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Evaluation of RheoCrete 222+ as Rust Preventative Concrete Admixture and DYNA Hardener as Rust Remover

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ISO 9001 Quality System Registered
Environmental ISO 14001 Certified System Registered

Background:

Sample of RheoCrete 222+, manufactured by BASF, was provided by Cortec Middle East for evaluation to determine if it behaves as a corrosion inhibitor, and to compare against Cortec MCI-2005. The hardener component of a 2K epoxy, DYNA coat, was also submitted for evaluation because it was witnessed to protect metal and remove rust in the field.

Method:

1. ASTM G180 Standard Test Method for Corrosion Inhibiting Admixtures for Steel in Concrete by Polarization Resistance in Cementitious Slurries
2. Immersion Testing, CC-029
3. FTIR Analysis, CC-006
4. GCMS Analysis
5. Salt Spray Environment, ASTM B117
6. Rust Removal Evaluation

Materials:

- Lab grade methanol
- GC grade methanol
- Lab grade calcium hydroxide
- Lab grade sodium chloride
- Deionized water
- Ten C1215 plugs for G180
- Helium carrier gas for GCMS
- ZnSe FTIR Plates
- Eight 1” x 3” 1008 Steel Panels
- Five 3” x 5” 1008 Steel Panels
- MCI-2005 (B# 06545)
- Hydrochloric Acid

Procedure:

1. ASTM G180 Standard Test Method
   - 0.5M sodium chloride concentration used
   - RheoCrete 222+ was tested at its recommended dose rate of 5 L/m^3 (as per RheoCrete 222+ data sheet). MCI-2005 was tested at its recommended dose rate of 0.6 L/m^3.
2. Immersion Testing
   - Test Solution: 3% NaCl, 0.42% $Ca(OH)_2$, comparative inhibitor concentrations
   - Temperature: 40 ± 2 °C
   - Exposure Time: 312 hours
   - Metal: 1008 Steel
3. GCMS Analysis done with RheoCrete 222+ in GC grade methanol
   - 2 minutes hold time at 40°C
   - 10°C/min ramp to 260°C
   - 15 minutes hold time at 260°C
4. FTIR Analysis done on ZnSe plates
5. Salt Spray on panels coated with DYNA hardener
   - Coat 1008 steel panels with DYNA Coat hardener and allow to dry
   - Expose coated panels to ASTM B117 salt spray conditions for 24 hours

- Evaluate the condition of the panels

6. Rust removal testing
   - Expose 1008 steel panels to ASTM B117 conditions for two hours to establish a layer of rust on the metal surface.
   - Apply DYNA coat and VpCI-422 to the metal surface.
   - Dab product from the metal surface at set intervals (2.5, 5, and 10 minutes)
   - Evaluate rust removal properties based on the remaining oxidation

ASTM G180 Results and Discussion:

ASTM G180 is a standardized test method used to qualify given admixtures for their ability to inhibit corrosion on steel reinforcement in concrete structures. The test is performed by mimicking the chemistry present in concrete, and consequently the chemistry steel reinforcement is exposed to.

First, mortar mixes are prepared and the liquid component is extracted. Then calcium hydroxide is added and CO_2-free air is purged through the solution for several days while stirring. A steel sample is exposed to the solution during this time, allowing it to form passivating layers or any other protection offered by the admixture. On the second day, sodium chloride is added to bring the solution to a 0.5 M concentration, and the stirring is stopped to encourage crevice corrosion. On the third day, electrochemical testing is performed by varying the potential applied to the metal sample and measuring the resulting current.

The results of the G180 standard test method are primarily interpreted from the experimentally derived polarization resistance (Rp). To qualify as a corrosion inhibitor in this test method, the average $\log_{10}(1/Rp)$ value must be 1.0 or less than that of the control. The Icorr and corrosion rate are largely just interpretations of the Rp.

	Control 1	**Control 2**	**Control Avg.**
Rp (kΩ)	3.565	2.776	3.1705
Avg. $\log_{10}(1/Rp)$	-0.498		
Icorr (mA/cm^2)	1.624	2.086	1.855
Corrosion rate (mpy)	0.814	1.046	0.93

	MCI-2005 1	**MCI-2005 2**	**MCI-2005 3**	**MCI-2005 4**	**MCI-2005 Avg.**
Rp (kΩ)	19.14	55.99	61.47	30.06	41.665
Avg. $\log_{10}(1/Rp)$	-1.574				
Icorr (mA/cm^2)	0.302	0.103	0.094	0.193	0.173
Corrosion rate (mpy)	0.136	0.056	0.043	0.087	0.0805

	RheoCrete 222+ 1	**RheoCrete 222+ 2**	**RheoCrete 222+ Avg.**
Rp (kΩ)	1.568	1.197	1.3825
Avg. $\log_{10}(1/Rp)$	-0.137		
Icorr (mA/cm^2)	3.693	4.836	4.2645
Corrosion rate (mpy)	1.688	2.209	1.9485

Table 1: Results from ASTM-G180 Standard Test Method. The control values were taken from previous data.

When evaluated with the ASTM G180 test method for polarization resistance (Rp) in cementitious slurries at the recommended dosage, RheoCrete 222+ results are well below those required to classify it as a corrosion inhibitor. Results for MCI-2005 exceeded the reuired criteria confirming its classification as a corrosion inhibitor.**Immersion Testing Results and Discussion**:

Immersion testing is a well-accepted method of corrosion testing and yields reproducible results with little effort. In essence, a test solution is made with the properties to be evaluated and pre-weighed metal panels are placed into the solution. These solutions are left to sit for two weeks at 40 ± 2 °C before collecting the metal panels and cleaning off the corrosion. Cleaning is performed with a concentrated hydrochloric acid solution since abrasive methods of oxide removal remove too much mass and in an inconsistent manner. Once clean, the panels are reweighed with an analytical balance to accurately determine the mass lost due to corrosion. Cleaning is also performed on a blank panel to determine the mass lost through the cleaning process.

The mass loss from cleaning, determined from the blank panel, is added to the final mass of each panel to adjust for the cleaning process. This corrected mass loss is used to determine the rate of corrosion of each sample (equation 1). Furthermore, the average corrosion rate of the experimental samples can be compared with the average corrosion rate of the control samples to determine the amount of inhibition offered (equation 2).

$$Corrosion\ Rate\ (mpy) = \frac{3.449 * 10^6 * W}{A * T * D}$$

Equation 1: Corrosion rate calculation formula. W is the mass loss in g to the nearest 1 mg, A is the area in cm^2 to the nearest 0.01 cm^2, T is the time of exposure to the nearest 0.1 h, and D is the density of the metal in g/cm^3.

$$1 - \left(\frac{Experimental\ Corrosion\ Rate}{Control\ Corrosion\ Rate}\right) * 100\%$$

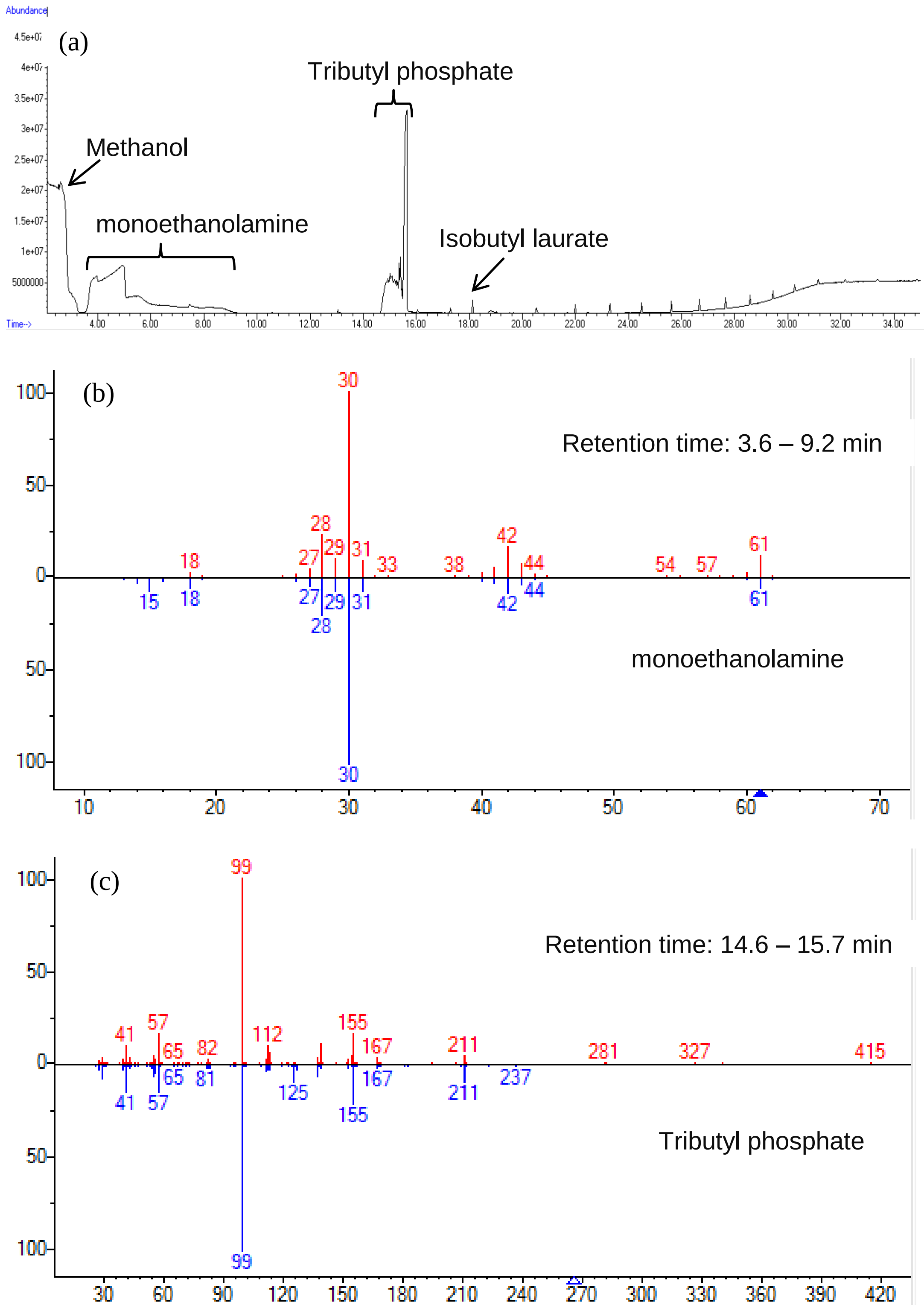
Equation 2: Inhibition equation

Sample	Product	Initial Mass (g)	End Mass (g)	Δ mass (g)	Corrosion Rate (mpy)	Avg Corrosion Rate (mpy)	Std. Dev.	Inhibition (%)
1	Controls	32.1972	32.1616	0.0356	1.9426	1.8635	0.0791	NA
2		32.1076	32.0749	0.0327	1.7844			
3	MCI-2005 0.40%	32.3483	32.3464	0.0019	0.1037	0.1110	0.0493	94.05
4		32.2382	32.2372	0.001	0.0546			
5		32.0157	32.0125	0.0032	0.1746			
6	RheoCrete 222+ 3.50%	32.1169	32.1025	0.0144	0.7858	0.7931	0.0068	57.44
7		32.197	32.1825	0.0145	0.7912			
8		32.2777	32.263	0.0147	0.8022			

Table 2: The results of the immersion testing.

The immersion testing performed for this report was done to simulate the conditions experienced in ASTM G180. To this end, a solution of 0.42% calcium hydroxide, 3.0% sodium chloride, and varying concentrations of inhibitor were mixed into deionized water. These conditions are conducive to the formation of pitting corrosion.

GCMS Results and Discussion:



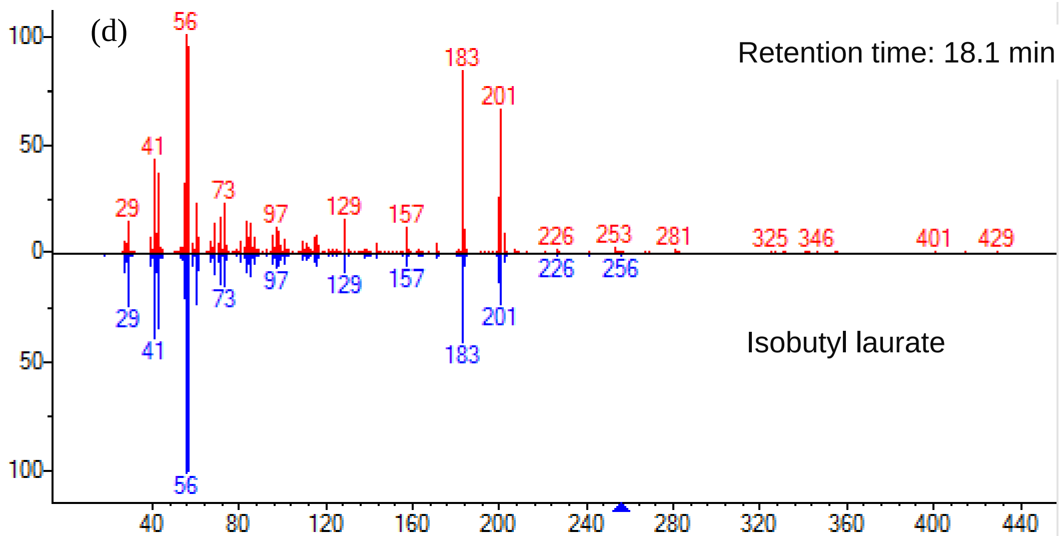


Figure 1: (a) The GC spectrum of RheoCrete 222+ (a) and (b, c, and d) MS spectra of individual components (top, corresponding to retention time shown in GC spectrum) compared with that of identified chemical species (bottom). Hysteresis of major component peaks in GC spectrum is due to water presence in RheoCrete 222+. Small periodical peaks in GC spectrum starting from retention time 17 min are chemicals from silica column.

Gas chromatography-mass spectrometry (GCMS) is a method used to separate the components of a **mixture** and subsequently identify the structures of these components. The machine performs this task by vaporizing a small sample of solution (1 µL) and passing it through a long column within an oven. By varying the temperature of the column, lighter, more volatile components can be separated from heavier, slower components.

Once the components have separated and reach the end of the column, they are hit with a beam of electrons, essentially breaking these components into smaller, charged fragments. Because the charge that every fragment receives is the same, they can be sorted by passing them through a charged region and then varying the voltage to search for specific mass-charge ratios (m/z). This entire process simply identifies the size of the charged fragments and the ratio of certain fragments with other, differently sized fragments. Compounds with very low volatility (e.g. inorganic salts) cannot be detected by GC-MS.

With the help of a library of compounds and their related spectra, the GCMS spectrum of RheoCrete 222+ was found (figure 1). Three major compounds were identified by the gas chromatograph, and, when analyzed via the mass spectrometer, monoethanolamine, tributyl phosphate, and isobutyl laurate were suggested by the software. RheoCrete 222+ disclosed monoethanolamine on its SDS at 10 to 30 %. Monoethanolamine is a well-known corrosion inhibitor for steel. Tributyl phosphate is widely used as air-detraining admixture. Isobutyl laurate is likely to be related to increasing concrete waterproofing capability, as mentioned in Patent WO 1996027695 A2.

FTIR Results and Discussion:

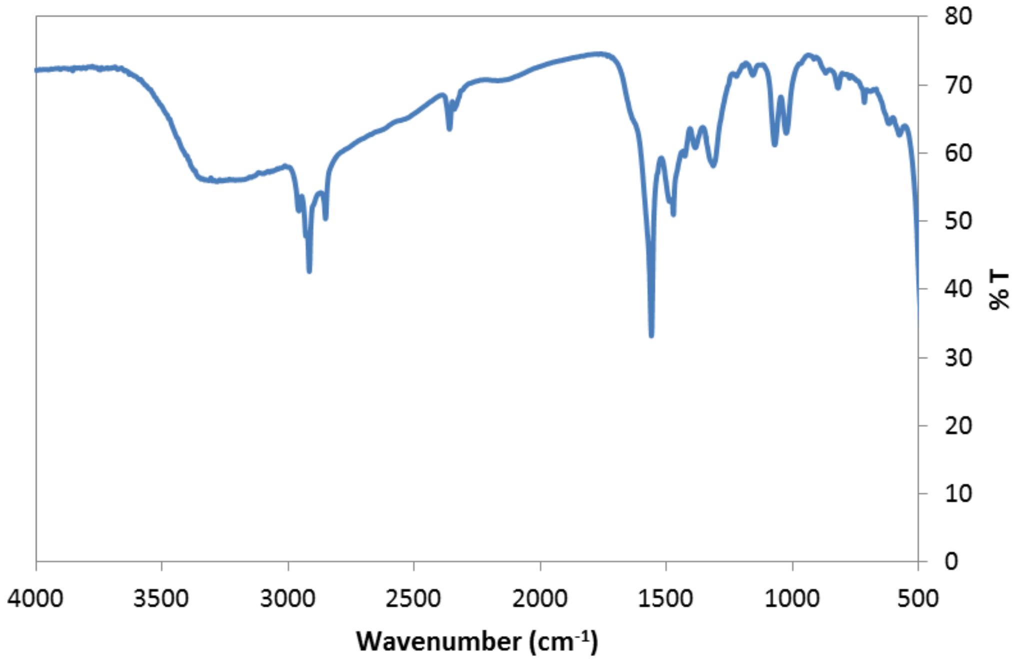
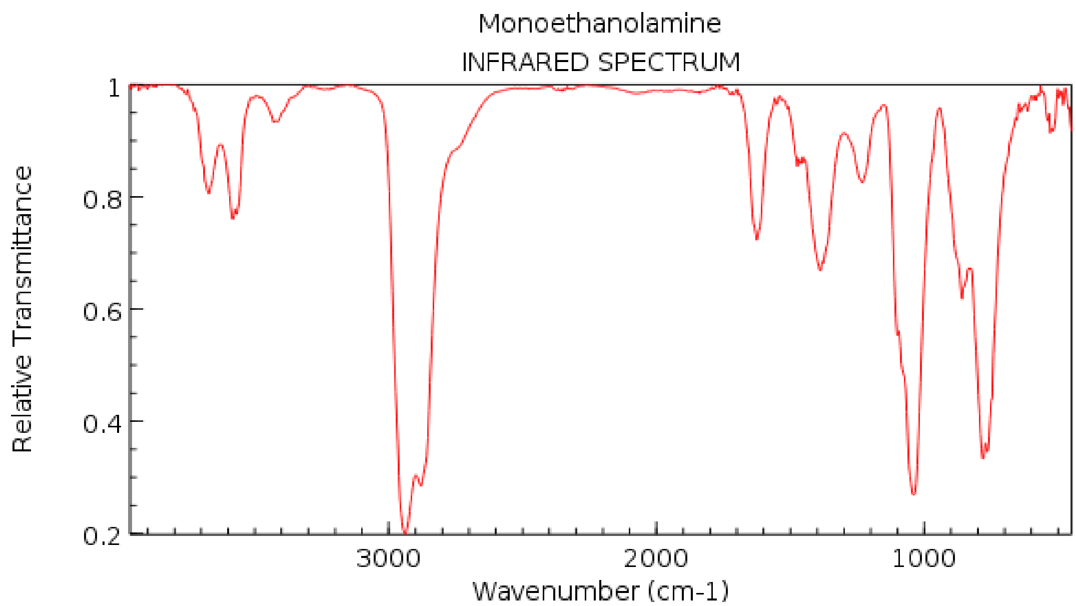
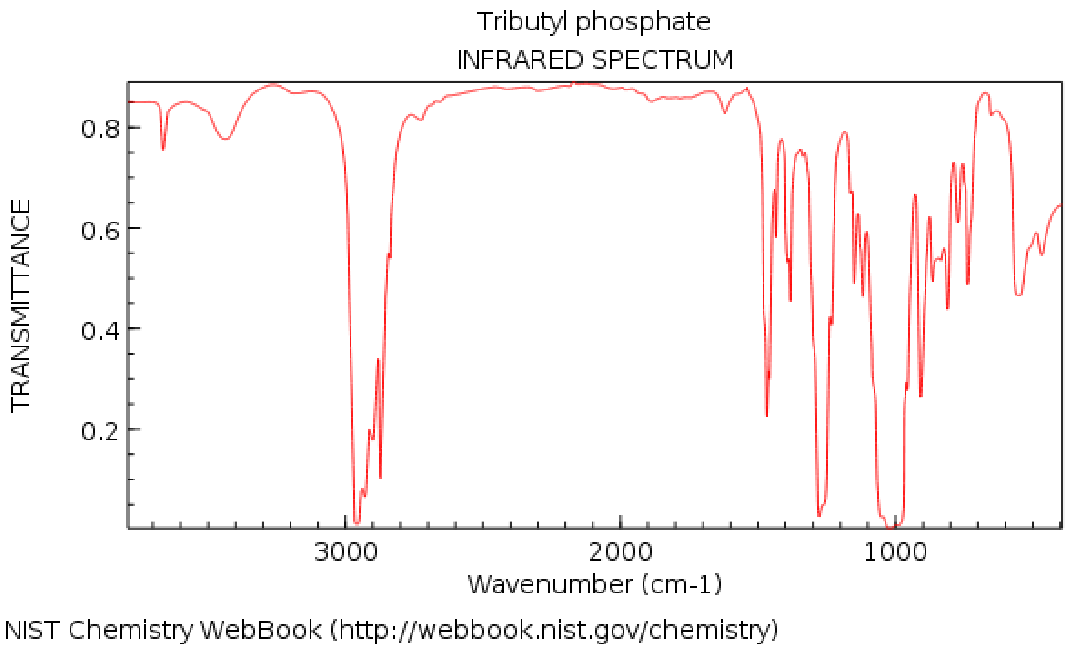


Figure 2: The FTIR spectrum of RheoCrete 222+ recorded at Cortec Laboratories



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)



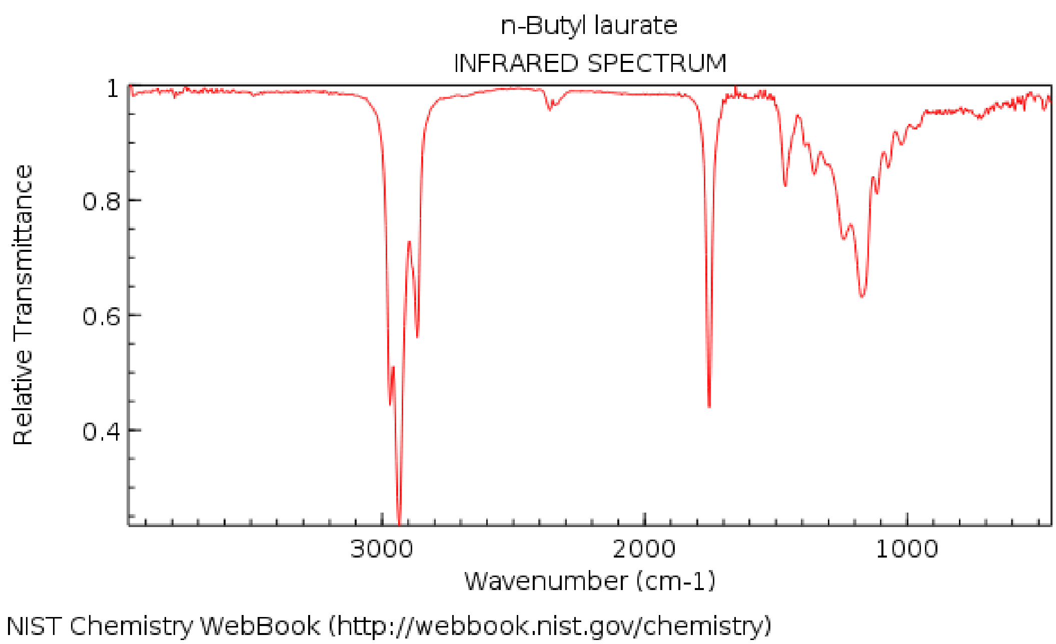


Figure 3: The reference FTIR spectrum of monoethanolamine, tributyl phosphate, and butyl laurate. Taken from NIST/EPA Gas-Phase Infrared Database.

Fourier Transform Infrared Spectroscopy (FTIR) is a common tool utilized by organic chemists to identify compounds of interest. Combined with results from GCMS or NMR (nuclear magnetic resonance) spectroscopies, FTIR can be effectively used to confirm the results of other techniques. FTIR spectroscopy is basically performed by passing a light beam through a given sample. Different molecular structures are excited by different frequencies of light, and this excitation results in the absorption of photons with different wavelengths. By varying the frequency of the light beam and measuring the amount of light seen on the other side of the sample, a plot of absorbance can be created. The utility of FTIR is in its ability to identify the functional groups of a molecule by their characteristic peak ranges and intensities.

Analysis of RheoCrete 222+ via FTIR has yielded results which relate to the reference spectra of tributyl phosphate. Characteristic peaks of monoethanolamines were not shown in RheoCrete 222+ spectrum due to the evaporation of monoethanolamine prior to FTIR measurement. Isobutyl laurate cannot be identified in RheoCrete 222+ spectrum due to its low concentration in the product (in GC-MS, its GC signal peak at 18.1 min is rather weak). The broad peak at ca. 3400 cm^{-1} is from water contained in RheoCrete 222+.

DYNA Filler 4100 Hardener Component Results and Discussion

Figure 4: The progression of the DYNA Filler 4100 hardener rust removal testing. Surface still has black oxide even after 10 minutes of cleaning. There is also a ring marking the edge of the product.

Figure 4: The progression of the VpCI-422 rust removal testing. No black oxide remains after 2.5 minutes of cleaning.

Figure 5: Steel panels coated with DYNA Filler 4100 hardener after 24 hours of exposure to ASTM-B117 conditions.

Conclusion:

At the recommended dosage of 5.0 L/m^3, RheoCrete 222+ did not perform as an effective corrosion inhibitor in both ASTM G180 and Immersion Testing.

Per ASTM C1582: *If Test Method G180 is used, the average polarization resistance, Rp, of the test specimens with the corrosion inhibitor shall be at least 8 times greater than that of the control specimens.* The average polarization resistance for MCI-2005 is 41.67 kΩ compared to 1.383 kΩ for RheoCrete 222+. While MCI-2005 exceeds that requirement, RheoCrete 222+ fails to show any improvement.

At the standard recommended dosage in ASTM G180, RheoCrete 222+ yielded corrosion rates of 1.949 mpy compared to 0.081 mpy for MCI-2005 and 0.930 mpy for the control.

In immersion testing, RheoCrete yielded 57% reduction in corrosion rates at its recommended dosage of 5.0 L/m^3 compared to a 94% corrosion rate reduction achieved by MCI-2005 at its recommended dosage of 0.6 L/m^3.

Analytical testing using GCMS and FTIR both revealed that – unlike MCI-2005 which is an amine carboxylate – RheoCrete 222+ is amino-alcohol based. Amino-alcohols are not referenced or recognized by ACI-212 Report on Chemical Admixtures for Concrete, while amine carboxylates are recognized, lab and field-proven and widely used.

Due to surface tension issues, DYNA Filler 4100 hardener does not provide adequate protection in ASTM-B117 conditions. While drying, it peeled away from the edges of the metal panels, causing the edges to be exposed to the aggressive, saline environment specified by ASTM-B117.

Rust removal testing did show DYNA Filler 4100 hardener to have some slight ability to remove rust from a metal surface, but the rate of removal was quite slow. VpCI-422 removed more rust in 2.5 minutes than DYNA Filler 4100 hardener removed in 10 minutes.