" (West Conshohocken, PA: ASTM).

12. ASTM D2196, "Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer" (West Conshohocken, PA: ASTM).

13. ASTM D1748, "Test Method for Rust Protection by Metal Preservatives in the Humidity Cabinet" (West Conshohocken, PA: ASTM).

ASTM-D1478 (Humidity Cabinet)
After 215 h of Testing

FIGURE 1 Panels at end of accelerated corrosion test; control (left) and sample with VCI-2 (right).

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Detecting Corrosion Inhibitor Migration Depth in Topically Treated Concrete Using Mass Spectrometry

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Direct analysis in real-time mass spectrometry (DART-MS) is an ambient atmosphere mass spectrometry technique. It allows quick analysis with minimum sample preparation. DART-MS was used to detect inhibitor penetration depths into a concrete interior when its surface received topical migrating inhibitor treatment. Two different concrete topical treatments were studied. One is a penetrating silane sealer. The other is a pure migrating inhibitor topical product. Concrete chips at various depths were taken at different times after the concrete surface was given a topical treatment. The analysis showed that five weeks after receiving the silane sealer, the corrosion inhibitor in the sealer was present at 1.2 in (30 mm) below the treated surface. Testing on concrete cores taken 12 weeks after the pure inhibitor topical treatment indicated that one inhibitor was detected as deep as 3 in (76 mm) below the treated surface. Both results indicate that migrating topical inhibitors penetrate into the concrete interior and become available for protection of embedded steel reinforcement.

Across America and the world, structures are being used longer than their original design life. Maintenance is often significantly delayed, leading to even more damage and increasing the cost of repairs while decreasing the useful service life.

The American Society of Civil Engineers (ASCE) releases a report card on the American infrastructure every four years, using a simple A to F school report card format. Since 1998, the grades have been near failing, averaging only Ds, due to delayed maintenance and underinvestment across most categories.[1] The average grade for the 2013 report is a D+, and an estimated investment of $3.6 trillion dollars is needed by the year 2020 to improve the infrastructure to a grade of B.[1]

Spearheaded by the American Concrete Institute (ACI) and the International Concrete Repair Institute (ICRI), durability models such as LIFE-365[†] have been developed in an effort to better evaluate life cycle performance of infrastructures and to reward practices that enhance durability and include eco-friendly designs.[2]

To meet the challenge of safely extending the existing infrastructure service life, migrating corrosion inhibitor (MCI) topical treatments have been developed since the mid-1980s.[3] The inhibitors are mostly in the family of vapor phase corrosion inhibitors (VCIs), or a blend of volatile corrosion inhibitors and contact corrosion inhibitors.[3] One of the advantages of topical treatment is its ease of _____

_____
[†]Trade name.

use on existing structures. It is also economical compared to other remedial procedures.

Studies on efficacy of topical corrosion inhibitor treatments have shown that this type of mitigation technique reduced corrosion rates by 93%,[4] or extended the life expectancy by more than 15 to 20 years.[5] Furthermore, x-ray photoelectron spectroscopy (XPS) analysis of the rebar embedded in concrete topically treated with corrosion inhibitors showed that the inhibitor penetrated into rebar surfaces and formed a protective layer.[5]

Construction engineers or contractors, however, often like to know how deep or how soon the corrosion inhibitors in topical treatment would migrate from a treated surface into the concrete interior and avail themselves for the protection of embedded rebar. A simple, straightforward detection method is desired.

Direct analysis in real time-mass spectroscopy (DART-MS) is a mass spectroscopy technique that uses an atmospheric pressure ion source to instantaneously ionize gases, liquids, and solids in open air under ambient conditions.[6] It allows analyzing samples in their native state with little or no preparation, and can produce rapid results. The ionized samples can be analyzed directly by mass spectrometer.[7] DART-MS has been used for analyses in the fragrance, pharmaceutical, foods and spices, forensic science, and health industries.

DART-MS was selected as a detection tool for MCIs in concrete due to its simple sample preparation requirements. The

added advantage of analyzing samples in ambient atmosphere vs. the high vacuum required in XPS makes DART-MS particularly suitable for analyzing VCIs.

Reported here are the results of DART-MS analysis on concrete specimens at various depths from concretes that received topical corrosion inhibitor treatments. Two topical treatments were studied. Treatment A is a silane sealer containing corrosion inhibitor. Treatment B is a water-based surface treatment product of corrosion inhibitors. Results of DART-MS analysis demonstrated that inhibitors from the surface treatment migrate into the concrete interior and can be detected as deep as 3 in (76 mm) below a treated surface, and avail them to the embedded steel reinforcement for their corrosion protection.

Experimental Procedures

Two corrosion inhibitor topical treatments were studied. Treatment A is a silane sealer containing MCI. Treatment B is a water-based surface treatment product of MCIs.

Table 1 describes concretes and the surface treatment they received prior to DART-MS analysis.

Treatment A was applied to a surface of a newly made concrete block (100 by 100 by 100 mm). Five weeks after the treatment, the block was cut lengthwise. Concrete chips at the surface, at 0.6 in (15 mm) and 1.2 in (30 mm) below the treated surface, were chiseled out for analysis.

Treatment B was applied to an existing concrete structure, circa 1920. The treated surfaces were the underside of an outdoor plaza floor and its supporting beams in a crawl space below grade. Cores were taken 12 weeks after the treatment. The analysis of two cores taken from the supporting beams (B1 and B2) and one core taken from the plaza floor underside (U) are presented here. Again, concrete chips at various depths were chiseled out of the cores for analysis. Table 2 illustrates the labeling of each concrete chip for Treatment B. Blanks—concrete that received no topical treatment—were also analyzed with DART-MS as controls.

TABLE 1. CONCRETE SPECIMENS AND CORROSION INHIBITOR SURFACE TREATMENT RECEIVED

Topical Treatment	A	B
Concrete Description	Type 1 Portland cement; water/cement ratio 0.45. Cured 28 days prior to receiving topical treatment.	Existing concrete structure, circa 1920.
Topical Treatment Dosage	125 ft² /gal (3 m²/L)	150 ft²/gal (3.68 m²/L)
Time Lapse Between Topical Treatment and Concrete Sampling	5 weeks	12 weeks
Depths Analyzed	Surface, 0.6 in, 1.2 in below surface	Surface, 0.6 in, 1.2 in, 1.8 in (48 mm), 2.4 in (61 mm), 3 in below surface.

TABLE 2. LABELING OF CONCRETE SPECIMENS (TOPICAL TREATMENT B)

| Specimens	Depth (in)	Note
B1-1	Surface	Beam
B1-2	0.6	Beam
B1-3	1.2	Beam
B1-4	1.8	Beam
B2-1	Surface	Beam 2
B2-2	0.6	Beam 2
B2-3	1.2	Beam 2
B2-4	1.8	Beam 2
U-1	Surface	Floor underside
U-2	0.6	Floor underside
U-3	1.2	Floor underside
U-4	1.8	Floor underside
U-5	2.4	Floor underside
U-6	3	Floor underside

An Accutof† time-of-flight (TOF) mass spectrometer operated in positive ion mode was employed for mass measurements. The mass spectrometer resolving power was ~6,000 as measured for protonated reserpine (m/z 609.2812). A mass spectrum of poly (ethylene glycol) with average molecular weight 600 (50 µL in 10 mL methanol [MeOH]) was obtained with each data acquisition as a reference standard for exact mass measurements. The atmospheric pressure interface was typically operated at the following potentials: orifice 1 = 30 V, orifice 2 = 5 V, ring lens = 10 V. The RF ion guide voltage was set to 300 V to allow detection of ions greater than m/z 30. The DART ion source was operated with helium gas at 400 °C. The mass range was m/z 30 to 600.

Concert samples were held in the gas stream for a few seconds, using a pair of forceps, taking care not to block the mass spectrometer sample cone entrance.

Results
Treatment A

Treatment A contained one inhibitor. Its manifestation in DART-MS was a peak at m/z 90.1. This peak was detected at the surface, at 0.6 in and at 1.2 in below the treated surface when the concrete was analyzed five
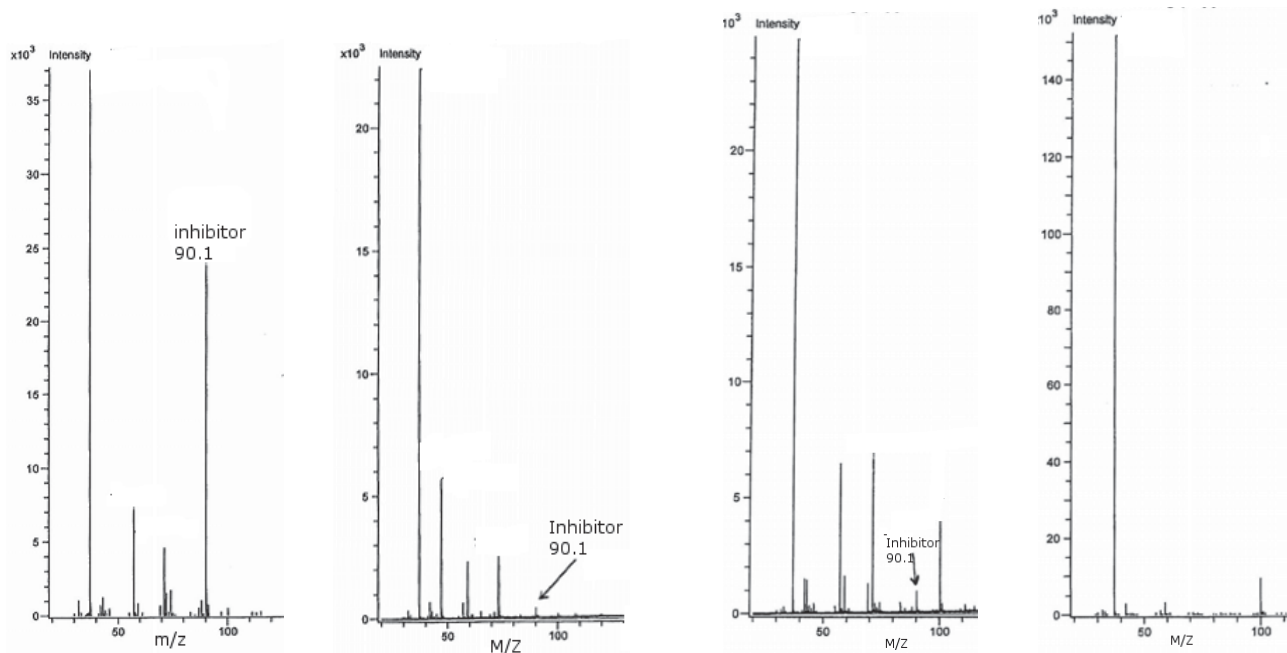
FIGURE 1. Mass spectra of Treatment A coated concrete at various depths casings.

TABLE 3. INHIBITOR DETECTION AT VARIOUS DEPTHS (TREATMENT B)

Specimens	Inhibitor I	Inhibitor II	Inhibitor III
B1-1	Yes	Yes	Yes
B1-2	Yes	Yes	Yes
B1-3	Yes	Yes	No
B1-4	Yes	Yes	No
B2-1	Yes	Yes	Yes
B2-2	Yes	Yes	No
B2-3	Yes	No	No
B2-4	Yes	Yes	Yes
U-1	Yes	Yes	Yes
U-2	Yes	Yes	No
U-3	Yes	Yes	No
U-4	Yes	Yes	No
U-5	Yes	Yes	No
U-6	Yes	Yes	Yes
Control	No	No	No

weeks after the topical treatment. This peak was not detected in untreated concrete (control) (Figure 1).

Treatment B

Treatment B contained a number of inhibitors. Inhibitor I manifested as a peak at m/z 62, Inhibitor II at 100.1, and Inhibitor III at 90.1. Table 3 shows a summary of inhibitor detection at various concrete chips.

DART-MS data in Table 3 shows that Inhibitor I and Inhibitor II were detected at all depths, as deep down as 3 in below the surface that received Treatment A. The only exception is Inhibitor II in specimen B2-3. One possible explanation for the absence of Inhibitor II in this analysis of B2-3 could be that the ion beam hit at not the cement paste but at the interior of an aggregate, since inhibitors mostly migrate within the cementitious material, but not aggregates. Inhibitors I and II were detected in all the treated concrete samples—two cores from the treated beams and one core from the treated underside of the plaza floor. Inhibitor III was detected less consistently at various depths. It was shown in all the surface specimens, and at 1.8 in depth in specimen B2-4 and at 3 in depth in U-6, but was absent in other specimens.

Penetration depth data of Inhibitor I and Inhibitor II in concrete indicate that these inhibitors are present at the depth of embedded rebar; they are available to be adsorbed onto the rebar surface to form a protective layer. This data corresponds to the XPS analysis of embedded rebar in topically treated concrete.[5]
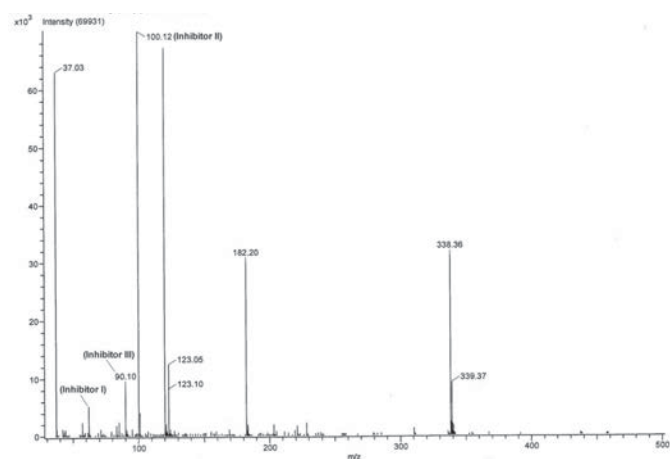
Representative mass spectra of Treatment B, of four concrete chips at different depths from core B1 (taken from the treated beam), and of a concrete chip taken from
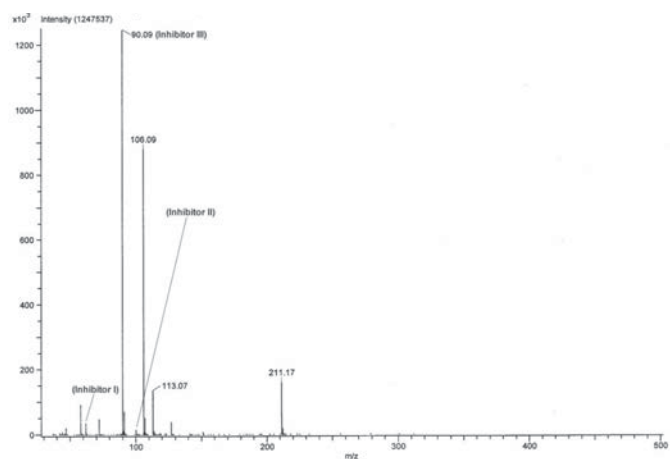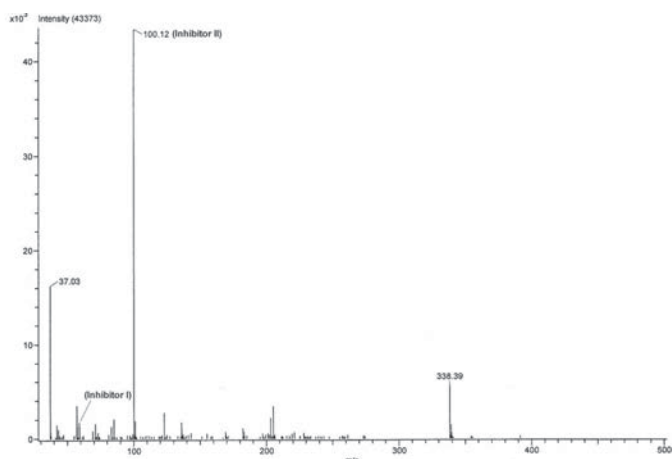
(a) **Mass** spectrum of Treatment B.
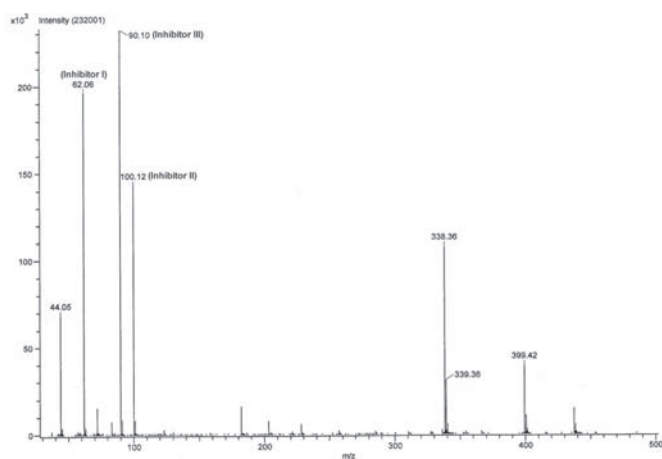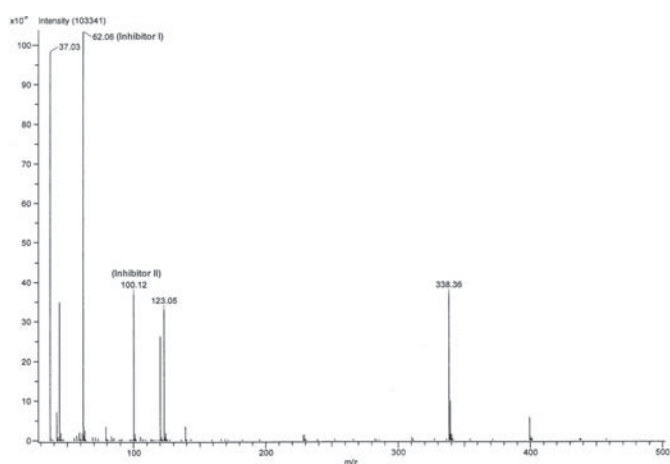
(b) **Mass** spectrum of concrete surface of treated beam.
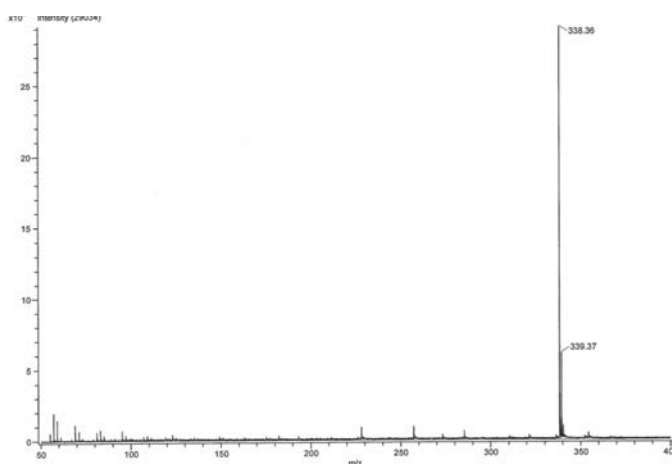
(c) **Mass** spectrum of concrete at 0.6 in below treated surface.

(d) **Mass** spectrum of concrete at 1.2 in below treated surface.

(e) **Mass** spectrum of concrete at 1.8 in below treated surface.

(a) **Mass** spectrum of untreated concrete (control).

FIGURE 2. Mass spectra of Treatment B coated concrete.

an untreated area of the beam (control), are shown in Figure 2.

Conclusions

DART-MS analysis of concrete chips, taken at various depths of concrete, shows that the inhibitors migrated to the concrete interior from the treated surface, to as deep as 3 in. The surface treatment could be in the form of a sealer containing corrosion inhibitor such as Treatment A; or in the form of a water-based corrosion inhibitor product such as Treatment B. Inhibitor migration occurs in newly made concrete and also in existing concrete structures, making the migrating inhibitor treatment a valuable tool in rehabilitating our aging infrastructure.

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Cortec® Films

Improved Packaging Film Incorporating Vapor Phase Corrosion Inhibitors and High Recycle Content

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Vapor phase corrosion inhibitors (VCIs) are used for safe and cost-effective protection of a wide range of metal articles. One large market includes packaging materials for storage and transportation of metal parts. Plastic packaging films can be readily impregnated with VCIs to provide corrosion protection, in addition to the basic physical barrier (against water, dirt, or vapors) afforded by the plastic. Generally, VCI-containing plastic films are recyclable. Likewise, they can be made from recycled plastics. However, when manufacturing with commercially available recycle streams, use of the recycled plastic is often limited by contamination and the extent of polymer degradation. This article discusses the benefits of using in-house recycling lines, including improved environmental profile, better quality, and cost savings. The results are supported by data and experience with in-house recycling lines at two production facilities.

Vapor phase corrosion inhibitors (VCIs) are a well-known and highly versatile range of products for the prevention of corrosion.[1] VCIs can be delivered to the target metal in a variety of ways. One common product is plastic packaging.[2] Plastic VCI films are a versatile and highly effective article for protection of items from corrosion. They are generally made from polyethylene (PE), which is readily available, cost effective, and usually recyclable.[3] Production of VCI films usually results in the production of at least some "scrap" film. This may be film of variable size produced during production start-up, or film that does not meet specifications. Scrap can be disposed of as trash, but is preferably recycled. The usual mode of recycling is to reprocess it (melt processing) into pellets that can be reused in production of new film.[3] It is often referred to as "repro." Reprocessing can be done in-house with dedicated machines or the scrap can be sent to external facilities that specialize in recycling. The quality of repro can vary considerably with the quality/purity of the scrap and the conditions used for reprocessing (particularly temperature and shear).[4] In this article, studies are cited on varying the source and quantity of repro and the effects on product quality. Results and commercial implications are discussed.

Experimental Procedures

Materials
PLASTIC RESINS
Commercial low-density PE (LDPE) and linear low-density PE (LLDPE) were used in proprietary combinations for the production of films. Slip and anti-block additives were used as necessary.

VCIs
VCIs were composed of proprietary formulations. The VCIs were added to the pellet blend as a master batch.

REPROCESSED PLASTIC RESINS
In-house reprocessed resin (repro) was prepared from VCI film scrap at two different facilities, using commercial re-granulator equipment. Some experiments utilized a commercial repro of LDPE. This was a clear material with a melt index of ~2 (2.16 kg, 190 °C). Sources varied.

Methods
MONOLAYER BLOWN FILM EXTRUSION
Films were produced on commercial blown film production lines in Cambridge, Minnesota, using standard melt processing temperatures in the range of 160 to 200 °C. Films contained a blend of commercial film-grade PE resins (LDPE and/or LLDPE). All samples contained a proprietary VCI, added as a master batch. Total concentration of active ingredients in the final film was ~2% by weight.

COEXTRUDED BLOWN FILM EXTRUSION
Films were produced on commercial blown film production lines in Beli Manastir, Croatia, using standard melt processing temperatures in the range of 160 to 200 °C. Films contained a blend of commercial film-grade PE resins (LDPE and/or LLDPE). All samples contained a proprietary VCI, added as a master batch. Total concentration of active ingre-

dients in the final film was ~1-2% by weight, depending on the specific film construction. The coextrusion die produced three layers (fed by three separate extruders).The general film construction included thickness/wt% of 25/50/25 for the three layers, respectively. VCI was added to one or more of the layers depending on the specific product.

PHYSICAL PROPERTY TESTING

The physical property testing was conducted with commercial testing instrumentation per the methods referenced below. These are primarily methods from ASTM for determining film thickness (caliper), ASTM D6988;[5] tensile properties, ASTM D882-02;[6] impact, ASTM D1709-04 Method A;[7] tear, ASTM D1922-06A;[8] coefficient of friction, ASTM D1894;[9] and seal strength, ASTM F88-99.[10] Puncture resistance was determined accord-

ing to Test Method 2065 of Military Standard 3010.[11] The results are generally shown with the number of digits in the instrument output report. However, for comparison purposes, differences between film sample results of less than about 10% are not considered significant. While the test methods can be quite precise, there is considerable variability in film samples due to small differences in composition and the effects of processing variables. In particular, physical properties of blown films are strongly dependent on orientation of the molecules in the film, which is a complex function of molecular structure, bulk melt viscosity/elasticity, processing temperatures, equipment design, cooling rate, processing speed, and blow up ratio (ratio of bubble diameter to die diameter).[12] Many material properties are measured in both the machine direction (MD) and transverse direction (TD), as these

properties are often different due to the different extent of orientation in these directions. For some properties, it is common for the MD and TD to be inversely correlated (as one increases, the other decreases).

VAPOR-INHIBITING ABILITY CORROSION INHIBITION TEST

The vapor-inhibiting ability (VIA) test measures the effectiveness of the VCI. Testing was performed by standard methods as previously described.[13] In brief; sanded carbon steel (CS) plugs are suspended from a modified lid in a quart jar. Strips of the test substrate, 1 by 6 in (25 by 150 mm) are hung from the inside of the lid, ensuring they do not come in contact with the plug. The jars are left to condition for 20 h at ambient temperature. After conditioning, a glycerol/water solution is added to the jars to accelerate cor-

TABLE 1. COMPARATIVE DATA—MONOLAYER FILMS							
Property	Direction	Units	No Repro	15% Blue Repro	20% Blue Repro	15% Blue Repro, 5% Clear	10% Blue Repro, 10% Clear
Caliper	—	μm	107.95	105.92	106.17	107.70	106.17
Breaking Factor	MD	kN/m	3.43	3.13	3.05	3.02	2.95
	TD		3.29	2.77	2.88	2.80	2.79
Tensile Strength at Break	MD	MPa	32.96	30.08	29.89	28.66	27.75
	TD		31.19	27.15	28.19	26.83	26.26
Elongation at Break	MD	%	739.54	655.21	720.65	645.45	663.60
	TD		833.85	734.19	833.80	761.28	777.69
Yield Strength	MD	MPa	15.17	9.28	9.49	9.77	8.89
	TD		14.21	9.98	10.47	10.18	10.43
Dart Drop Impact Resistance	—	Grams	623.30	728.06	737.94	693.03	687.47
Puncture Resistance	—	N	32.52	32.29	34.03	29.98	32.61
Tear Strength	MD	mN	6,621.69	5,570.38	4,848.58	4,958.42	4,252.32
	TD		16,632.67	14,906.64	15,691.20	15,659.82	14,969.40
Coefficient of Friction	—	Static	0.20	0.52	0.49	0.55	0.50
	—	Kinetic	0.27	0.53	0.51	0.56	0.51
Seal Strength	—	kN/m	NA	1.70	1.64	1.60	1.60
Razor Blade (Steel)	—	—	Pass	Pass	Pass	Pass	Pass
Razor Blade (Copper)	—	—	Pass	Pass	Pass	Pass	Pass
VIA	—	—	Pass 3, 2, 3	Pass 2, 2, 2	Pass 2, 2, 3	Pass 2, 3, 3	Pass 2, 2, 3

TABLE 2. COMPARATIVE DATA—MONOLAYER FILMS

Property	Direction	Units	20% Blue Repro	15% Blue Repro, 5% Clear	15% Blue Repro
Caliper	—	μm	103.63	104.17	102.92
Breaking Factor	MD	kN/m	2.70	2.83	2.91
	TD		2.94	2.73	2.67
Tensile Strength at Break	MD	MPa	26.72	27.98	28.47
	TD		29.10	27.13	26.37
Elongation at Break	MD	%	622.70	715.11	737.55
	TD		733.96	792.60	773.75
Yield Strength	MD	MPa	9.05	9.40	9.30
	TD		10.37	10.14	9.98
Dart Drop Impact Resistance	—	Grams	742.03	719.53	701.20
Puncture Resistance	—	N	30.96	30.83	31.09
Tear Strength	MD	mN	6,966.89	64,96.16	6,904.13
	TD		15,377.38	15,377.38	15,942.26
Seal Strength	Left	kN/m	1.78	1.69	1.50
	Center		1.33	1.37	1.34
	Right		1.75	1.77	1.64

TABLE 3. COEXTRUDED FILMS

Property	Direction	Units	No Repro	40% Repro (Mid Layer) In House	40% Repro (Mid Layer),30% In House, 10% Commercial
Caliper	—	μm	100	100	100
Breaking Factor	MD	N	61.68	60.61	55.07
	TD		60.93	65.67	56.05
Tensile Strength at Break	MD	MPa	22.72	21.92	22.00
	TD		24.63	24.02	22.50
Elongation at Break	MD	%	674.40	694.10	687.40
	TD		796.40	878.40	806.20
Tear Strength	MD	mN	6,696.96	8,580.48	6,121.44
	CD		21,346.56	17,893.44	15,382.08
Impact Puncture	—	N	17,605.68	17,684.16	16,428.48
	—	J	1.51	1.52	1.42
Coefficient of Friction	Kinetic	—	0.20	0.21	0.21
	Static	—	0.22	0.23	0.23

rosion and left to sit at ambient temperature for 2 h, then in a 40 °C oven for 2 h. The plugs are removed and rated on a scale of 0 (heavily corroded) to 3 (no visible corrosion). A grade of 2 or 3 is considered passing.

Razor Blade Corrosion Inhibition Test

This test measures the effectiveness of the film in preventing corrosion when in direct contact with a metal surface. Testing was performed by standard methods as previously described.[13] In brief, CS panels are cleaned in methanol and dried. Two drops of deionized (DI) water are placed on the metal panel and covered with the substrate of interest. After 2 h, the substrate is removed and the panels are inspected. Panels with any sign of corrosion, pitting, or staining are deemed to "fail" the test. A second test is conducted with copper panels. The method is the same except that a 0.005% (by weight) sodium chloride (NaCl) solution is used instead of water and the test time is extended to 4 h.

Results

Monolayer Films

The films compared in Table 1 were produced on a machine with an 8-in (200-mm) diameter die, with a blow up ratio of 2:1. The "blue repro" is material made in-house from VCI scrap. The "clear repro" is commercially purchased material containing no VCI. The table shows a comparison of films containing up to 20% repro (in various combinations) with a comparable formulation containing all virgin resins (no repro).

All of the samples passed the corrosion inhibitor tests. Most of the physical property results are not considered to be significantly different. The differences in the coefficient of friction values are due to different levels of slip and anti-block additives in the formulations (not to the use of repro). There are possibly real differences between samples for yield strength, tear strength, and tensile strength at break, with the repro containing formulations showing slightly reduced properties. However, all films are perfectly acceptable for use.

There were no significant physical property differences between the samples using in-house (blue) repro and those using commercial (clear) repro. However, the samples made with the commercial repro had a large number of "unmelts." These are physical defects in the film due to small pieces of plastic (~10 to 100 μm) that are visible in the film and create a rough feel to the surface. Unmelts may be caused by contamination in the resin, often from higher melting plastic contaminants in the reprocessing feed stream.

Table 2 shows results for a similar experiment run on a larger film line, with a die 20 in (500 mm) in diameter. The table compares films with 15 to 20% repro, in various combinations. Again, there were no significant differences between the physical properties at 15% or 20% repro, or with in-house vs. commercial repro. Again, however, the film made with commercial repro showed a large number of unmelts.

Coextruded Films

The films compared in Table 3 were produced on a machine with a 400-mm diameter die, with a blow up ratio of 2:1. The repro is used at 40% in the center layer, which makes up 50% of the film structure, so the repro makes up 20% of the bulk film composition. Here again, the differences between physical properties of the films are mostly not significant, with the possible exception

of cross direction (CD) tear strength. The sample with all in-house repro appears to have somewhat better properties than the one made with commercial repro. The commercial repro used in this study was from a different source than the material used in the monolayer films. In the coextruded films, there was no significant increase in unmelts in films made with the commercial repro.

The data in Table 4 show an experiment with a different grade of film. This uses only 10% repro in the center layer (5% of film). It again shows no significant degradation of film physical properties.

Conclusions

It is shown by the data presented in this article that it is feasible to make VCI packaging films using repro resins with no or minimal compromises in physical properties. Films containing up to 20% repro were demonstrated. In-house produced repro is generally superior due to its contribution of VCI to the final product, along with better consistency and generally reduced levels of contamination. From a cost perspective, commercial repro is generally about half the price of virgin resin. In-house repro can be significantly lower in cost, depending on the specific equipment used and local labor costs.

One further advantage of in-house reprocessing is the elimination of shipping; either one-way (purchase of commercial repro) or two-way (shipping scrap to the preprocessor and the return transit of the repro to the film facility). This produces significant environmental advantages in addition to the cost savings. The structure of coextruded films makes them especially well suited for incorporation of repro, as it can be "buried" in the middle layer with even less effect on bulk physical properties and VCI performance. Depending on the quality of in-house repro, it is likely that loading levels significantly greater than 20% can be achieved with good processability and film performance.

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TABLE 4. COEXTRUDED FILMS

Property		Units	No Repro	10% Repro (Mid Layer) In House
Caliper	—	μm	100	100
Breaking Factor	MD	N	59.76	60.25
	TD		61.83	58.92
Tensile Strength at Break	MD	MPa	24.13	23.25
	TD		26.70	24.89
Elongation at Break	MD	%	448.00	432.60
	TD		949.40	928.50
Tear Strength	MD	mN	5,127.36	4,604.16
	CD		16,847.04	16,376.16
Impact Puncture	—	N	19,567.68	19,724.64
	—	J	1.69	1.70
Coefficient of Friction	Kinetic	—	0.22	0.22
	Static	—	0.24	0.24

Evaluation of Impressed Current Cathodically Protected Tank Bottoms in the Presence of Vapor Phase Corrosion Inhibitor

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This work aims to assess the effectiveness of an amine carboxylate-based vapor phase corrosion inhibitor (VCI) on the protection of storage tank bottoms against soil-side corrosion, as standalone and in combination with an impressed current cathodic protection (ICCP) system. It also attempts to determine the effect of VCI on instant-off potential. Lab-scale tanks simulating the environment of single bottom storage tanks sitting on washed sand with a high-density polyethylene (HDPE) liner and ICCP system were considered. The corrosion rate for each tank was monitored using an electrical resistance probe corrosion monitoring system. Natural and instant-off potentials of tank bottom steel plates were also monitored throughout the experiment using a temporary copper/copper sulfate ($Cu/CuSO_4$) reference electrode. Corrosion rate data from electrical resistance probes indicated that amine carboxylate VCI slurry is effective in mitigating corrosion on carbon steel bottom plates. The corrosion rate was reduced by 82.5% and 89.7% as standalone and in combination with ICCP, respectively. The study also indicated a shift of the instant-off potential, which might need to be considered by CP operators in the case of using a VCI in supplementing ICCP for protection of storage tank bottoms.

Soil-side corrosion is a principal cause of storage tank failure and imposes a major environmental and operational challenge worldwide. Several techniques have been adopted to mitigate soil-side corrosion of aboveground storage tank (AST) floors, such as bituminous sand, impressed current cathodic protection (ICCP), and coatings. However, the total effectiveness of these techniques, as standalone or combined, have been questionable in providing the required protection, especially against pitting corrosion.

Al-Sulaiman[1] discussed the possibility of a bituminous layer trapping moisture and corrosive species between the underside of the tank floor and construction pad, resulting in a corrosive environment. The author also highlighted the likelihood of the bituminous layer when combined with CP to shield protection current and render the CP system ineffective, at least partially. Yu[2] concluded that inevitable air gaps between the construction pad and tank bottom plates block CP current at that location and consequently prevent its uniform distribution on the underside surface of the tank bottom. Chatterjee[3] emphasized that underside coating of bottom plates alone cannot prevent corrosion due to unavoidable defects during its application and deterioration during tank operation.
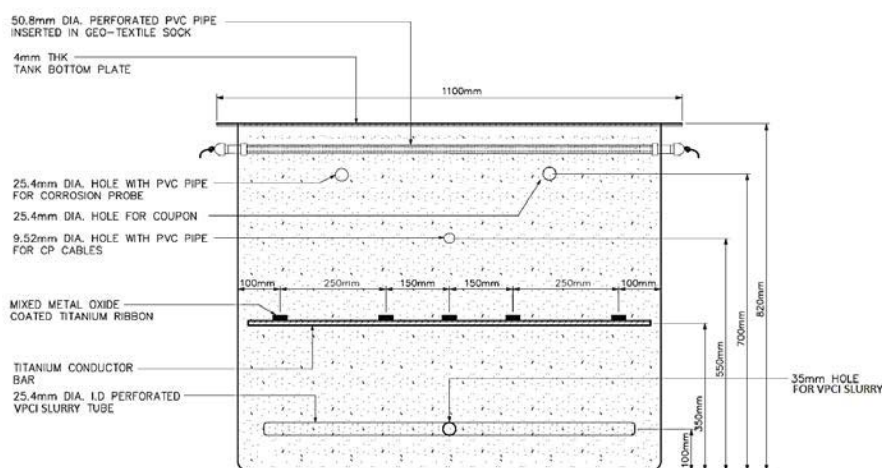
There is a growing industrial awareness

FIGURE 1. Section view of lab-scale tank.

about the importance of finding a viable solution to supplement the performance of the aforementioned techniques in an attempt to achieve a comprehensive corrosion protection scheme for the tank bottom. One promising solution is the use of amine carboxylate-based vapor phase corrosion inhibitors (VCIs). An amine carboxylate VCI is a chemical substance that acts to reduce soil-side corrosion by a combination of volatilization from a VCI material, vapor transport in the headspace between floor plates and the tank pad atmosphere, and condensation onto surfaces in the space. The condensation process includes adsorption, dissolution, and hydrophobic effects on metal surfaces, where the rate of soil-side corrosion of bottom plate surfaces is thereby inhibited.

VCI material comes in a powder form composed of fine white crystalline amine carboxylate-based material infused with silica to eliminate clumping and ensure smooth fogging application through the tank floor. It also comes as a thin liquid solution, delivered into the interstitial spaces under the tank floor through injection pipes placed in the sand layer. During tank construction, VCI powder enclosed in a pouch constructed from a breathable membrane is used. This breathable pouch allows the VCI molecules to sublimate through the membrane, diffuse through the sand layer, and form a molecular layer on the tank bottom plates that provides soil-side corrosion protection.[4]

One of the first publications that confirmed the potential of using VCI material for soil-side corrosion protection, including pitting, of AST bottoms was written in 1993 by Rials et al.[5] Since then, several other published technical articles have recommended and/or confirmed the viability of VCI as a potential solution for this chronic industrial problem.[4-12] The use of VCI in protecting tank bottoms against soil-side corrosion has been classically coupled with the use of electrical resistance (ER) probes to monitor their impact on the corrosion rate data before and after injection. Unlike other indirect corrosion monitoring systems, ER probes are designed to evaluate and continuously monitor the corrosiveness of the surrounding
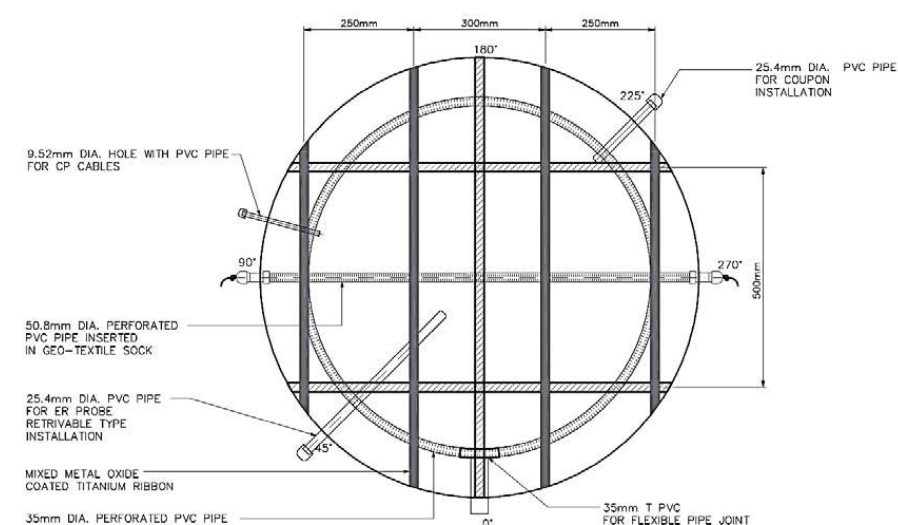

FIGURE 2. Plan view of lab-scale tank.

FIGURE 3. Electrical resistance probe used for the experiment.

environment under the tank floor. In most cases, ER probes are used as the primary corrosion rate monitoring technique. They are usually installed away from the inhibitor injection point to confirm inhibitor diffusion and evaluate the overall effectiveness of VCI material.[4,7-8,11-12] However, to our best knowledge, the interaction and effect of introducing such chemicals under the tank floor on the instant-off potential of an ICCP-protected storage tank bottom and soil-side corrosion haven't been investigated.

An experiment was designed to assess the effectiveness of amine carboxylate-based VCI slurry in protecting single storage tank bottoms against soil-side corrosion. The experiment also looked into the effect of VCI slurry on the instant-off potential when installed in combination with the ICCP system.

Experimental Procedures

Six lab-scale tanks simulating the environment of single bottom storage tanks sitting on sweet sand with a high-density polyethylene (HDPE) liner and ICCP system were constructed and examined

for 120 days. Plastic tanks 1 m in diameter were cut off their tops and filled with washed sand having an average resistivity of 35,000 Ω·cm. Each tank was fitted with a 35-mm in diameter perforated VCI slurry dispensing ring positioned 100 mm above the tank bottom. A mixed metal oxide (MMO) anode grid was placed 270 mm below the steel plate. An ER probe was placed about 100 mm below the steel plate. Slotted monitoring polyvinyl chloride (PVC) pipe 50 mm in diameter was also installed in each tank. After compacting and leveling, a 4-mm thick sandblasted round steel plate was placed over the sand. The plates were weighted down with cement blocks and sealed with caulking. Figures 1 and 2 show an illustration of the test tank design.

Figure 3 shows the ER probe selected for this experiment. This probe configuration was chosen for compatibility with the PVC access pipe, which was installed under the steel plate of each tank. Data from the probes were taken on a daily basis by connecting to a data logger supplied by the probe manufacturer.
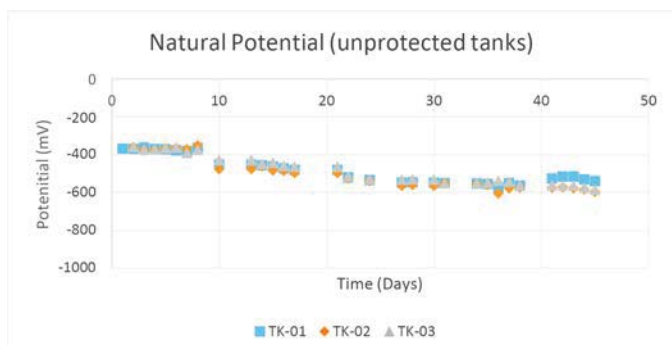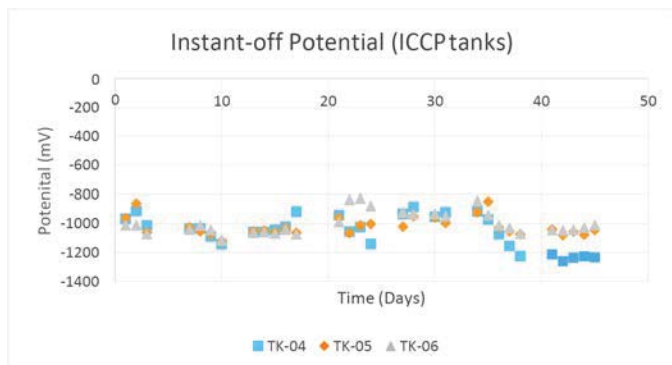
FIGURE 4. Natural potential of unprotected tanks during pre-injection phase.
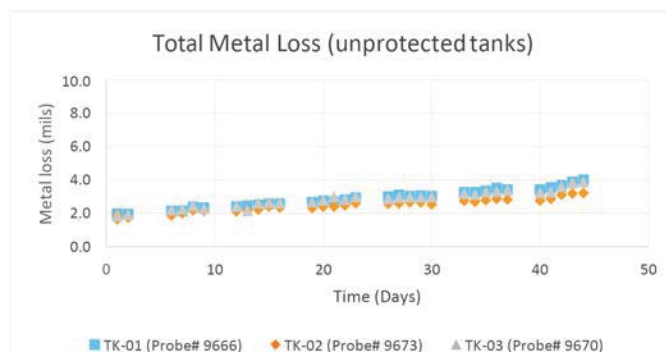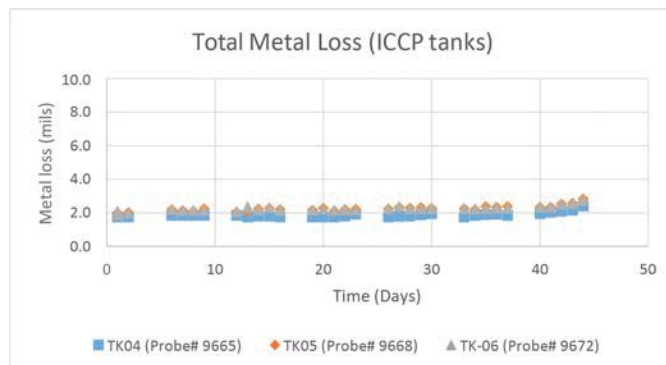

FIGURE 5. Total metal loss of ER probes installed in unprotected tanks during pre-injection phase.

FIGURE 6. Underside steel plate of unprotected tanks at the end of pre-injection phase.

FIGURE 7. Natural potential of ICCP-protected tanks over time during pre-injection phase.

FIGURE 8. Total metal loss of ER probes installed in ICCP-protected tanks during pre-injection.

FIGURE 9. Underside steel plate of ICCP-protected tanks at the end of pre-injection phase.
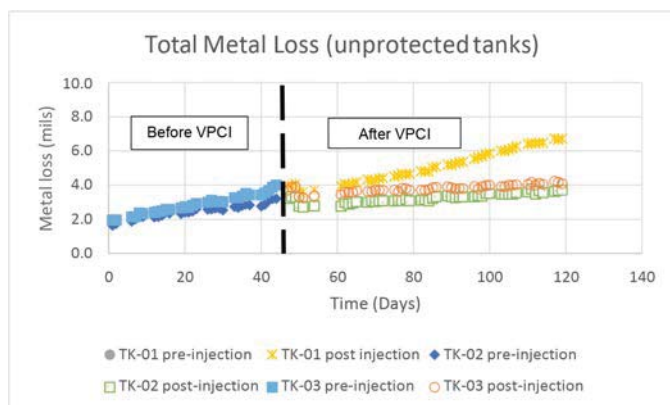
FIGURE 10. Comparison between total metal loss of ER probes installed in unprotected tanks before and after injection of VCI slurry.
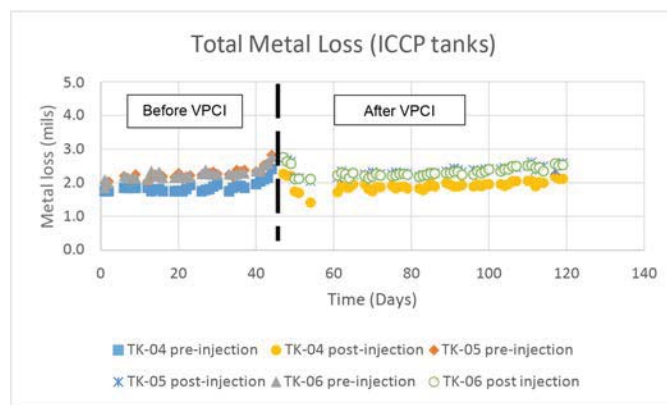

FIGURE 11. Total metal loss of ER probes installed in ICCP tanks before and after injection of VCI slurry.

TABLE 1. CORROSION RATE DATA RESULTS

| Tank Category	Tank Tag # and Probe ID	Corrosion Rate Before VCI Application (mpy)	Corrosion Rate after VCI Application (mpy)	Percentage of Corrosion Rate Reduction After VCI Application
Unprotected Tanks	TK-01 (probe # 9666)	15.44	6.39	58.6%
	TK-02 (probe # 9673)	10.73	0.91	91.5%
	TK-03 (probe # 9670)	15.44	0.40	97.4%
ICCP Tanks	TK-04 (probe # 9665)	2.52	0.29	88.4%
	TK-05 (probe # 9668)	3.80	0.29	92.3%
	TK-06 (probe # 9672)	3.50	0.40	88.5%
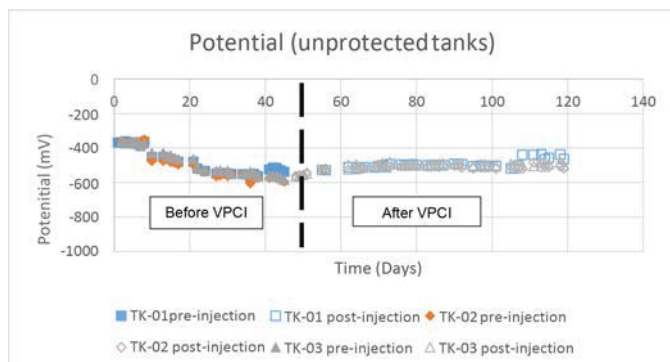
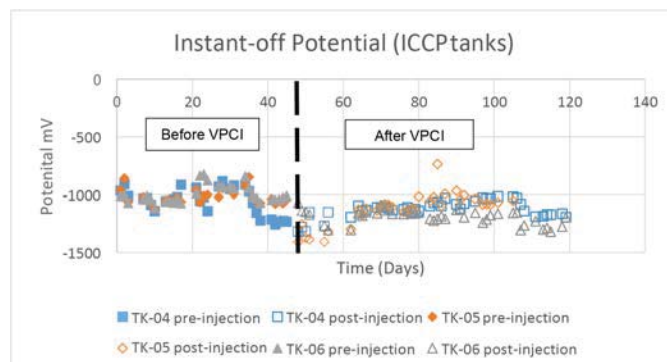**FIGURE 12.** Change in potential of unprotected tanks before and after injection of VCI slurry.

FIGURE 13. Change in instant-off potential of ICCP tanks before and after injection of VCI slurry.

The natural potential of the six tanks was measured and recorded using a copper/copper sulfate (Cu/CuSO4) reference electrode. The six tanks were randomly split into two groups; three tanks had their ICCP system activated and the other three hadn't. The input current for the ICCP tanks was adjusted to 29 mA until −850 mV instant-off potential was achieved.

The experiment was divided into two phases; pre-injection and post-injection of VCI slurry. During the pre-injection phase, corrosion rate data were collected and the natural potential for unprotected tanks and instant-off potential of ICCP tanks were monitored for 45 days. When steady state was achieved, the tanks were opened and the status of each steel plate was photographed. Plates were put back into their original place and sealant was reapplied. VCI slurry was injected through the preinstalled dispensing ring in all tanks. The effect on metal loss of the ER probes and the instant-off potential of the steel plates was monitored for 75 days.

Results
Pre-Injection Phase
The natural potentials of the unpro-tected tanks (TK-01, TK-02, and TK-03) continued to shift in the negative direction until it stabilized at an average of −551 mV after approximately 20 days (Figure 4). Corrosion rate data from the ER probes installed in non-CP protected tanks showed an average corrosion rate of 15.5 mpy as calculated per Equation (1) from the data in Figure 5.

$$CR = \frac{M2 - M1}{\Delta T} \times 365 \qquad (1)$$

where ΔT is the lapse time in days between total metal loss between M1 and M2.

The high corrosion rates from the ER probes were confirmed by the actual status of the steel plates. Upon removal of the steel plates from the unprotected tanks, it was observed that the internal surfaces were covered with sand and corroded, especially at the center area (Figure 6). ICCP protected tanks (TK-04, TK-05, and TK-06) showed an average instant-off potential of −1,024 mV (Figure 7), satisfying the −850 mV instant-off protection criteria. Corrosion rate data from ER probes installed in control tanks showed an average corrosion rate of 3.2 mpy as calculated per Equation (1) from the data in Figure 8.

The low corrosion rate is in line with the fact that protection criteria were achieved. However, visual inspection of the underside surface of the plates revealed considerable levels of corrosion (Figure 9). Despite meeting the −850 mV instant-off protection criteria, the actual status of the underside surfaces showed otherwise. The corrosion morphology looked similar to the unprotected tanks.

This might be attributed to the fact that the CP system was not commissioned during and after the construction of tanks for a period of about two weeks. Similar challenges, even on a larger scale, exist in real life, where tanks take from several months to years to be boxed up and their CP systems commissioned. Tank bottom plates are usually left without any protection during this time. In other cases, lack of availability of a power supply hinders activation of the CP system for several years at the job site.

Post-Injection Phase

After injection of VCI slurry through the dispensing ring, a noticeable effect was observed on the metal loss of ER probes in both unprotected (Figure 10) and ICCP protected tanks (Figure 11). The average corrosion rate of ER probes installed in TK-02 and TK-03 reduced from 13.1 mpy to 0.66 mpy, with an average percentage reduction of 95%. However, the corrosion rate in TK-01 didn't reflect the same level of effect after VCI application where the corrosion rate was reduced from 15.44 to 6.39 mpy, a 59% reduction only. For ICCP-protected tanks, the average corrosion rate of ER probes went from 3.2 mpy to 0.3 mpy, with an average percentage reduction of 90%. It is worthwhile to note that the introduction of VCI

slurry under the tank plate helped maintain an average corrosion rate under 1 mpy in all tanks, excluding TK-01. Table 1 summarizes the corrosion rates of the individual ER probes before and after VCI application. It is worthwhile to note that the reduction in the corrosion rate of all ER probes not only confirmed the ability of VCI molecules to diffuse through a compacted sand layer over a short period of time and protect the underside of the tank floor, but also diffused through the corrosion product layer on the tank floor and hence reduced the corrosion rate of pre-rusted steel.

It was noticed that VCI slurry shifted the average potential of unprotected tanks from −550 mV to −500 mV (Figure 12). For ICCP tanks, each tank reacted differently to the VCI slurry (Figure 13). In TK-05, the average instant-off potential shifted temporarily from −1,020 mV before injection, to −1,205 mV for the first 19 days before it started to go back to the original value through the end of the experiment. TK-06 also showed a transient behavior, where its instant-off potential shifted in the negative direction from an average of −1,000 mV to reach a value of −1,300 mV on day 16 after injection. However, the instant-off potential shifted in the positive direction to stabilize at an average of −1,200 mV until the end of the experiment.

Prior to injection of VCI slurry, TK-04 showed an average instant-off potential of −1,004 mV for about 36 days. A sudden shift in the negative direction of the instant-off potential was noticed on day 37 and continued for seven days before injection of VCI slurry to reach −1,318 mV. After the introduction of VCI slurry, no clear change was noticed until the end of the experiment. However, if the average instant-off potential for all tanks was considered before and after injection in Figure 13, it can be concluded that an overall shift of 150 mV in the negative direction occurred. Although the findings might not be conclusive in terms of an exact value of the potential shift and whether this shift is permanent or transient, the CP operator can expect a shift in the instant-off potential of the protected tank. Therefore, a longer study should be conducted to answer such queries.

Conclusions

Soil-side corrosion on ASTs, including those protected by CP, can present a chronic

challenge to operating companies. There is a growing industrial awareness about the importance of finding a viable solution to supplement the performance of the aforementioned technique. One promising solution is the use of an amine carboxylate-based VCI. This experiment was designed to assess the effectiveness of an amine carboxylate-based VCI system on the protection of AST bottoms against this type of corrosion as standalone and in combination with an ICCP system. The experiment also looked into the effect of VCI slurry on the instant-off potential and in turn the protection criteria of an ICCP system. The obtained results led to the following conclusions:

- Despite having a CP system satisfying the protection criteria of −850 mV instant-off potential, the tanks showed signs of soil-side corrosion. This might be partially attributed to the CP system not being commissioned as soon as the tanks were constructed, allowing the corrosion process to start. Due to the spontaneous protection mechanism of an amine carboxylate VCI system, it might be advantageous to introduce amine carboxylate VCI material into the tank sand pad to provide protection of the underside of tank bottom plates during construction and until the CP system gets commissioned.

- ER corrosion rate probes can be used to evaluate the corrosiveness of the environment under an AST and indicate the effectiveness of VCI in reducing and controlling soil-side corrosion.

- VCI slurry can be effectively introduced and distributed through a designed online injection system under existing and new ASTs.

- VCI slurry alone showed the ability to reduce the corrosion rate by 82.5%, which makes it a viable solution to protect against soil-side corrosion, especially for tanks without a CP system or when the existing CP system is deficient.

- VCI slurry in combination with ICCP showed a synergetic effect on the corrosion rate and helped maintain it below 0.5 mpy, with an average reduction of 89.7%. This suggests that supplementing new and existing CP systems with VCI material is therefore advantageous to operating companies. The introduction of VCI slurry may have

an effect on instant-off potential and this might need to be considered by CP operators in the case of using VCI slurry in supplementing an existing ICCP system. However, an experiment for longer duration or actual field trials is required to confirm the value of this effect and whether it is transient or permanent.

Acknowledgements

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