CAAP Final Report

Date of Report: April 9, 2016
Contract Number: *DTPH5614HCAP05*
Prepared for: DOT and PHMSA
Project Title: Improved Coatings for Pipelines
Prepared by: Texas Engineering Experimental Station
Contact Information: Dr. Hung-Jue Sue, 1-979-845-5024, hjsue@tamu.edu
For period ending: *March 31, 2016*

Business and Activity Section

1. Summary of student participation and business interactions

We have met with our business partners, ShawCor and Dow Chemical (now Olin), at the end of each quarter. Our students traveled to visit Dow Chemical in Freeport. Our final meeting was at ShawCor in Toronto.

We have received several batches of test panels from Shawcor. After applying our coatings, these were shipped back to ShawCor for testing. Olin supplied raw materials and formulation advice. ShawCor provided information on pipeline test protocols and the market for coatings.

We have met with the Pipeline Research Council International in Houston, Texas, to discuss this project with PRCI leadership.

Fan Lei, the PhD student who did most of the work within Texas A&M, will be graduating by the end of the year. Peng Li recently (March 2016) received his PhD. Zhiyuan (Alex) Jiang, a PhD student, is producing 100 g of ZrP nanoplatelets for ShawCor to test after the contract expires.

2. Summary of progress towards goals

The goals of this project were to prepare an epoxy coating containing fully exfoliated nanoplatelets, prepare test panels, characterize the coating morphology, and determine whether the nanoplatelets offer advantages over unfilled controls.

We have been gratified to discover that our postulated improvements in coatings properties from well-exfoliated nanoplatelets have largely been realized. We have demonstrated that dramatic improvements in scratch resistance are achievable. Accelerated corrosion tests (cathodic disbondment and hot water immersion) are also improved with the well-aligned nanoplatelets addition. Although nanoplatelet-filled coatings have been reported in the past, the improvements compared to conventional fillers have been modest.

Note that there are several technical problems to overcome before our coatings can be used commercially. These are delineated in the ‘Proposal for further work’ section below. We are applying for continued funding to be able to address these issues and move our new technology towards commercial reality. Nevertheless, we have proven for the first time that significant improvements in scratch resistance and corrosion protection are possible with nanoplatelet fillers.

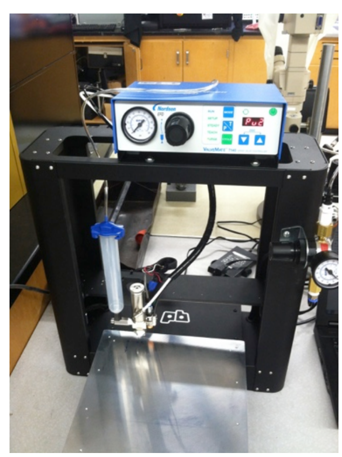
3. Detailed technical progress

Test protocol
At our kick-off meeting the major topic for discussion was which epoxy formulation to investigate and how to test the coatings. Commercial coatings are complex formulations with up to seven or more components including epoxy resins, hardeners, catalysts, pigments, fillers, and other additives. We were reluctant to simply add our ZrP nanoplatelets into such a complex formulation for several reasons.

- The fillers would make it difficult to determine the nanoplatelets morphology using transmission electron microscopy.
- We have no experience with exfoliation of nanoplatelets in the presence of macroscopic fillers. A requirement for property improvements with nanoplatelets is that they align parallel to the surface of the substrate. Isotropic fillers might interfere with this alignment.
- The exfoliation process is quite sensitive to the chemistry and dielectric properties of the surrounding media. Inert fillers such as mica will not likely cause a problem, but we were not sure.

We decided to use a simple two-part formulation consisting of bis-F diglycidyl ether (D. E. R.™ 354 from Dow Chemical) and diethyl toluenediamine (Epicure™ W from Momentive as the hardener. Occasionally the bis-F epoxy resin was replaced with bis-A diglycidyl ether (D. E. R. 383) for higher T_g (glass transition temperature) with the tradeoff of higher viscosity. Because we are using an aromatic amine as the curing agent, a relatively high temperature (~200 °C) is required for cure. Commercial coatings for pipelines that are applied in the field are generally cured at 100 °C or lower. Furthermore, the viscosity of the formulation was too high to easily spray, so a solvent (acetone) was added. Again, solvents are generally not added to commercial formulations. Given that the goal of this work was to demonstrate that nanoplatelets gave useful improvements in coatings, we felt these compromises were acceptable compromises. Some work was performed to reduce the cure temperature using aliphatic amine hardeners such as D. E. H.™ 615, but the pot life was short at room temperature and we reverted to Epicure W.

The next discussion was the choice of substrate to coat for testing. Shawcor thought it would be best if we overcoated one of their proprietary epoxy coatings. We termed the Shawcor coating as a primer. We would use the panels with no overcoat (but with the primer) as controls. This test protocol had the advantage that we could use thin overcoats (15 to100 µm), reducing the requirements for ZrP nanoplatelets. We were initially concerned that the adhesion between the primer and our overcoat, but this was not a problem. There was never an adhesive failure either in the hot water immersion tests or the scratch tests.



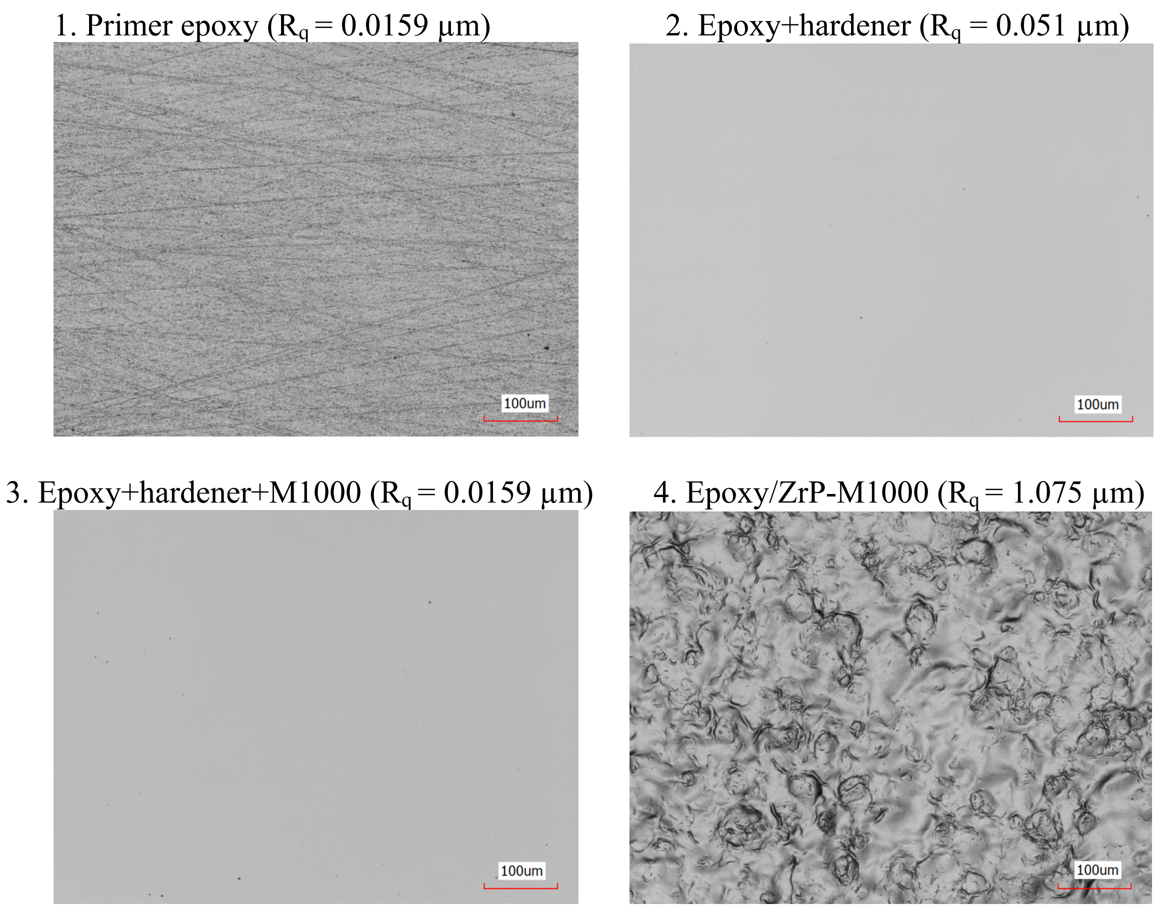
Coating procedure and spray robot
Our initial coatings were applied using a small hand-sprayer. Although this gives acceptable results, we felt that we needed a method that would give better precision. Our thought was to purchase an inexpensive 3D printer, modify it, and attach a high quality spray head. This has proven to be successful. We spent ~$5,000 total for parts to build the spray robot. Most of this cost was for the Nordson spray controller and spray head. The driver applications written for 3D printing were not useful for our purposes, and so we developed our own. With our custom

application we are able to adjust the spray pattern, speed on both axes, number of layers, wait time between layers, and other parameters.

There are also numerous spray-head parameters that can be adjusted that affect the quality of the coatings, including the nozzle dimensions, liquid pressure and flow, the atomizing air pressure, and others. This required considerable time to optimize, but we are now able to prepare reproducible coatings of good quality. We are able to achieve an average surface roughness for our epoxy/ZrP-M1000 coatings of 1 µm, which both Dow and Shawcor have said is adequate.

In Figure 1 below are 4 images of the test panels. The first image is of the panels as received from ShawCor that have only the primer coat. The second image is a coating with only epoxy (D. E. R. 354) and hardener (Epicure W). The third image is a coating with epoxy, hardener, and Jeffamine™ M1000. Finally, the fourth image is the full formulation with the ZrP/Jeffamine M1000 nanoplatelets. The nanoplatelets add to the surface roughness (root mean square roughness of ~1 µm) is within acceptable limits.

Figure 1: Surface roughness characterization



One persistent problem is circular defects in the coatings that are likely due to the escape of trapped solvent that remains before cure. The concentration of these defects is not so high that the coated panels can’t be tested. We partially solved this problem by keeping each layer thin

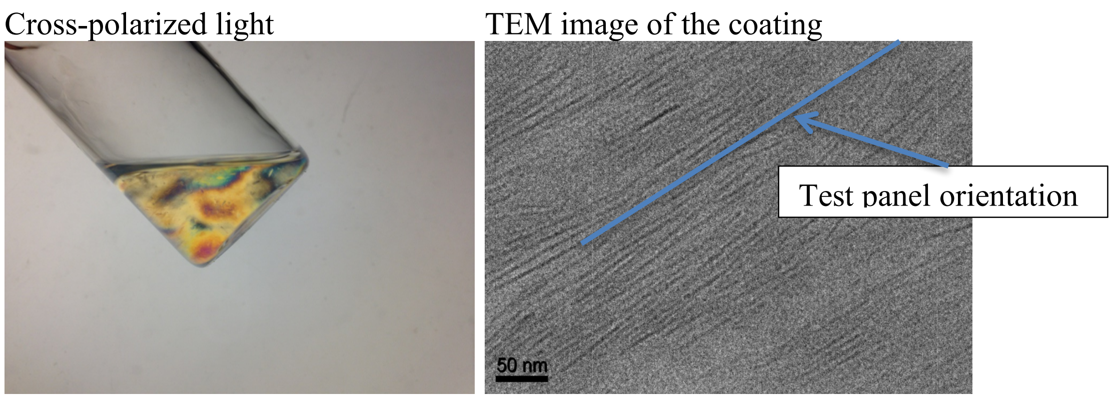
(~20 µm). A possible improvement to the sprayer that we did not implement was to heat the platen so that solvent can evaporate at a faster rate as the coatings are applied. The ultimate solution would be to eliminate the solvent in our formulations. Our industrial partners have made it clear that solvents are not desirable for commercial applications.

Formulation and cured morphology

The ZrP nanoplatelets were prepared from $ZrOCl_2 \cdot 8H_2O$ using a procedure outlined in the literature (H. –J. Sue, et al, Nature Comm., **2014**, *5*, 3589). A key part of the exfoliation process is the surfactant which initiates separation of the ZrP nanoplatelets and stabilizes them. The surfactant used throughout was Jeffamine™ M1000, which is a polyol (copolymer of ethylene oxide and propylene oxide) with an amine at one end. The ZrP nanoplatelets have an acidic site that forms an anion-cation pair with the amine surfactant.

The morphology of the nanoplatelets is important for reducing diffusion of water and oxygen through the coatings. Accordingly, one of our first tasks was to characterize the coatings using transmission electron microscopy (TEM). In Figure 2, an optical image of the formulation using polarized light is shown. The regions of color indicate that there is some local order in the suspension before cure. The TEM image at right is a cross-section of the coating after cure.

Figure 2: Comparison of epoxy coatings with and without ZrP nanoplatelets



Our results from cathodic disbondment tests at Shawcor have been mixed. Our preliminary tests using D.E.H. 615 (aliphatic amine) as the hardener have shown improved results vs controls. More recent tests using Epicure W (aromatic amine) as the hardener did not give significantly different results.

Hot water immersion tests performed by Shawcor have shown that our coatings give improved results ('adhesion rating' from 1 to 2) that they deem significant. ShawCor attributes to the reduction in water diffusion rates through the coatings.

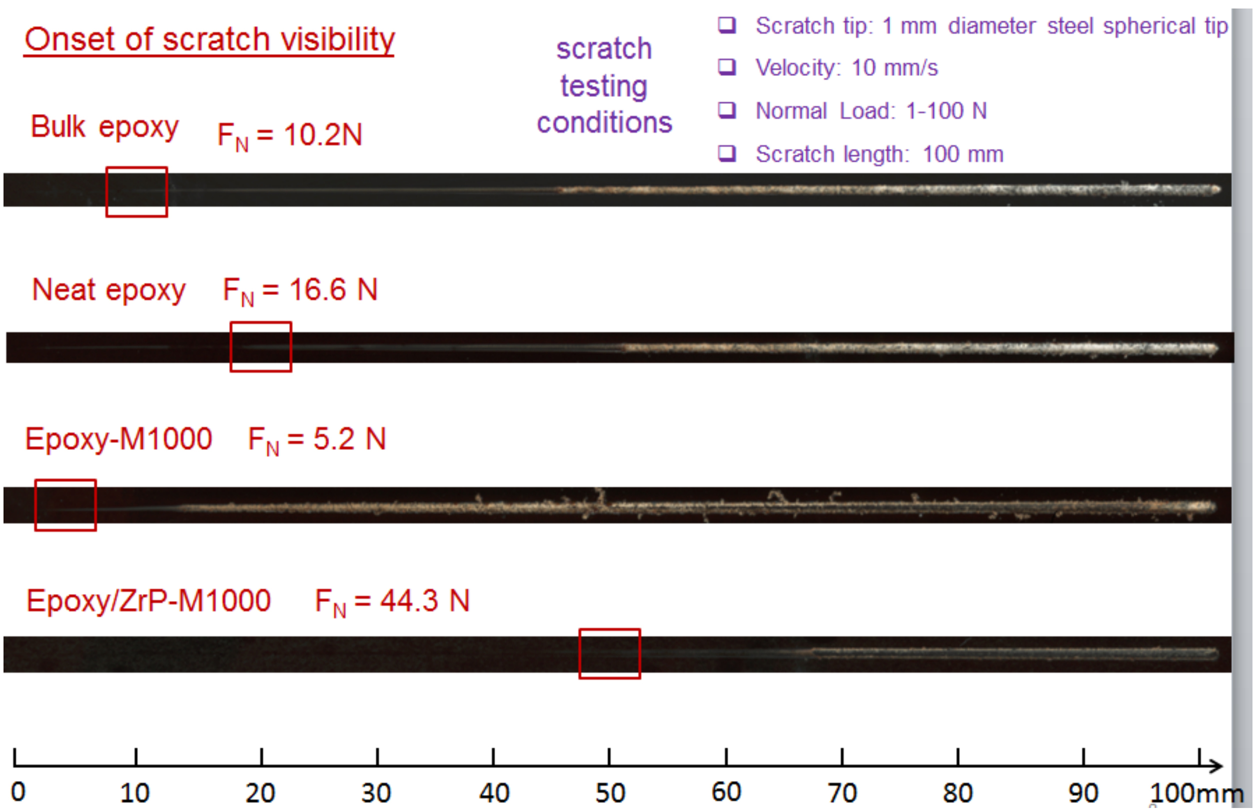
Coating scratch resistance measurements

We used our scratch machine (ASTM D7027) to compare coating formulations with and without ZrP nanofillers. A 1 mm diameter steel sphere was used with a speed of 10 mm/s, and a normal load increasing from 1 to 100 N.

In Figure 3 below, images from our laser confocal microscope of scratch surfaces for 1) the primer coat, 2) the 'neat' epoxy with hardener only, 3) epoxy, hardener, and Jeffamine M1000, 4) the complete formulation with ZrP. The panels, precoated with a proprietary epoxy coating by Shawcor, were subjected to a heat-treatment using the same schedule as our 'epoxy-M1000' formulation. The purpose of this was to ensure that the properties of the 'bulk' coatings didn't change after we added an additional coating and heat-treated it. When the 'bulk' coating was tested using the scratch machine using the same protocol shown in Figure 1, a visible scratch was observed starting at 10.2 N.

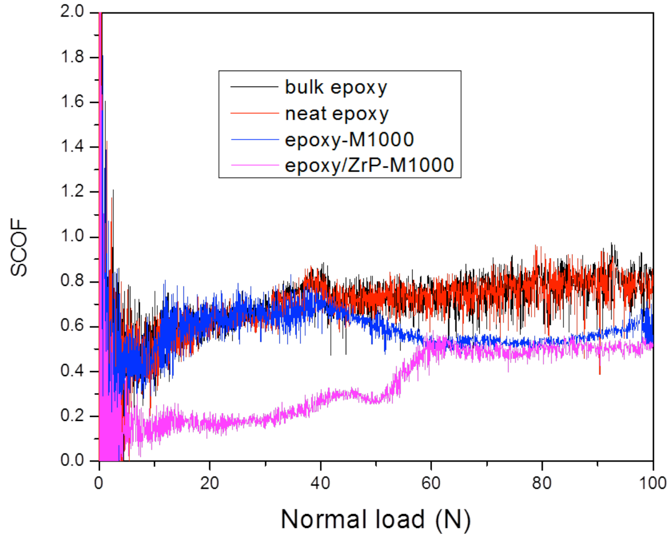
Red rectangles are used to highlight the areas where the onset of scratch visibility starts. The force required to cause visible damages increases from 16.6 (neat epoxy) to 44.3 N when ZrP is added, indicating significantly improved scratch resistance. Multiple tests show the results have low standard deviation.

Figure 3: Comparison of epoxy coatings with and without ZrP nanoplatelets.



The coefficient of friction (COF) for the epoxy/ZrP coating was also significantly reduced from the other three coatings as shown in Figure 4 (magenta line). The COF is low (~0.2 to 0.3) until the head plows through the overcoat at ~50 mm. This corresponds with the 'onset of visibility' as shown in Figure 3.

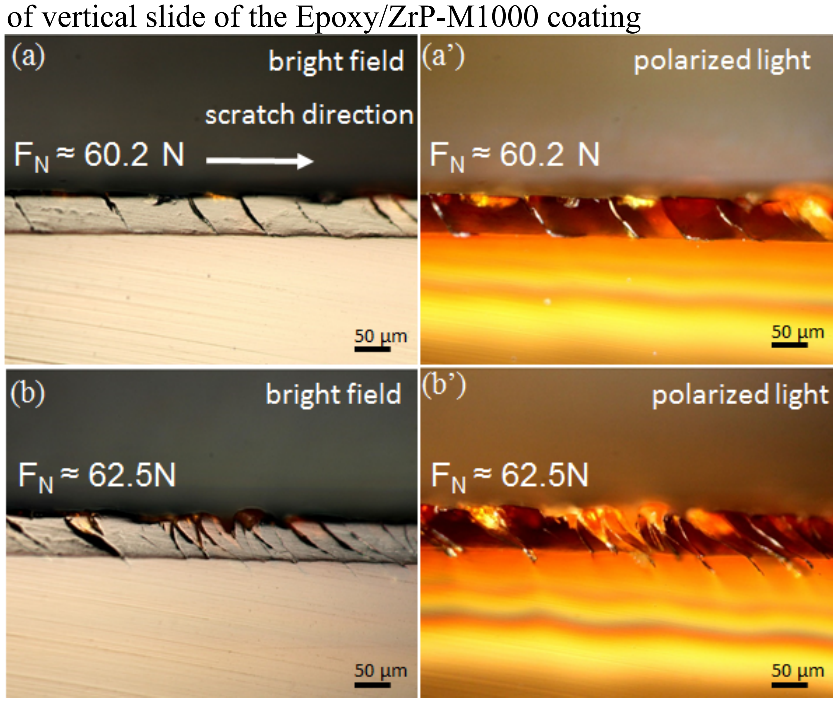
Figure 4: Coefficient of friction measurements



One concern that we discussed early in the project was adhesion between our nano-filled top-coat layers and the 'bulk' coating. We now have data that show that in the case of the epoxy/M1000 formulation, the adhesion is actually excellent.

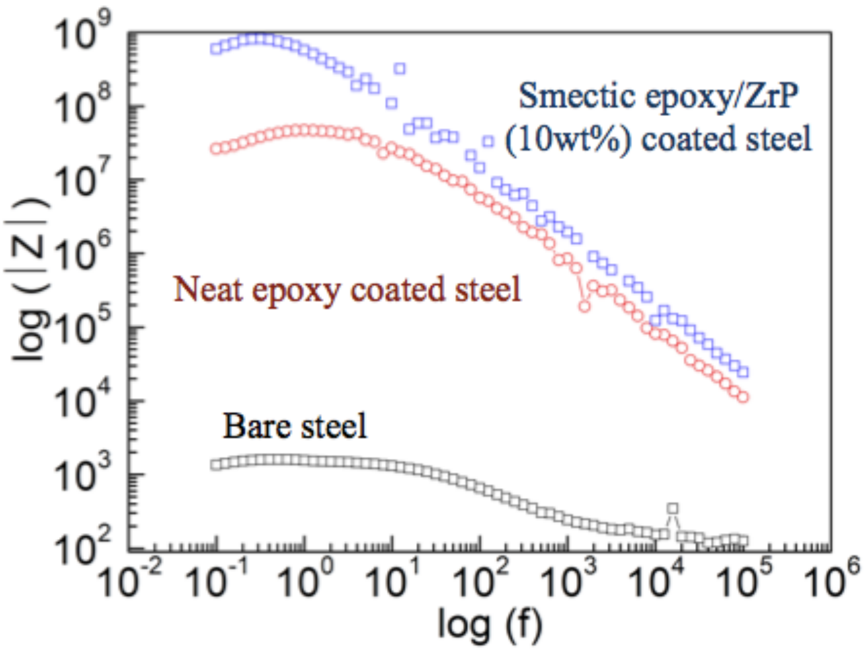
In Figure 4 an image taken of a vertical slice of the scratch is shown, specifically the portion of the scratch just after it is visible on the top surface. At a force of 60.2 N (top two images a and a') cracks form in the overcoat but stop at the primer. With slightly more force (62.5 N, bottom two images b and b') cracks propagate into the primer. There is no evidence of adhesive failure between the overcoat and the primer.

Figure 5: Image of vertical slide of the Epoxy/ZrP-M1000 coating



One of the panels was tested by electrochemical impedance spectroscopy (EIS) using a saturated calomel electrode as reference. The results are shown in Figure 6 below. A bare steel panel and a panel coated with only the neat epoxy (no ZrP) were used as controls. ShawCor said that the results were promising, but further work is required.

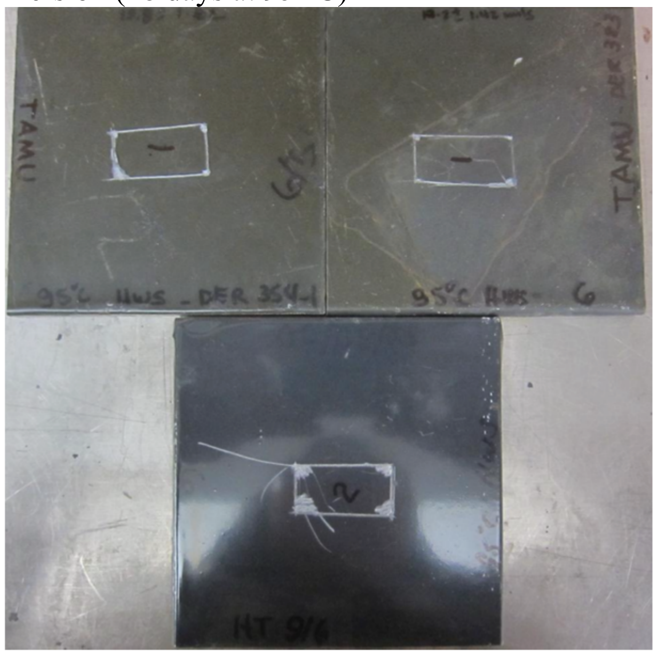
Figure 6: Electrochemical Impedance Spectroscopy (EIS)



Hot water immersion test results

Two separate series of test panels have shown that our ZrP overcoat improves the hot water immersion test results of Shawcor's proprietary coating (the most recent test results are shown above in Figure 7). The two images at the top are two formulations that contain ZrP that have been over-coated onto Shawcor's proprietary epoxy coating. The image at the bottom is a panel that has not been overcoated. The two panels that have been overcoated show improved adhesion of the epoxy coating to the steel.

Figure 7: Hot Water Immersion (28 days at 95 °C)



Adhesion Rating improved from 2 to 1

As ShawCor explained, the water boil test is mostly a result of water diffusion through the coating. A reasonable hypothesis is that the ZrP nanoplatelets slow the rate of water diffusion, and improve the test results. The cathodic disbondment test is more complex, and ‘holidays’ play a role.

In the most recent HWI test with a second proprietary primer, improvements were not observed. We suspect that this is due to instability of the primer coat to the conditions used to cure the overcoat (200 °C for 6 h). Reducing the cure temperature of our ZrP formulation is one of the goals of the future research.

Cathodic disbondment test results
A 28-day cathodic disbondment test was conducted at Shawcor. After 28 days at 65 °C, a disbondment of 10.1 mm resulted for the ZrP-epoxy panel, and 17.3 mm for the control panel. Dennis said that the results were “excellent” but that we will need to test more panels for the results to be conclusive.

Figure 8: Cathodic Disbondment

ShawCor discussed the new cathodic disbondment test results at room temperature, 50, 65, 80, and 95 ºC (see "Shawcor Overcoat test results 09-2015.doc"). In summary, there was not a significant difference between 'uncoated' samples and those over-coated with our epoxy/ZrP-M1000 coating. Dennis suggested that our coatings may not be sufficiently thick to see an effect. This will be left for future work.

4. Proposal for further work

The result so far show that the technology has promise, but further work is required to develop a coating that can be field tested. We propose the following studies. For all of this work, preliminary tests will be made for T_g, cure rate, pot life, and formulation viscosity before any coating is performed. Select formulations will then be applied to steel panels and tested.

- ZrP/surfactant:
  - We will investigate different surfactants with the goal to reduce the proportion of surfactant and to minimize the impact of the surfactant on the epoxy cure chemistry. In previous studies we have shown that exfoliation using $(n\text{-Bu})_4NOH$ is possible. If we can replace a portion or all of the Jeffamine M1000 with $(n\text{-Bu})_4NOH$ or other surfactants, we would reduce the impact that the monofunctional amine has on the T_g. Also, because the molecular weight is less, the proportion of ZrP would increase.
  - Jeffamine M1000 is based on a polyol produced using a mixture of ethylene oxide (EO) and propylene oxide (PO). The EO/PO determines the lipophilicity of the polyol, which in turn influences the compatibility of the exfoliated with the other components in the formulation. The molecular weight of the polyol (1000 g/mol in the case of M1000) also has an effect. A variety of Jeffamines with different molecular weights are available.
  - There are a few different procedures to make ZrP that yield nanoplatelets with different aspect ratios. Is ZrP with a 300:1 aspect ratio significantly better than with 100:1 ratio? If so, we might be able to reduce the amount of ZrP needed, and therefore minimize the problem with interference with cure chemistry.

- Epoxy/hardener:
    - Once our understanding of the ZrP/surfactant is more complete, we will be able to focus on optimizing the epoxy and hardener choice with the goal of reducing cure time and temperature. Ideally we would like to have a sprayable formulation that can be cured at 100 °C in an hour, and gives a T_g of 50-80 °C.
- Solvent:
    - Solvents are not used in commercial formulations. In addition, the acetone that we have used is the major cause of 'holidays' (pits and pinholes) in the coatings. Our current formulations are 'pourable' at 25 °C, and so we suspect that we will be able to delete the solvent and still be able to apply with a spray procedure. The non-Newtonian viscosity of formulations with ZrP is a desirable feature because it allows for high-shear spraying. Once the coating is applied, shear is low and viscosity is high, therefore dripping is minimized.
- Coating preparation:
    - Our ability to prepare good quality coating with few 'holidays' is critical for reliable test results, and of course the ultimate application. Removal of solvent will help considerably. We may also need to find a low dust environment to apply the coatings and cure them.

Appendix:

- Quarterly expense report from ShawCor and from Olin

ShawCor
ENERGY SERVICES • GLOBAL SOLUTIONS

March 29, 2016

Dr. Hung-Jue Sue
Texas A&M University
College Station, TX 77843-3123
+1 979 845 5024

RE: 6th quarter industrial support for DOT pipeline project DTPH5614HCAP05

Dear Dr. Sue:

Our 6th quarter support for the quarter for staff time, expenses, and materials is $6909.50. A breakdown of this total is shown below.

Project Activity	**Contributed Cost in $**
Staff time for coating formulation, testing, evaluation, meetings	6909.50
Materials, sample preparation, consulting	
Travel expenses	
Total	6909.50

Sincerely,

Dennis Wong, PhD, P Eng
ShawCor Ltd
25 Bethridge Rd
Toronto
Ontario
M9W 1M7
+1 416 744 5807
dwong@shawcor.com

MONTHLY REPORT #615

COPY 1 - 2

Standard Form 1035 September 1973 4 Treasury FRM 2000 1035-110	PUBLIC VOUCHER FOR PURCHASES AND SERVICES OTHER THAN PERSONAL	Voucher No. 6 Schedule No. 0 Sheet No. 1 OF 1

U.S. Department, Bureau, or Establishment

Texas A&M / Department of Transportation

Texas A&M/Department of Transportation

		Total Budget	**$25,000**
BILLING PERIOD:		**01/01/16 through 03/31/16**	
DIRECT COSTS:		Current Period	Total-To-Date
	HOURS	31	63
Labor		$1,799.55	$3,921.88
Materials & Supplies		$0.00	$0.00
Subcontracts		$0.00	$0.00
Travel		$0.00	$122.11
Other Direct Costs		$0.00	$0.00
Total Dow Direct Costs		**$1,799.55**	**$4,043.99**
Laboratory Overhead	0%	$0.00	$3,865.29
Total Direct Cost + Lab Overhead		**$1,799.55**	**$7,909.28**
Admin. Services Expense @	0%	$0.00	$895.44
TOTAL COSTS		**$1,799.55**	**$8,804.72**
Cost Share Dow		$0.00	$0.00
Total Cost Share		$0.00	$0.00
Spent in Excess of Incremental Funding		$0.00	$0.00
Excess Spending Cleared		$0.00	$0.00
Total		$0.00	$0.00
***** TOTAL AMOUNT DUE**		**$1,799.55**	**$8,804.72**

I certify that, to the best of my knowledge and belief, the data above is correct and that all outlays were made in accordance with the agreement conditions and that payment is due and has not been previously requested.

Date Request Submitted:

See attached

Joseph Cawley
Finance Manager

Telephone:
267-684-6941

**** 10/05/15 Agreeement transferred from The Dow Chemical Company to Olin Corporation ****

Printed on: 4/26/2016

Mundell, Kristy (KR)

From: Cawley, Joseph T (J) - Olin
Sent: Monday, April 25, 2016 9:50 AM
To: Mundell, Kristy (KR)
Subject: FW: March 2016 Government Contract Spending Reports

Not sure if I approved this or not....but I'm giving the financial approval for this.

From: Jean, David (DL) - Olin
Sent: Thursday, April 21, 2016 1:14 PM
To: Cawley, Joseph T (J) - Olin; Turakhia, Rajesh (R) - Olin
Subject: RE: March 2016 Government Contract Spending Reports

Can't access the folder, but I think I remember this being discussed prior to Day 1, and Lingyun was working with Dow on the right resolution.

Dave

From: Cawley, Joseph T (J) - Olin
Sent: Thursday, April 21, 2016 12:10 PM
To: Turakhia, Rajesh (R) - Olin; Jean, David (DL) - Olin
Subject: FW: March 2016 Government Contract Spending Reports
Importance: High

Are you guys familiar with the gov't contact.? Dow is looking for financial approval for what we are spending. I understand Lingyun He already given her approval.

From what I understand, someone in Epoxy forward this data to the dow research and they do the filing.

The reports are located on the following server: \\USNT42\govtcont.

Core Team:	#614	#615	#617
R&D Directors	P. Vosejpka/J. Robacki	R. Turakhia	P. Vosejpka
Program Manager	D. Bank	R. Turakhia	M. Mirdamadi
Principal Investigator	M. Mirdamadi	L. He	M. Mirdamadi
Operations Manager	M. Smit	M. Thompson	B. Cooper
Finance	L Sonby	C. Vasquez	M. Pridoehl
Finance Manager	P. Pierce	J. Cawley	P. Pierce
External Technology	M. Dibbs	M. Dibbs	M. Dibbs

From: Mundell, Kristy (KR)
Sent: Wednesday, April 06, 2016 10:07 AM
To: Vosejpka, Paul (PC); Robacki, Jeff (JM); Bank, Dave (DH); Mirdamadi, Mansour (M); Smit, Mark (M); Sonby, Lea (LQ); Pierce, Paul (P); Dibbs, Mitch (M); Turakhia, Rajesh (R) - Olin; He, Lingyun (L) - Olin; Thompson, Marla (MJ); Vasquez, Christopher (CM); Cawley, Joseph T (J) - Olin; Cooper, Beth (B); Pridoehl, Michele (ME)

Cc: Baier, Gretchen (G); Quencer, Brett (BM)
Subject: March 2016 Government Contract Spending Reports
Importance: High

The March 2016 government contract spending reports are available for your review.

The reports are located on the following server: \\USNT42\govtcont

The Program Manager (highlighted in red below) is required to confirm their review of contracts expenses and approve prior to invoicing. Please respond back to this email confirming the review and approval of expenses no later than April 13th, 2016.

Core Team:	#614	#615	#617
R&D Directors	P. Vosejpka/J. Robacki	R. Turakhia	P. Vosejpka
Program Manager	D. Bank	R. Turakhia	M. Mirdamadi
Principal Investigator	M. Mirdamadi	L. He	M. Mirdamadi
Operations Manager	M. Smit	M. Thompson	B. Cooper
Finance	L. Sonby	C. Vasquez	M. Pridoehl
Finance Manager	P. Pierce	J. Cawley	P. Pierce
External Technology	M. Dibbs	M. Dibbs	M. Dibbs

If you have any questions regarding the reports, please do not hesitate to contact me.

Kristy Mundell
The Dow Chemical Company
Functional Controllers: U.S. Government Contracts
1776 Building
Midland, Michigan 48674 USA
Phone: (989) 638-9831 Fax: (989) 636-1705
e-mail: krmundell@dow.com