



# **High Build Polyurea Coatings**

## **Final Report**

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## Acronyms and Abbreviations

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<b>Term</b>	<b>Definition</b>
CARC	Chemical Agent Resistant Coating
CTMA	Commercial Technologies for Maintenance Activities
DOD	Department of Defense
EPA	Environmental Protection Agency
GVSC	Ground Vehicle Systems Center
JAB	Joint Assault Bridge
NCMS	National Center for Manufacturing Sciences
NCO	Isocyanate (from the chemical formula $N=C=O$ ; Nitrogen, Carbon, and Oxygen)
NDSU	North Dakota State University
ODASD-MR	Office of the Deputy Assistant Secretary of Defense, Materiel Readiness
OEM	Original Equipment Manufacturer
PATTI	Pneumatic Adhesion Tensile Strength Testing Instrument
TACOM	Tank Automotive Command
TARDEC	tank and Automotive Research, Development, and Engineering Center
VOC	Volatile Organic Compound



# 1. Executive Summary

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In 2016 a Department of Defense (DOD) contracted study reported corrosion has a cost impact of \$20.6 billion to the various Service branches. In addition to the high costs to rehabilitate corroded assets, military readiness also has the potential to be affected by taking critical weapon systems out of action and creating safety hazards. Further, capital investments and facilities may also experience structural failures related to corrosion.

In 2022, these challenges still exist and new ways of protecting defense assets are continually being sought. DOD vehicles, weapons systems and associated support equipment are protected from environmental degradation by systems of metal pretreatments and coatings designed to inhibit corrosion. These coatings systems also provide camouflage and electromagnetic signature attributes to protect the warfighter. However, these coating systems are typically less than 125 microns in total thickness. Accordingly, impacts from rocks, debris, tool drops, and general wear and tear can easily breach the coating layers exposing bare metal surfaces which will quickly oxidize. Exposure to environmental elements will accelerate the oxidation or rusting of the asset until it is no longer suitable for its intended purpose without remedial action.

Polyurea coatings represent an established technology uniquely suited to address this need and this project sought to collect data illustrating performance limits of existing formulations and conduct research and development aimed at incorporating additional performance attributes. Polyurea coatings have been employed in the private sector for many years to address similar challenges but have been underutilized within the defense community. For example, spray applied polyurea coatings are often applied to the interior surfaces of truck beds to protect from impacts, abrasion and tool scrapes while also providing a slip resistant surface. Nissan was the first automotive Original Equipment Manufacturer (OEM) to pioneer the use of spray applied bedliners in its 2007 Titan pick-up truck. Prior to this spray applied bedliners were only an aftermarket accessory. Today these liners are standard option for consumers and are ubiquitous.

PPG and North Dakota State University (NDSU) researchers collaborated in this project. The team's collective results described in this report show benchmarking performance against standard coating stack-ups without polyurea, alternative crosslinking chemistries which yield similar performance attributes, physical chemistry testing regimes that were developed specifically for this project and finally formulation modifications designed to impart direct to metal performance features.

A standard Army coating stack will include pretreatments on steel and aluminum surfaces, typically in accordance with TT-C-490 requirements, an epoxy corrosion inhibiting primer conforming to MIL-DTL-53022 or 53030 and finally a chemical agent resistant coating (CARC) topcoat conforming to MIL-DTL-53039 or 64159. These systems typically perform well in standard test methods performed on flat metal coupons as described in the relevant specifications. However, real world abusive environments experienced by tactical vehicles can dramatically compromise the coating system leading to bare metal exposure and subsequent corrosion. Examples include undercarriage rock and debris impacts while traveling over rough terrains, tool and equipment drops in cargo areas and general abrasion from constant movement of troops and equipment.

This project first sought to benchmark performance of a coating stack consisting of zinc phosphate pretreatment, corrosion resistant epoxy, polyurea high wear coating and lastly a CARC topcoat. Due in part to the high film thickness of polyurea high wear coatings, the results demonstrated very

significant improvements in corrosion resistance when the high wear coating were included in the stack. Further, the compression resistance of polyurea was determined to exceed anticipated needs for coatings in extreme environments such as mobile bridging applications.

A characteristic of polyurea coatings is the extremely fast cure kinetics such that plural component application equipment must be used and cure times can be measured in seconds. This is the result of the rapid condensation reaction between isocyanate pre-polymers and primary amine functional reactants. This project also examined the use of acetoacetate functional prepolymers reacted with amine reactants. This reaction is equally fast at ambient temperatures but has the potential to replace some or all of the isocyanates used in conventional polyurea coatings. Since workers exposed to isocyanates have the potential to develop skin sensitization substituting with acetoacetate functional materials may reduce worker exposure.

Lastly the project made significant progress toward direct to metal polyurea compositions which would enable eliminating the corrosion resistant epoxy and pretreatment steps. If implemented as a new coating type within the MIL-PRF-32440 specification such a system would increase productivity in repair processes and mission readiness via reduced equipment downtime.

Funding for the collaborative effort was secured through the National Center for Manufacturing Sciences (NCMS) Commercial Technologies for Maintenance Activities (CTMA) Program and the Office of the Deputy Assistant Secretary of Defense, Materiel Readiness (ODASD-MR).

## 1.1 Results

As will be described in Sections 3.1 thru 3.4 three major conclusions may be reached as a result of this project. First, existing qualified high wear polyurea coating systems perform well in combination with standard epoxy primers and CARC topcoats. Adhesion, corrosion, resistance to temperature extremes were all observed to be significantly better than coating stacks without high wear polyurea. Further, in some applications these coatings might be expected to withstand compressive forces in excess of 30,000 PSI. Testing developed by NDSU researchers suggests existing products will meet this requirement.

Secondly, while alternative chemistries can be developed which match the cure speed of polyurea, trade-offs are required based on the team's evaluation. For example, elongation of polyurea films can be dramatically increased via the addition of acetoacetate crosslinkers to replace some of the isocyanate prepolymers but this comes at a significant reduction in Young's modulus. Conversely, Young's modulus may be increased through addition of reactive thiol crosslinkers but elongation and flexibility were observed to be reduced.

Lastly, modest formulation changes point to the possibility of developing direct to metal high wear polyurea systems. This would reduce time, materials and labor associated with asset repairs. In addition, high wear polyurea systems are often formulated without organic solvents so system volatile organic compounds (VOCs) could be significantly reduced via the introduction of a direct to metal polyurea formulation.

## 1.2 Benefits

The work completed under this project benefits the DOD by providing increased confidence that polyurea coatings qualified to MIL-PRF-32440 may be used in a wide range of physically demanding applications. Increased DOD usage of these coatings is certain to provide long term protection of expensive assets and significantly extend service life beyond that of conventional coating stacks which do not include a polyurea mid-coat.

The work completed in this project also benefits the public at large. In particular, direct to metal polyurea formulations developed in this project have extensive utility in applications such as heavy-duty equipment including farm and construction vehicles. Likewise, emergency responder vehicles, tractor trailers and fleet vehicles such as moving vans may benefit from the technology as a means of increasing protection from corrosion and reducing process time for OEM manufacturing and aftermarket repair processes.

The primary benefits to the defense community were to document the extreme performance features of polyurea coatings and to advocate for their increased usage across Army asset management. The project team also demonstrated direct to metal systems which would simplify repair processes and increase mission readiness. While not explicitly described in MIL-DTL-32440, coatings of this nature should be considered when specification revisions are made as a new type or class of high wear coating.

For the public sector the direct to metal polyurea would also be of interest and work continues at private expense to optimize formulas of this type for applications such as trailer builders and heavy-duty equipment. In addition to productivity enhancements a direct to metal polyurea would offer end users a 0 VOC alternative to conventional coating stacks, thus benefiting the environment and reducing greenhouse gas emissions.

## 1.3 Technology Transition

The relevant specification, MIL-PRF-32440, was revised in September of 2020 and a number of commercially available products have been approved based on Army validation testing (including PPG's **Dragonhide® 1000 Polyurea Coating**). The direct to metal version described in Section 3.4 would represent a new type and specification revisions would need to be captured to utilize this material in DOD applications.

Outside the scope of this project, PPG is supporting production of a training video sponsored by Tank Automotive Command (TACOM) to increase awareness of polyurea coatings technology. Given the unique plural component application equipment required for polyurea, this training video will be an important tool to introduce depot level painters to the benefits of polyurea and the basic operation of plural mix equipment. Filming of this video is expected to start in Q4 2022, and PPG is providing space and equipment at the PPG Springdale, PA development center to facilitate. As needed PPG will also support additional video productions to provide more in-depth training related to polyurea application.

## 1.4 Recommendations

As described previously, a direct to metal polyurea with the same adhesion, corrosion resistance and cure speed as standard polyurea coating stacks would be very desirable to end users and simplify coating repair processes. A recommendation would be to continue to optimize direct to metal polyurea formulations first envisioned in this project and revise specifications to accommodate their usage.

A further recommendation would be to complete the TACOM sponsored training video being prepared outside of this project and widely distribute to depot level repair technicians. The benefits of polyurea were clearly demonstrated in this project but there needs to be increased awareness about the technology, availability of high-quality application equipment, training on how to use the equipment and lastly broader application of polyurea to protect assets in the harshest of environments.

## 1.5 Invention Disclosure

Invention Disclosure Report(s):

DD882 Sent to NCMS

No Inventions (Negative Report)

## 1.6 Project Partners

- United States Army Ground Vehicle Systems Center (GVSC)
- PPG Industries, Inc.
- North Dakota State University (NDSU)
- National Center for Manufacturing Sciences (NCMS)

## 2. Introduction

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### 2.1 Background

The United States Army recently finished operational testing of a new, mobile assault bridge, the Joint Assault Bridge (JAB), which is designed to cross battlefield barriers as wide as 18 meters. It began being fielded to combat troops in 2021. The JAB is built on an M1 Abrams tank chassis and features a hydraulic launching mechanism for deploying the Heavy Assault Scissor Bridge, which is capable of extending across gaps and trenches on the battlefield. The JAB can be seen during performance test in Figure 1. The Army plans to field the JAB between fiscal 2021 through fiscal 2027, Elizabeth Miller, the service's product manager for Bridging, said in the release. In addition to the 1st ABCT of the 1st ID, the 278th Armored Cavalry Regiment's Brigade Engineering Battalion, Tennessee Army National Guard, is also slated to receive JABs in mid-2021.

<https://www.businessinsider.com/the-armys-newest-vehicle-is-actually-a-big-mobile-bridge-2020-12?op=1>

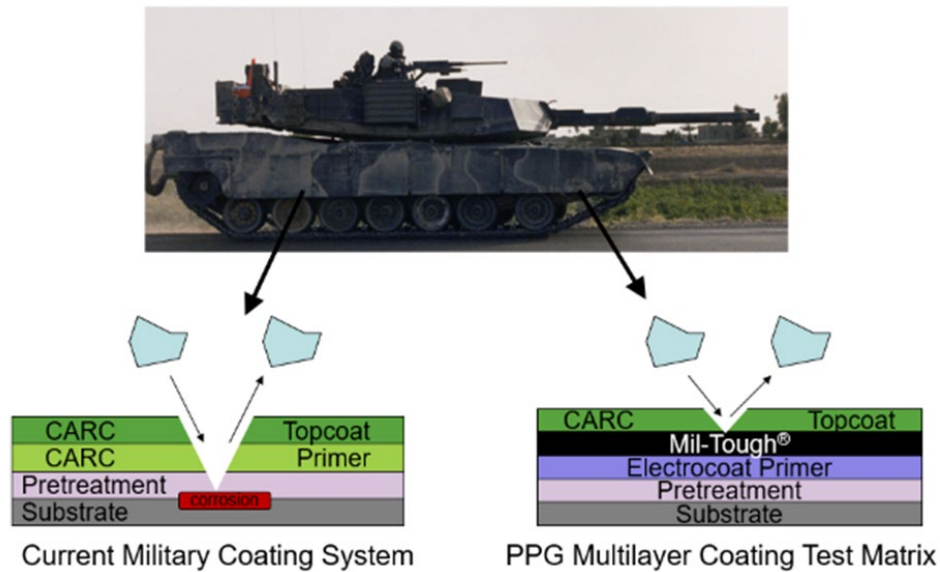


**Figure 1. The JAB Successfully Completed Initial Operational Testing in November 2020**  
*U.S. Army Operational Test Command Photo*

From the beginning of this project the JAB and similar mobile bridging platforms were seen as an excellent example of where polyurea might be employed to protect assets. Not only are there enormous forces during the deployment of the bridge, after it's deployed tactical vehicles and tanks traverse its span exposing the painted surfaces to additional wear and abrasion forces. Once the troops have traversed the barrier, the M1 Abrams drives over the bridge and using hydraulics re-installs the bridge for use in the next barrier. Based on the weight of the bridge itself, Ground Vehicle Systems Center (GVSC) experts have suggested the coatings may be experiencing compressive forces as much as 30,000 psi during deployment.

Previous work conducted by PPG also inspired the further investigation of this project. In 2008 PPG proposed and demonstrated performance advantages of incorporating polyurea into military asset

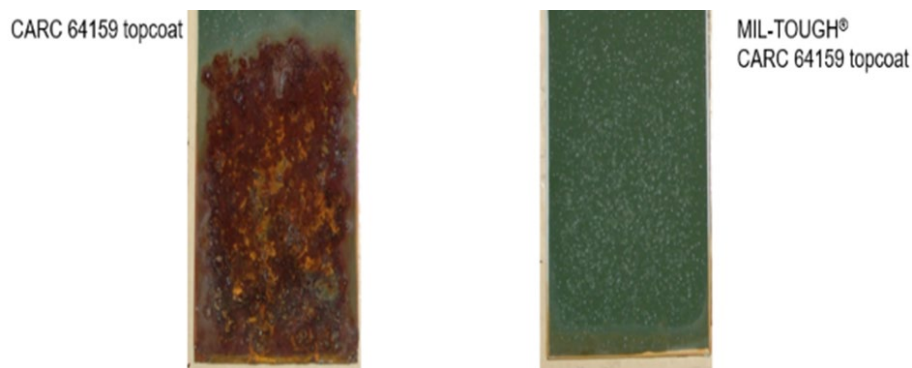
coating stacks. The work conducted at that time is conceptually shown in Figure 2 where the polyurea coating was applied over an electrodeposition primer and then topcoated with a standard CARC topcoat. The polyurea, then under the tradename Mil-Tough™, was expected to absorb energy of debris impacts and prevent coating failure to the metal surfaces.



**Figure 2. Original Concept for Incorporating Polyurea in Military Coating Stack**

To prove this hypothesis, PPG prepared panels which included zinc phosphate pretreatment, cationic electrodeposition primer (ED6280) and either CARC topcoat or Mil-Tough polyurea plus CARC topcoat. The panels were cured then subjected to 80 cycles of a modified “chip-scab” test wherein panels were submitted to alternating exposures of wetting and drying cycles coupled with a gravelometer impact test. In this test SCAB stands for Simulated Corrosion Atmospheric Breakdown and 18 cycles of gravelometer impacts were used.

As predicted the coating system without polyurea quickly had coating failures which exposed bare metal whereas the polyurea systems had topcoat only failures. The test panels were then further exposed to two years atmospheric exposure at PPG’s Ft. Lauderdale exposure farm. Results are shown in Figure 3 where the advantages of a polyurea mid-coat are clearly illustrated.



**Figure 3. Results of Chip-Scab Testing Followed by Two Year Atmospheric Exposure**  
 On left is CARC system stack without polyurea mid-coat, on right is same system with polyurea inserted between topcoat and electrodeposition primer.



While the results of this test were dramatic, cationic electrodeposition is primarily used at defense OEM such as Oshkosh or General Dynamics. At the depot level where most repair operations occur, liquid spray applied coatings are by far the primary coating systems. Therefore, this project sought to, in part, repeat similar testing with a focus on post production repair processes.

## 2.2 Purpose

The work completed under this project was expected to provide the DOD with increased confidence that polyurea coatings qualified to MIL-PRF-32440 may be used in a wide range of physically demanding applications. Increased DOD usage of these coatings is certain to provide long-term protection of expensive assets and significantly extend service life beyond that of conventional coating stacks which do not include a polyurea mid-coat.

The work also had as an objective the exploration of novel rapid cure, high wear resistance coatings with a focus on imparting additional benefits such as incorporation of novel corrosion inhibitors or direct to metal adhesion characteristics. Coatings with these new and desirable features could then be proposed as additional qualification types within a revised MIL-PRF-32440 specification.

## 2.3 Scope/Approach

Corrosion is a persistent problem affecting nearly all infrastructure, vehicles, and equipment used for commercial and military applications. Coatings designed for corrosion prevention ensure the reliability and long-term performance of metallic substrates by slowing or stopping the electrochemical reactions that adversely impact the appearance and structural integrity of the metal. However, once a protective coating is penetrated, its ability to provide corrosion resistance is compromised.

The goal of this project is the development of state-of-the art chip and wear resistant coatings for demanding applications such as Army Bridging systems and other TACOM ground vehicle systems to reduce corrosion risk in high wear and impact areas. Prototype(s) developed in the project will be CARC system stack-ups with a polyurea intermediate layer (e.g., pretreatment-primer-polyurea-topcoat) or a polyurea topcoat (e.g., pretreatment-primer-polyurea) on representative substrates to be used to comparatively test polyurea coating systems versus other existing chip and wear resistant technologies.

### Task 1: Baseline Performance Establishment

PPG will collaborate with Tank and Automotive Research, Development, and Engineering Center (TARDEC) to develop a matrix of target substrates and coatings stacks for evaluation and related target metrics for coating system performance. Metrics will contain, at a minimum, corrosion resistance, adhesion, coating durability, film thickness, and chip/wear resistance. Coatings stacks will include specified CARC pretreatments, primers, and topcoats as relevant.

### Task 2: Coating System Assessment

*2.1 – Baseline Testing:* Using the matrix established in Task 1, PPG will evaluate baseline developmental coatings stacks. Materials in evaluation will include polyurea and polyurethane coatings in combination with CARC topcoats and will be compared to baseline CARC coatings stacks.

*2.2 – Developmental Formula Testing:* As needed, developmental formulas will be prepared and evaluated using criteria developed in Task 1.

**Task 3: System Recommendations**

PPG will prepare a summary of the test results and provide a recommendation for further demonstration activities, including stack-up advantages and disadvantages, cost, ease of application, environmental safety and occupational health concerns, etc.

## 3. Project Narrative

### 3.1 Materials and Application Tools

MIL-PRF-32440 covers chip-, impact-, wear-, and abrasion-resistant coatings for use on areas of military vehicles or ground support equipment which may encounter diminished service life through damage. Examples of subject areas are bed liners and cargo beds of trucks, undercarriages of ground support equipment, torsion bars, and other areas subject to chipping, impact, wear, or abrasion, which may compromise the established quality and function of the OEM part.

PPG chose to use both aliphatic and aromatic polyurea compositions for much of the experimental work conducted in this project. Aliphatic polyurea formulas are characterized by excellent outdoor weatherability and in commercial applications they are usually used without a topcoat. In contrast, aromatic polyurea such as PPG's *Dragonhide* 1000 product, are UV sensitive and will exhibit chalking and blushing upon UV exposure unless protected by a topcoat. In DOD applications the aromatic polyurea is often topcoated with a MIL-DTL-53039 or MIL-DTL-64159 Chemical Agent Resistant topcoat.

For experimental purposes two application techniques were employed. The spray application of the polyurea was accomplished using a VOB-150ASP air assisted pneumatic spray gun as shown in Figure 4. The system holds two 150ml cartridges containing the isocyanate and amine side separately in the pack A and B respectively. An air assisted pneumatic plunger pushes the two components through a static mixer at a 1:1 volume mix ratio which is then atomized and sprayed onto the panels targeting 30-50mil thickness. This system is suitable for low volume polyurea application where quality of finish is not critical and neither component needs heated prior to application.



Figure 4. Portable Plural Component System for Spray Application of Polyurea Samples

Polyurea free films were generated using a smaller pneumatic gun with a similar setup to the one described above. The application method has a smaller volume and no atomization step but does utilize static mixer at a 1:1 volume mix ratio. The mixture was then extruded onto a Teflon mold in a back-and-forth pattern until the mold was filled resulting in a roughly 3mm thick film. Samples prepared in this manner were suitable for analytical testing of material properties and cure kinetics but not suitable for coating properties such as adhesion or corrosion resistance.

A third application method entails the use of more expensive plural component systems which would be used in OEM or depot level applications. An example would be Graco's hydraulic Reactor 2 H-XP2 which increases yield and allows for high output spraying as shown in Figure 5. Systems like this are typically used by OEM's or applicators that spray at high volumes. This high-pressure system applies up to 1.5 gal (5.7 liters) per minute and has heated fluid delivery lines for viscous materials. It also includes the "Reactor Connect" app which provides communication and system control from a linked smart phone.



Figure 5. Graco H-XP2 System for High Volume Production of Polyurea Coating

## 3.2 Benchmarking Control Formulations

### 3.2.1 Impact and Wear Resistance

Applications such as the mobile bridging described in Section 2.1 are expected to expose the polyurea films to extremely high compressive forces. To examine polyurea resistance to forces of this magnitude samples of both aliphatic (Durabed) and aromatic (*Dragonhide*) polyurea where

prepared on steel panels. The panels were degreased with acetone and Kim-wipes prior to application of the coatings. Both samples cured within seconds, however after spraying a minimal of 24 hours wait period was implemented before the wear resistant test were performed.

For a wear test, a cylindrical steel bar of (238.39 g and dimensions of 50.8 mm x 15.875 mm) was placed on either the coated steel substrate or a free film; illustrated in Figure 6.



Figure 6. Sample, Cylindrical Steel Bar, Low Frame Shimadzu Universal Testing Machine

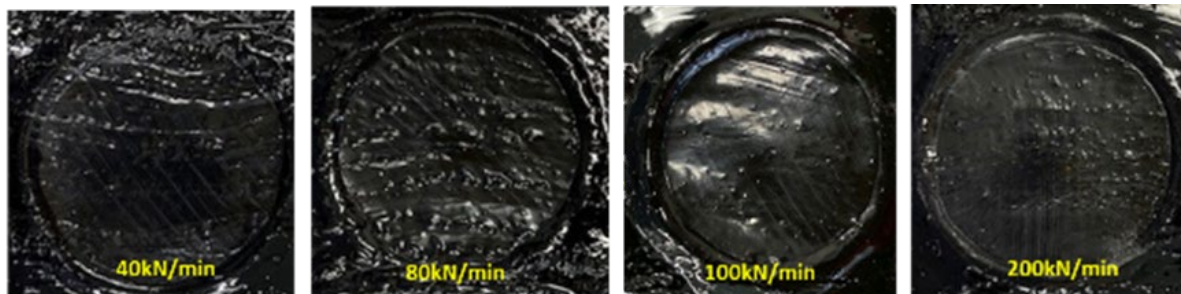
Force was increased at controlled rates up until a maximum force was reached. Three different types of wear resistance experiment were performed:

1. **Wear Resistant of Free Film:** A wear experiment was performed on free film 19-KTB-1007-1. Force was increased at a rate of 20 kN/min and the test was stopped at 150 kN after the coating fractured.
2. **Wear Resistant of Coatings on Substrate – Effect of Force Rates:** Wear resistant experiments were performed on Aliphatic Durabed and Aromatic *Dragonhide* coated steel substrate. The rate of force was incrementally increased from 20kN/minute to 200 kN/minute for both coating systems in order to evaluate the effect of force rates on wear resistant. The maximum force for each experiment was 400 kN. These results are shown in Table 1. In terms of both adhesion and physical damage to the coatings, the aromatic polyurea performed better than aliphatic polyurea throughout most of the testing with no visible damage as shown in Figure 7.
3. **Wear Resistant of Coatings on Substrate – Instrument Limitation:** Wear resistant experiments were performed on Aliphatic Durabed and Aromatic Bedliner coated steel substrate. The rate for force was 100 kN/min and the maximum force of 510 kN is the machine limitation. While the aliphatic polyurea exhibited significant damage under these conditions, the aromatic product showed no visible signs of damage.

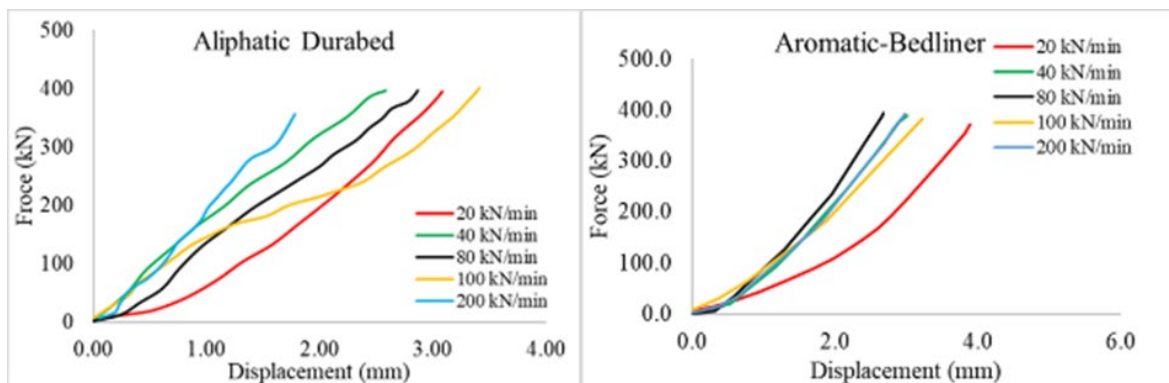
The result of wear experiments 2 and 3 are reported in Table 1. The force vs. strain (displacement) curve for experiment 2 and 3 are extrapolated and reported in Figure 8.

**Table 1. Wear Resistance of Steel Coated with Aliphatic and Aromatic Polyurea**

Sample Name	System	Thickness (mm)	Rate (kN/min)	Max Force (kN)	Displacement (mm)	Adhesion	Physical Damage of Coating Post Wear Test
19-KTB-1003-13	Aliphatic: CAT133 + Durabed BDL1724E	3.5	20	400	3.08	intact	Mild damage
		3.56	40		2.58	intact	Mild damage, 2 cracks
		3.68	80		2.86	intact	Damage, 4 cracks
		3.34	100		3.14	Loss of adhesion	Noticeable damage, crack (>20) within coating
		NA	200	1.78	intact	Very mild to no damage	
		NA	100	510	2.98	intact	Noticeable damage; multiple crack (>14) in coating
19-KTB-1003-2	Aromatic: CAT250 + Dragonhide 1000 BAP1724H	4.12	20	400	3.9	Coating fully adhered to substrate after test	Damage, 4 cracks
		4.18	40		3		No visible signs of damage
		5.24	80		2.7		
		4.43	100		3.2		
		3.81	200	3			
		3.13	100	510	2.89		



**Figure 7. Images of Aromatic Dragonhide After Wear Test; Maximum Force of 400kN**



**Figure 8. Force vs. Displacement Curve of Various Rate of Aliphatic Durabed and Aromatic Dragonhide Coated Steel Substrates**

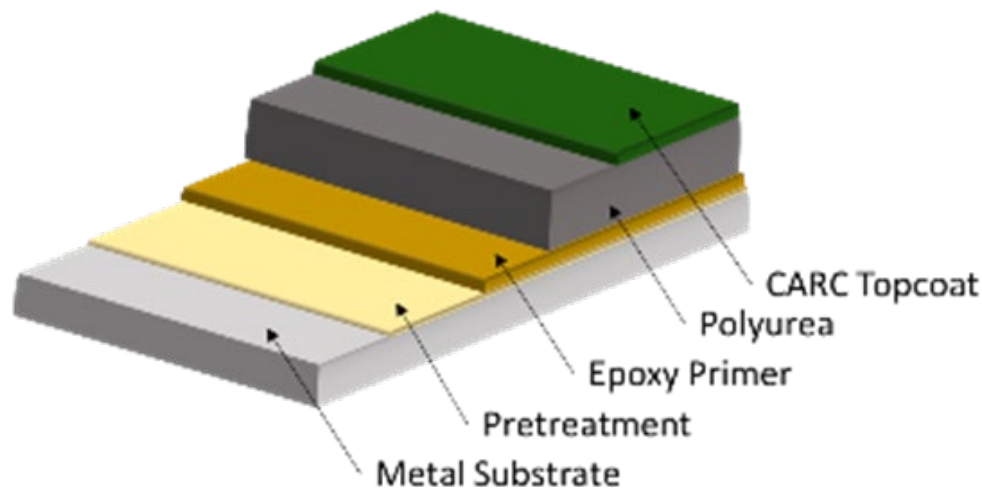
Based on Table 1 and Figures 7 and 8, the Aromatic *Dragonhide* showed higher resistance to the compression-based wear tests. For rates of force between 40 kN/min and 200 kN/min, and maximum force of 400 kN, the aromatic coatings showed no visible signs of damage. Above 40kN/min, the aromatic coatings have more uniform displacement compared to aliphatic Durabed. It is also apparent that as the rate of force increases, the circular indentation left by the cylindrical bar becomes more visible and deeper.

As for the Durabed, the amount of damage observed in the coating increases as the rate of force increases from 20 kN/min to 100 kN/min for maximum force of 400 kN. At 100 kN/min, loss of adhesion to the substrate is also observed, as well as a very deep circular indentation on the tested area.

Increasing the maximum force to 510 kN at a rate 100 kN/min resulted in results similar to the previous experiment. Aromatic *Dragonhide* outperformed the Aliphatic Durabed showing no signs visible of damage. The overall total displacement of both coatings is approximately 3 mm.

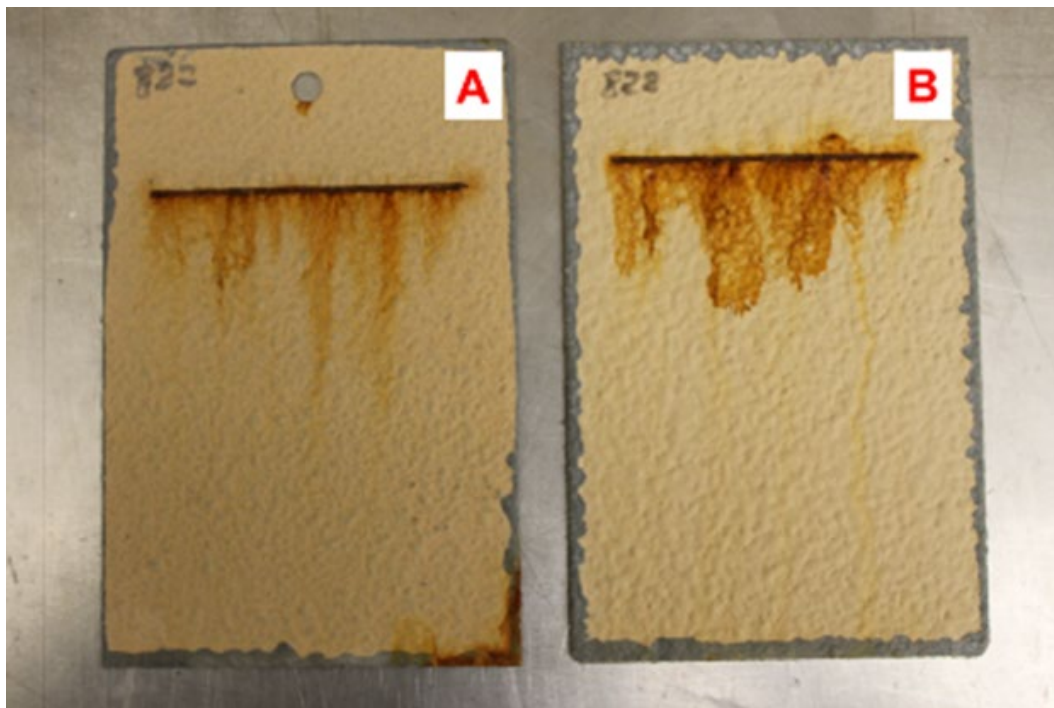
### 3.2.2 Corrosion Resistance

The standard system of coatings as prescribed by MIL-PRF-32440 is shown in Figure 9. In addition to the polyurea coating a pretreatment and epoxy primer layer is included for adhesion and corrosion protection.

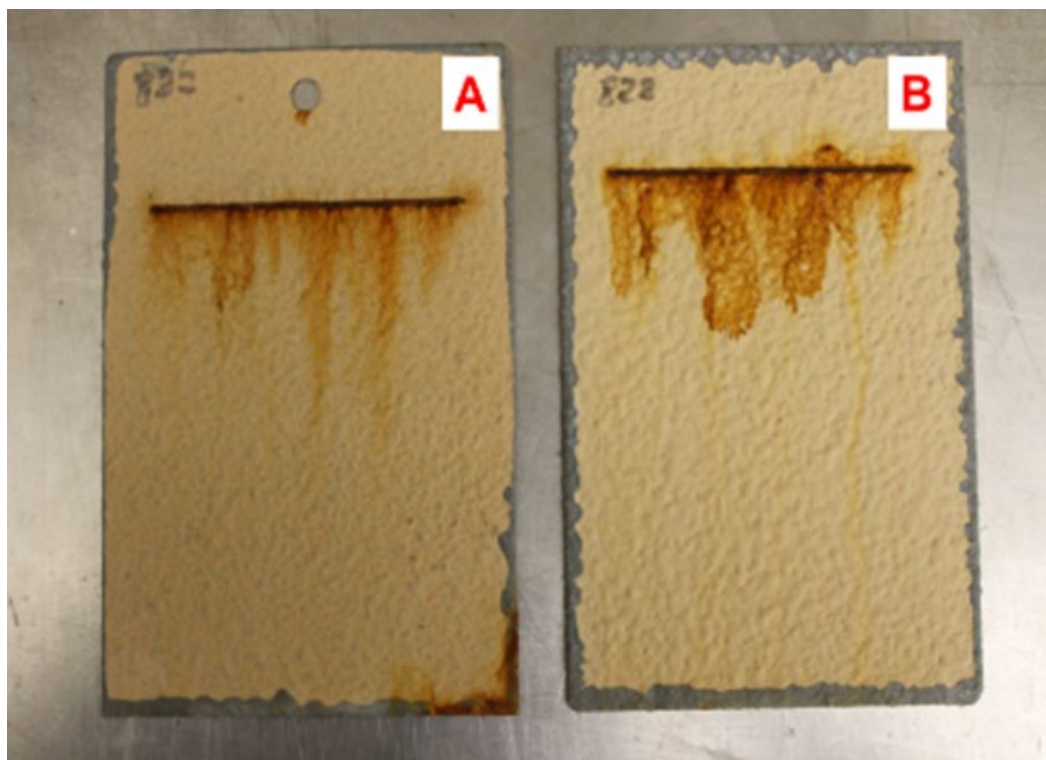


**Figure 9. Coating Stack as Described in MIL-PRF-32440**

This system of coatings performs exceptionally well for chip and corrosion resistance. The specification requires 30 cycles of GMW14872 cyclic corrosion testing with no blistering or delamination. Our testing attempted to stress the system by extending the cyclic corrosion testing to 120 cycles. Further, a 2 mm wide scribe was made through the entire coating stack to bare metal as a means to induce corrosion. As seen in Figures 10 and 11, both aliphatic and aromatic polyurea perform exceptionally well with either MIL-DTL-64159 (water based CARC topcoat) or MIL-DTL-53039 (1K moisture cured CARC). Corrosion is evident within the bare metal scribed area but does not creep beyond the scribe. Further, no blistering or delamination is observed even after 120 cycles of GMW14872.



**Figure 10. Aliphatic Polyurea (28 mils) With Either WB (A) or 1K Solvent Based CARC Topcoat (B) After 120 Cycles GMW14872**



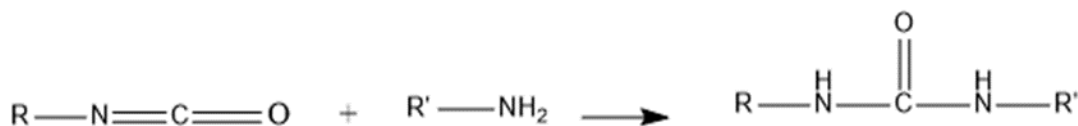
**Figure 11. Aromatic Polyurea (28 mils) With Either WB (A) or 1K Solvent Based CARC Topcoat (B) After 120 Cycles GMW14872**



### 3.3 Alternative Crosslinking Approaches

#### 3.3.1 Acetoacetate-Amine-Isocyanate

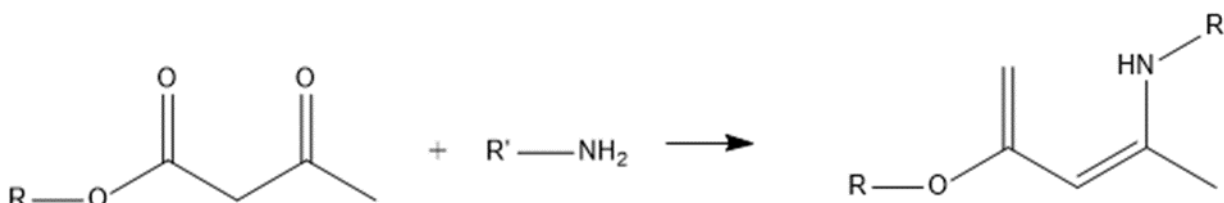
Polyurea coatings result from the very rapid condensation reaction between polyfunctional isocyanates and polyfunctional amine prepolymers. Figure 12 below illustrates a simplified reaction scheme for the crosslinking chemistry.



**Figure 12. Generalized Amine-Isocyanate Reaction Scheme**

The reaction proceeds extremely quickly even at low temperatures such that dry to touch times can be measured in seconds. Performance properties are manipulated via selection of the isocyanates and amine resins, by adjusting stoichiometric ratio of amine to isocyanate and/or by addition of hydroxyl functional materials as a partial replacement for amines.

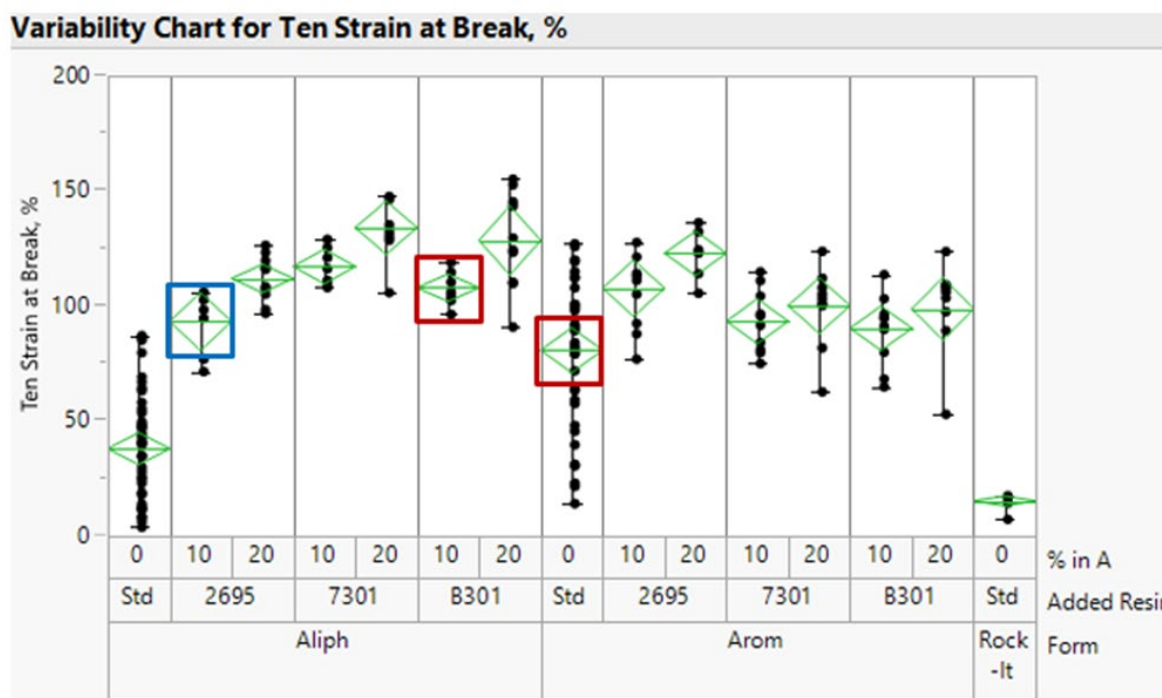
However, the commercially available range of isocyanate prepolymers is somewhat limited and isocyanates exposures can result in skin sensitization. For these reasons PPG researchers chose to investigate alternative curing reactions which might provide the same speed of cure while reducing or eliminating the isocyanate component. An excellent example is the reaction between polyacetoacetate and polyfunctional amines. A simplified reaction scheme is shown in Figure 13.



**Figure 13. Simplified Reaction Scheme for Acetoacetate – Amine Reaction**

Acetoacetate functional materials are compatible with isocyanate crosslinkers so they can be blended at any ratio without unintended side reactions that might affect stability. Acetoacetate functional polymers are readily prepared from virtually any hydroxyl functional polymer via reaction with tertiary butyl acetoacetate with liberation of t-butanol. As a result, acetoacetate crosslinkers may be prepared from a wide range of starting materials including acrylic and polyester polyols. Additionally, acetoacetylation mitigates hydrogen bonding between hydroxyl groups so the resulting polymers exhibit significant viscosity reduction. Crosslink density, glass transition temperature and modulus are a few of the polymer properties that can be manipulated via partial replacement of isocyanate crosslinkers with acetoacetate crosslinkers. Lastly, since the acetoacetate-amine reaction can be just as fast as the isocyanate-amine reaction the resulting coatings maintain desirable cure response.

The following experimental results illustrate how acetoacetate modification can have dramatic effects on resulting coating properties. Both aliphatic and aromatic polyurea systems were used in this experiment. Acetoacetate functional resin were selected from a polyester resin developed by PPG (2695) and two commercially available resins from King Industries (7301 and B301). The level of acetoacetate was selected as a replacement for 0, 10 or 20% of the isocyanate equivalents. Application was via the standard plural component cartridge system and the acetoacetate was blended with the isocyanate. As can be seen in Figure 14, increasing levels of any of the acetoacetate resins results in a significant increase in elongation. In this experiment elongation of the aliphatic polyurea increased from about 40% to about 130% depending on choice and loading level for the acetoacetate resin. The aromatic polyurea exhibited an increase from about 80% to over 125% elongation.



**Figure 14. Effect of Acetoacetate Functional Crosslinkers on Polyurea Elongation**

Young's modulus is useful in characterizing the force required to break a material and thus of importance to understand in a material that will be subjected to physically challenging environments. On average the aliphatic polyurea will exhibit a Young's modulus on the order of 300 MPa whereas the aromatic polyurea is much lower at around 40 MPa. Figure 15 illustrates dramatic changes in modulus that result from addition of acetoacetate functional materials as a partial replacement of isocyanate. Note that the left and right sides of this image represent the same data, but the right half has been scaled to show detail of the lower YM samples. In this case even small additions of acetoacetate result in very significant reductions in Young's modulus. In terms of performance attributes of interest to the Army this is clearly the wrong direction. However, the observation is of potential value in commercial polyurea applications where the elongation may be of more importance than the force to break the material.

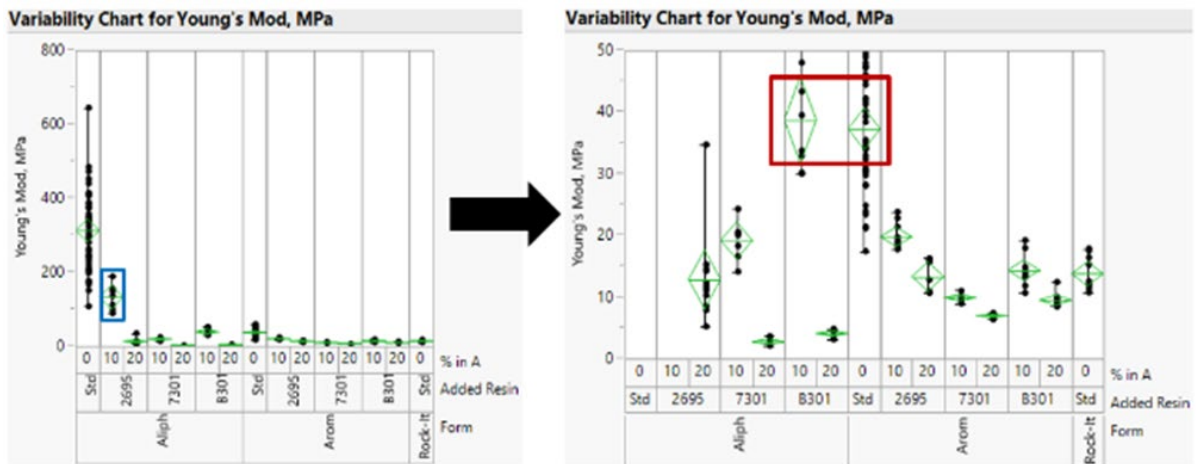


Figure 15. Effect of Substituting a Portion of Polyisocyanate with Polyacetoacetate Crosslinker

### 3.3.2 Polythiol-Amine-Isocyanate

Polythiols, organic compounds characterized by  $-SH$  functional groups, will also rapidly react with polyisocyanates to create a polythiourea linkage. Particularly in combination with amine co-reactants, the cure kinetics can be even faster than standard polyurea systems. PPG explored this crosslinking chemistry in an effort to discern if unique performance properties might be achieved.

A multi-functional, polythiol crosslinker was selected based on its fast reactivity with aromatic and aliphatic isocyanates. During the test, however, the reaction was too fast, and the material gelled as it was exiting the static mixer. Upon closer review of the polyurea formulations, it is believed the presence of tin catalysts with an excess of amine pushed the crosslinking reaction to happen instantly. Future tests focused on eliminating the tin catalyst and finding the right balance of amine and crosslinker functionality.

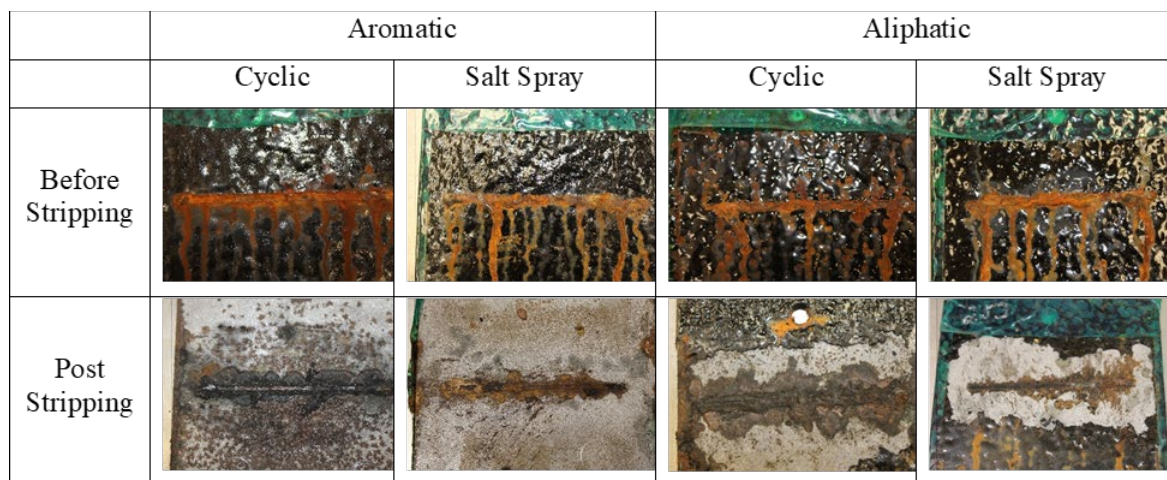
While still extremely fast to cure a few samples were prepared and able to be tested. The reactive polythiol material demonstrated a significant increase in shore D hardness and Young's modulus but in this case elongation was observed to decrease as the resulting polythiourea was too brittle. While interesting chemistry, this particular approach was abandoned to explore developmental formulas with direct to metal performance.

### 3.4 Direct to Metal Approaches

With the qualification of the *Dragonhide* 1000, focus shifted towards process improvement through the direct to metal application of polyurea thereby eliminating the need for a primer. Beyond just reducing material cost and waste, eliminating the primer would result in reduced application time which, in combination with polyurea fast dry time, would result in very fast start to finish applications. This proposed system of direct to metal polyurea would be a significant departure from the MIL-PRF-32440 specifications but if successful could offer significant productivity enhancements to both military and commercial customers.

Initial benchmarking focused on using the qualified *Dragonhide* 1000 and another commercial PPG aliphatic polyurea. To determine corrosion performance ASTM B117 salt spray testing was performed for up to 1512 hours and GMW14872 cyclic corrosion was performed for up to 60 cycles.

Additionally, Pneumatic Adhesion Tensile Strength Testing Instrument (PATTI) adhesion tests were done to measure adhesion to the substrate. The initial results (Figure 16) show little to no signs of blistering or corrosion on the surface but do show significant corrosion under the surface. Between the two systems the *Dragonhide* 1000 shows better scribe creep, however, it also suffers from significant face blistering when applied as a direct to metal coating. This face blistering is much less evident when using the aliphatic formulation as a direct to metal coating. The PATTI adhesion in the aliphatic system was also much higher with ~1100 PSI compared to the ~600 PSI seen in the aromatic system.



**Figure 16. GMW14872 and ASTM B117 Corrosion Results for Aromatic and Aliphatic Polyurea Coatings Applied Direct to Metal**

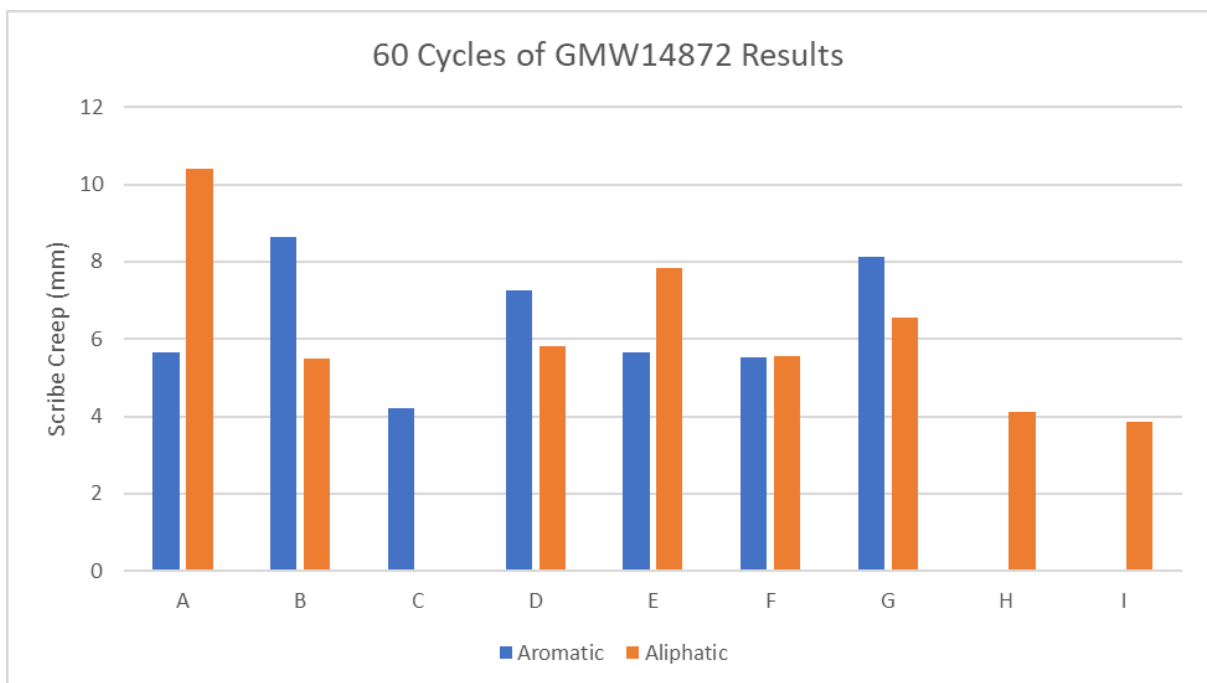
Using this as a starting point the first thought was to improve the corrosion properties through the introduction of corrosion inhibitors. To investigate this a simplified formulation was created preserving the resin composition of the formulation and replacing all the non-critical additives and pigments with the corrosion inhibitor or interest. Table 2 describes the range of corrosion inhibitors screened for this experiment. As in previous testing, a large 2 mm wide scribe was etched through the coatings to bare metal surface to serve as an initiation point for corrosion propagation.

**Table 2. Candidate Corrosion Inhibitors for Direct to Metal Polyurea Formulations**

Composition	Code
Control	A
Metal oxide 1	B
Mixed metal-organic salts	C
Mixed metal phosphosilicate	D
Zinc phosphate/Organic zinc complex	E
Metal oxide 2/Zinc phosphate	F
Metal oxide 2/Ion exchanged silica	G
Ca organic salt	H
Zinc organic salt	I

For the aromatic system, the mixed metal phosphosilicate (Inhibitor C) demonstrated encouraging results in GMW14872 cyclic corrosion testing (Figure 17), ASTM B117 (Figure 18) and with respect to PATTI adhesion (Figure 19). Further, this inhibitor prevented face corrosion which could be seen in other samples after chemically stripping the polyurea from the steel substrate. Unfortunately, the mixed metal phosphosilicate inhibitor was incompatible with both the isocyanate and amine components of the polyurea leading to poor stability and very high viscosities. Attempts to stabilize the inhibitor by pre-reacting with a monofunctional amine were unsuccessful. The remaining inhibitors had little effect on the scribe creep and in several situations resulted in worse results. Missing data points from Figures 17, 18 and 19 were samples that could not be sprayed due to system stability and high viscosity.

Within the aliphatic system, there was a greater effect seen in the scribe creep. A majority of the inhibitors reduced the scribe creep in cyclic corrosion. They also appear to improve the PATTI adhesion results, which is well above the specification requirement already. In particular, the Ca and Zn organic salts showed the largest effect. However, the aliphatic system did have a much worse baseline corrosion results and the improvements to performance were still well below acceptable levels. In addition, the largest benefit to using an aliphatic system over an aromatic system is the improved weathering resistance from the aliphatic system. Since the polyurea is going to be overcoated with a CARC topcoat or used in under carriage applications with minimal UV light exposure, the increased cost does not make sense. This, in combination with the poor corrosion performance, led us to focus on the aromatic formulations going forward.



**Figure 17. GMW14872 Corrosion Scribe Creep Results for Candidate Corrosion Inhibitors in Direct to Metal Polyurea Formulations**

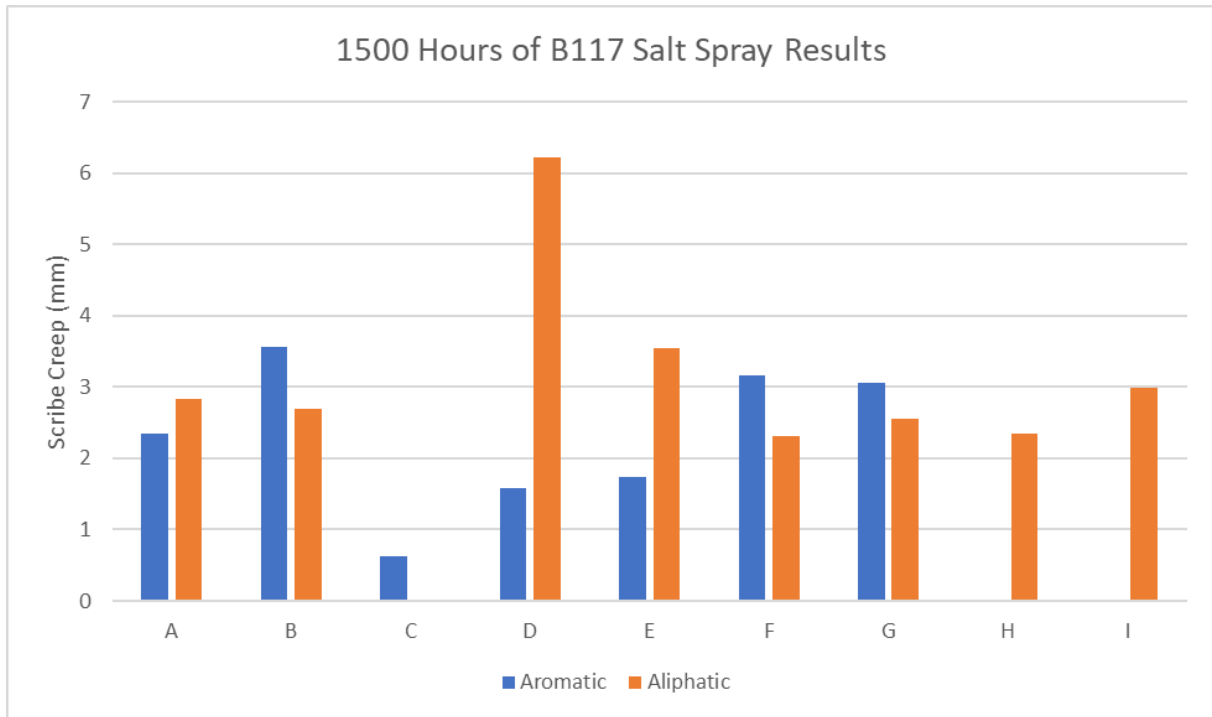


Figure 18. ASTM B117 Corrosion Scribe Creep Results for Candidate Corrosion Inhibitors in Direct to Metal Polyurea Formulations

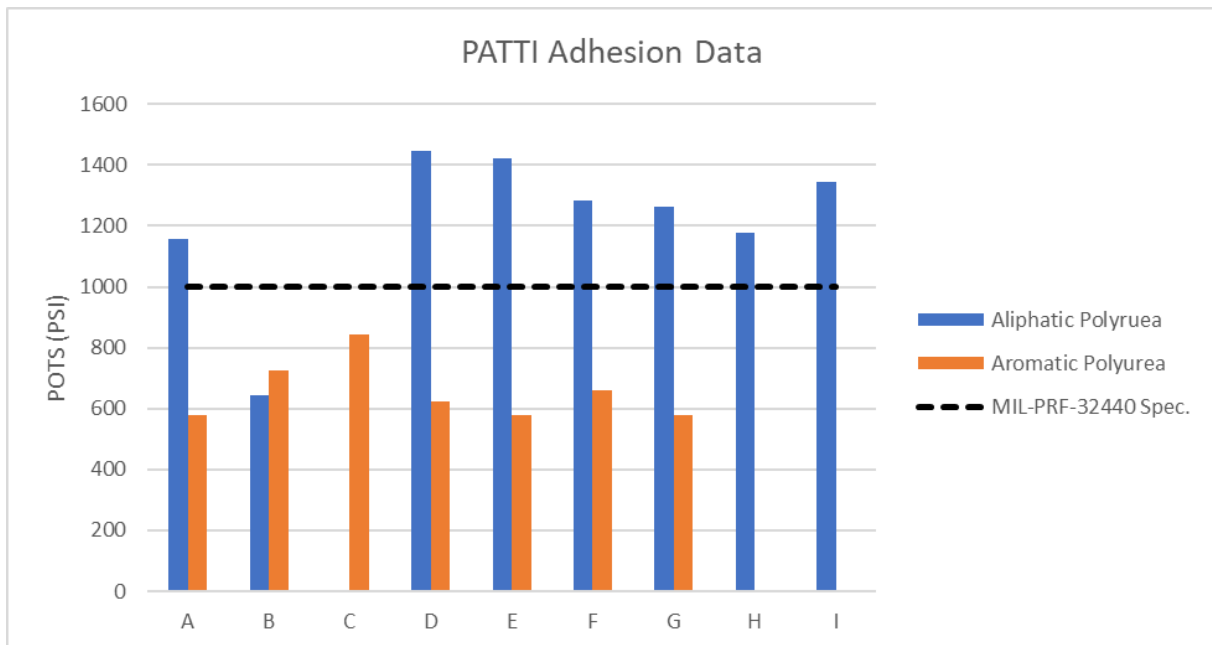
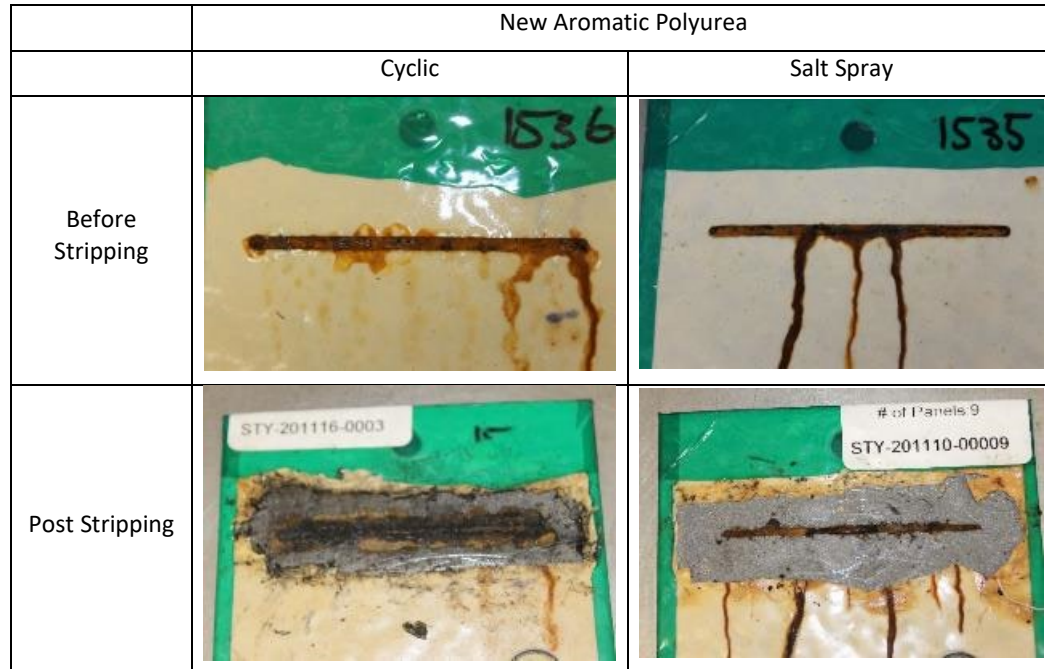


Figure 19. PATTI Adhesion Results for Corrosion Inhibitors in Direct to Metal Polyurea Formulations

Seeing the poor results from the current commercial systems as direct to metal coatings, a new slower curing aromatic polyurea system was investigated. The idea was that a slower reacting formulation would have more time to form interactions with the substrate to form hopefully resulting in better adhesion and corrosion properties. Initial benchmarking has shown improved adhesion and corrosion results. The baseline PATTI adhesion results had shown over 1400psi exceeding the specification requirements and the results seen from the aliphatic polyurea in previous experiments. The new formulation also showed almost no scribe creep after B117 salt spray and improved cyclic corrosion over previous systems (Figure 20). Despite these results significant face corrosion was observed throughout the panel as well as a greater amount of blistering along the scribe.

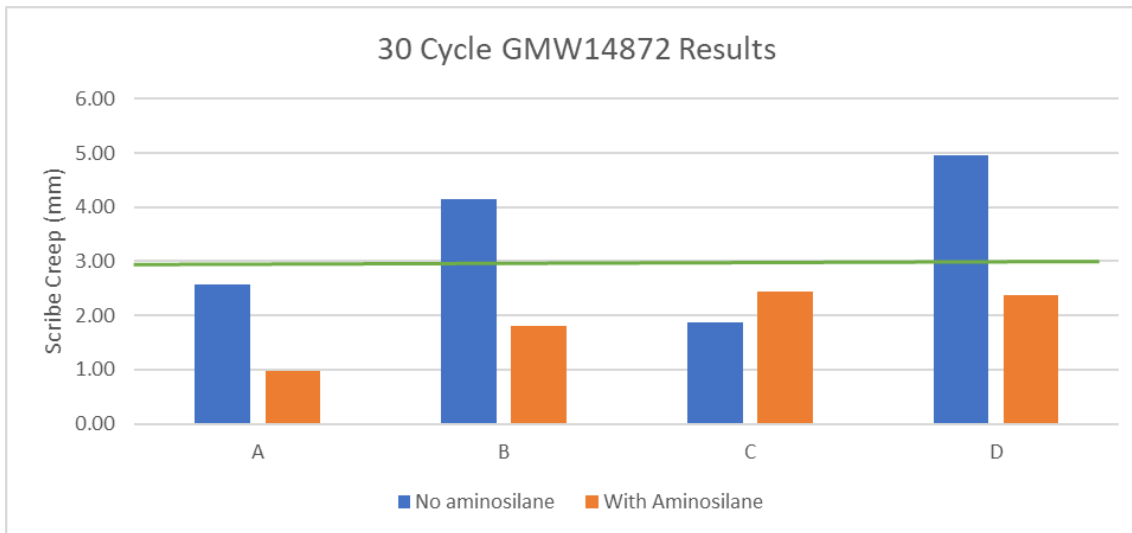


**Figure 20. GMW14872 and ASTM B117 Corrosion Results for New Aromatic Polyurea Formulation**

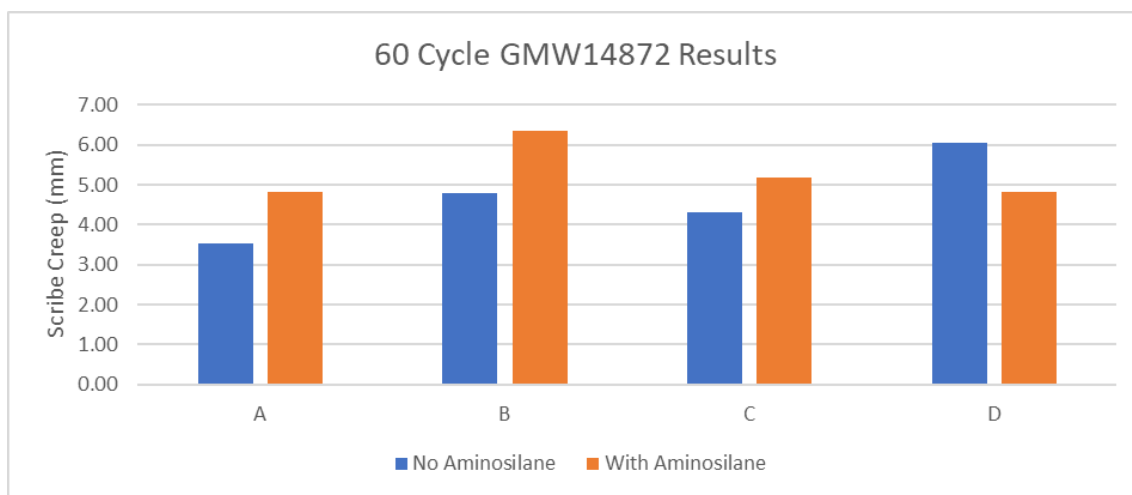
Incorporation of the best performing adhesion promoters and corrosion inhibitors was attempted to improve the deficiencies in the new system (Table 3). The corrosion inhibitors were added in combination with the amino alkoxy silane adhesion promoter and alone. Outside of the zinc organic salt no system showed a benefit to the corrosion properties in the system and most showed worse results in the longer cyclic corrosion testing. The corrosion inhibitors alone also did not prevent the face corrosion. Similarly, the adhesion promoter by itself did not show a large benefit to the scribe creep results but was able to prevent the face corrosion. In fact, none of the samples which contained the amino alkoxy silane showed significant face corrosion in the timeframe tested. Additionally, there does not appear to be any benefit to the combination of the adhesion promoter and corrosion inhibitor with the adhesion promoter by itself showing the best results. Figures 21 thru 24 illustrate scribe creep performance for the various inhibitor systems with and without amino silane adhesion promoter. Of note, the requirement within MIL-PRF-32440 is 30 cycles of GMW14872 testing with a scribe creep of 3.0mm or less. In this experiment the cyclic corrosion testing was extended for an additional 30 days.

**Table 3. Candidate Corrosion Inhibitors for New Aromatic Polyurea System**

Composition	Code
Control	A
Zinc phosphate/Organic zinc complex	B
Zinc organic salt	C
Mixed metal phosphosilicate	D

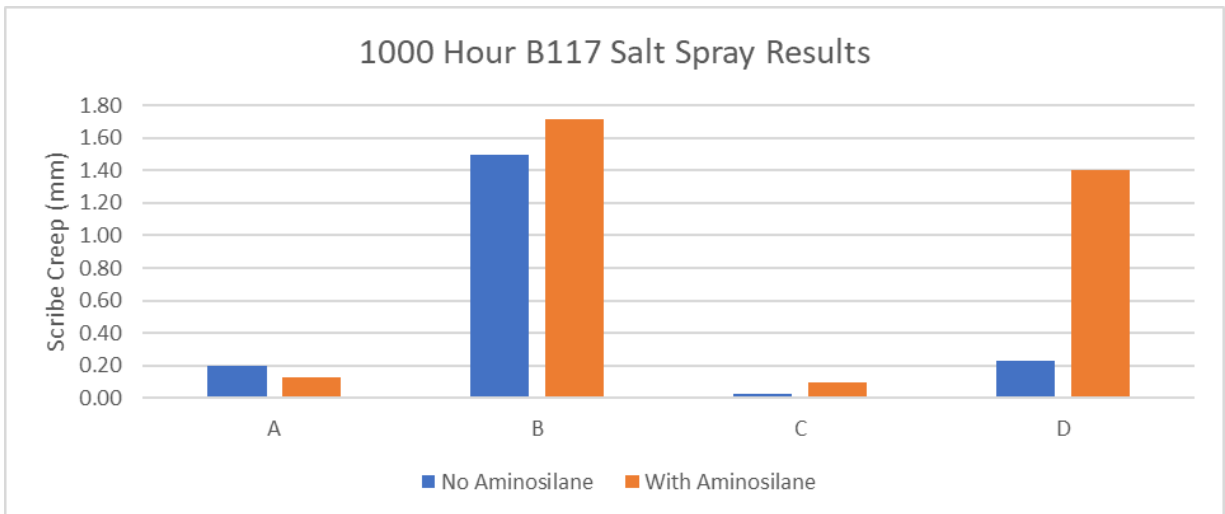


**Figure 21** Scribe Creep Measurements for New Aromatic Polyurea with Various Inhibitor Systems After 30 Cycles GMW14872

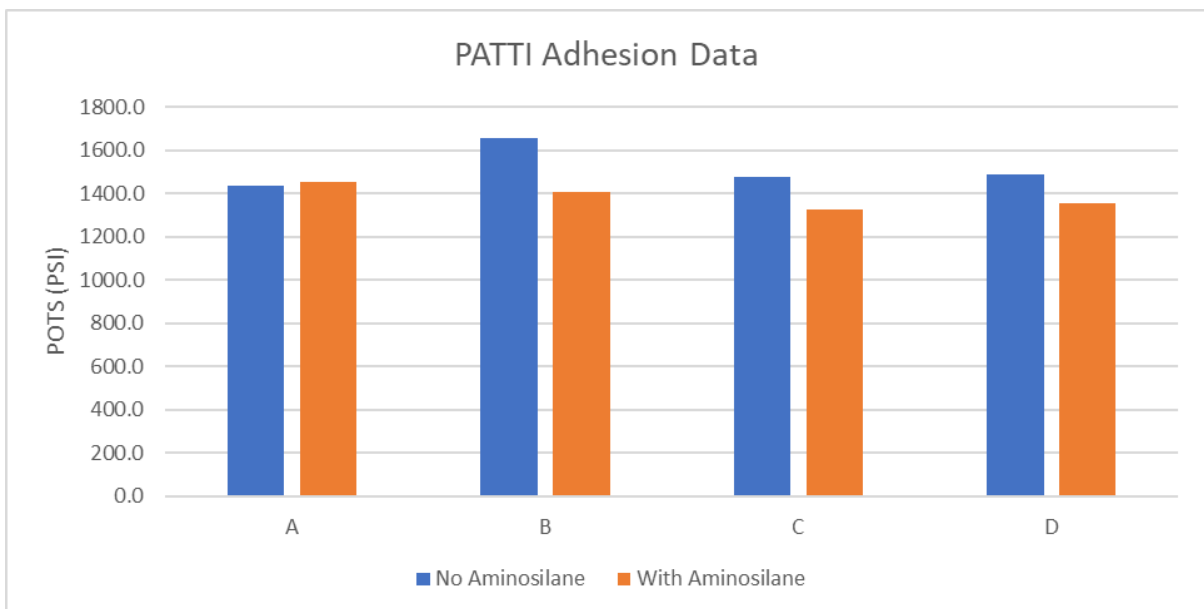


**Figure 22.** Scribe Creep Measurements for New Aromatic Polyurea with Various Inhibitor Systems After 60 Cycles GMW14872e



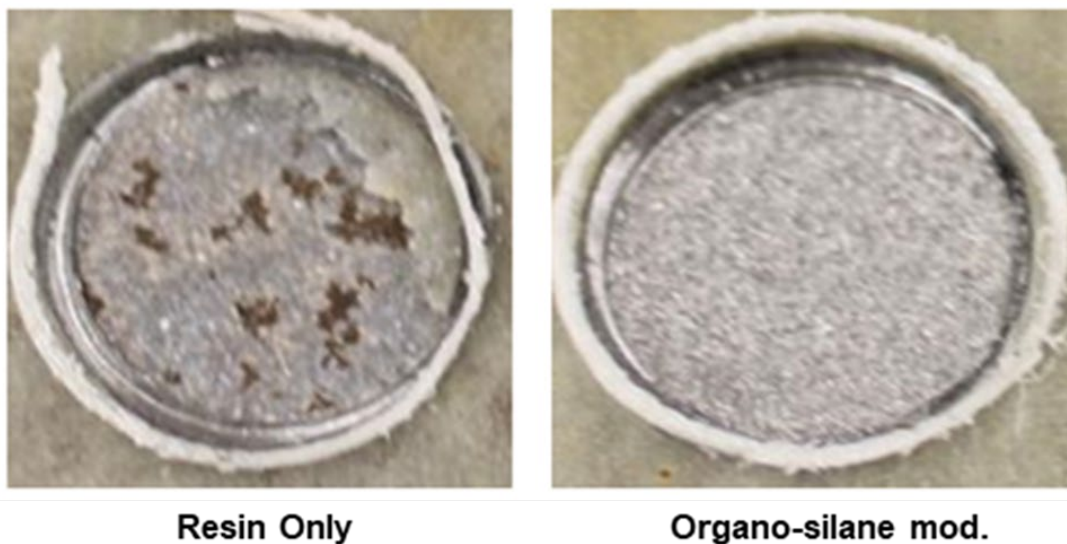


**Figure 23. 1008 Hours B117 Scribe Creep Measurements for New Aromatic Polyurea with Various Inhibitor Systems**



**Figure 24. PATTI Adhesion Results for New Aromatic Polyurea with Various Inhibitor Systems**

Figure 25 illustrates the improvement in face corrosion observed when amino silane adhesion promoter is added to the formula. The image shows a ½ inch circle of polyurea which has been removed from the panel after 60 cycles of GMW14872 cyclic corrosion testing. The small spots of red rust which appear for the resin only system are eliminated when amino silane is added.



**Figure 25. Example of the Amino-Alkoxysilane Effect on Face Corrosion After 60 Cycles of GMW14872**

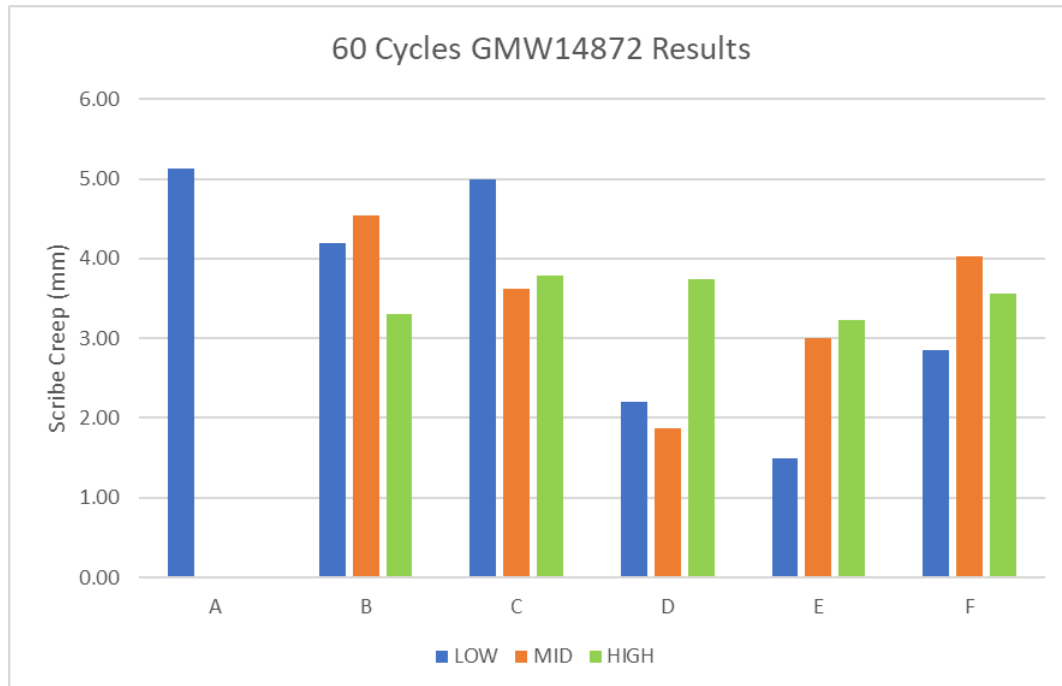
To gain a greater understanding of the effect of corrosion inhibitors in the system higher loadings of the corrosion inhibitors were investigated. For this ladder three different loadings of corrosion inhibitor were investigated. Candidate inhibitors are shown in Table 4. The low loading is the amount used in the previous experiment which is based on replacing the non-critical pigments within the control formulation. The medium and high loading were roughly two and three times that amount respectively. It should be noted that due to the strict requirement for a 1:1 volume mix ratio in the cartridge gun used for the spray application the higher loadings of corrosion inhibitor also have a different equivalence ratio between the amine and isocyanate resulting in a higher proportion of NCO in the system. While not optimal to change multiple variables at once it is unavoidable in this situation.

**Table 4. Candidate Corrosion Inhibitors for Re-Evaluation at Higher Loadings**

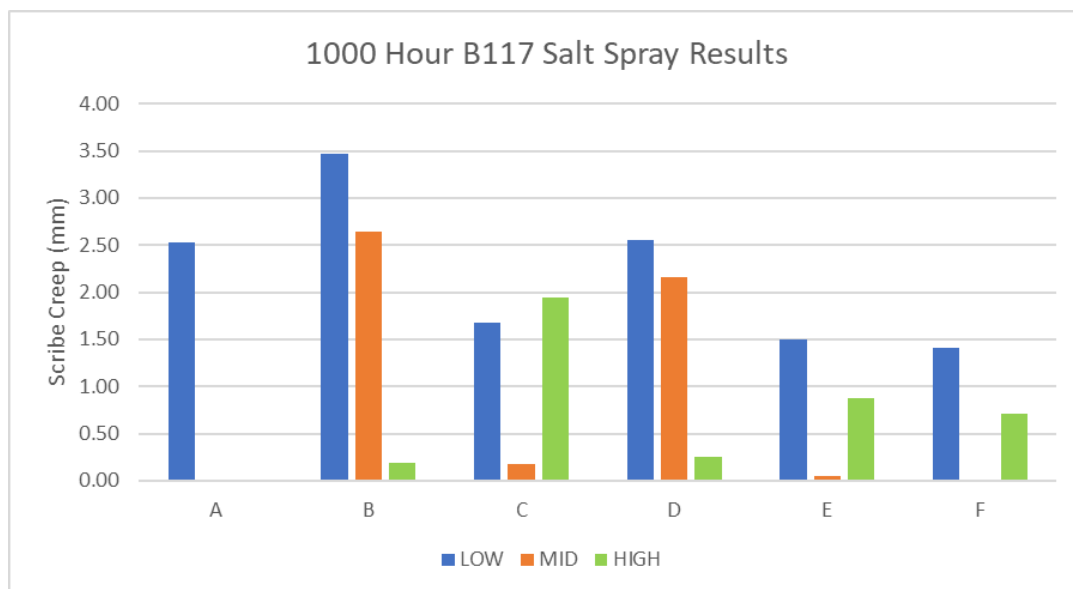
Inhibitor	Code
Control	A
Metal Oxide	B
Mixed metal phosphosilicate	C
Zn phosphate/Organic Zn complex	D
Zinc organic salt	E
Organic Inhibitor 2	F

The scribe creep results from the GMW14872 did show improvement over the control in most cases, as seen in Figure 26, with the zinc phosphate/organic zinc complex and the zinc organic salt corrosion inhibitors showing the greatest reduction. In these systems the higher loadings did not appear to offer any benefit to the corrosion properties and were generally worse than what was seen at the

lowest loadings. The metal oxide and mixed metal phosphosilicate inhibitors did show benefit to an increase in loading, but the benefits were relatively small. The scribe creep results from the B117 salt spray (Figure 27) did show a larger effect from the loading, with an increasing amount of inhibitor generally showing a decreasing amount of corrosion. Unfortunately, the varying loadings did not appear to prevent the face corrosion as well as the amino-alkoxy silane did. Given those results, it appears that addition of the silane additives is the best method for corrosion reduction.

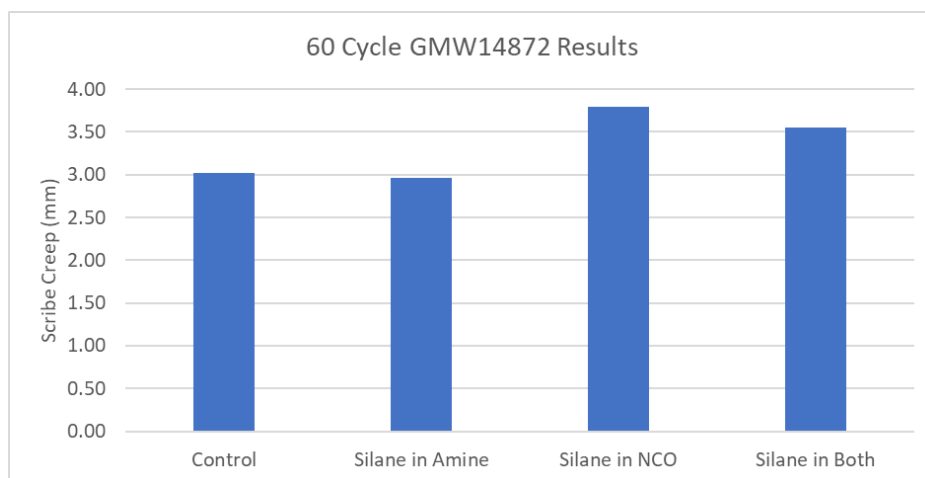


**Figure 26. Scribe Creep Results for the Corrosion Inhibitor Ladder Study After 60 Cycles GMW 14872 Cyclic Corrosion**

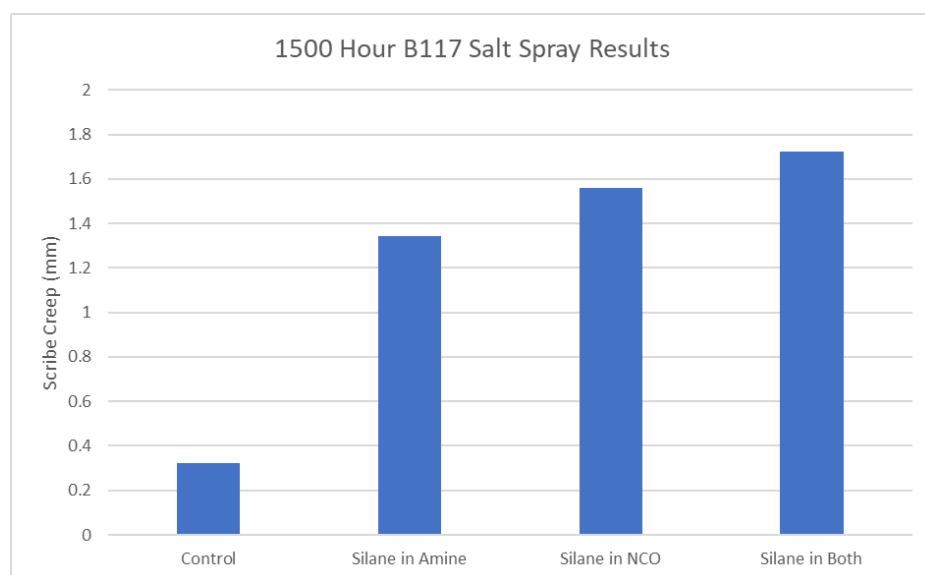


**Figure 27. Scribe Creep Measurements for the Corrosion Inhibitor Ladder Study After 1008 Hours ASTM B117 Salt Spray**

While the corrosion inhibitors had shown mixed results and did not prevent the face corrosion, all of the formulations containing the amino-alkoxysilane did stop this phenomenon. Generally, these additives are placed on the amine side of the formulation, since they are reactive with the isocyanate. However, we wanted to investigate whether they would still provide the same or better benefits if placed in the isocyanate package. Doing this would have the effect of reducing the equivalent weight of that package and allow us to do the same on the amine portion through the addition of more additives. This would allow greater formulation latitude while maintaining crosslink density. The corrosion results in Figures 28 and 29 show that the amino-alkoxysilane can in fact be placed on either side and prevent the face corrosion. The other results were largely similar in terms of scribe creep and adhesion as well. While putting the amino silane in the isocyanate component of the formulation would enable increased formulation latitude and make subsequent formula modifications easier to explore it would also be creating a new isocyanate/silane hybrid polymer that would need to be registered with the Environmental Protection Agency (EPA) and other regulatory bodies where the product might be used. Accordingly, making an aminosilane part of the amine component of the polyurea formulation makes more sense.



**Figure 28. Effect of Amino Silane Additions on GMW14872 Cyclic Corrosion Results**



**Figure 29. Effect of Amino Silane Additions on ASTM B117 Salt Spray Results**

## 4. Conclusions

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This project achieved a number of important goals. First, polyurea coatings qualified to MIL-PRF-32440 may be expected to provide exceptional performance when used and applied in accordance with specification requirements. In fact, the chip and abrasion resistance of polyurea coatings argues for much more use within the defense community. Polyurea coatings qualified to MIL-PRF-32440 cannot be matched for performance in high wear environments such as mobile bridging, under carriage components, vehicle trailers and other applications where traditional coatings would fail almost immediately. This robust performance in harsh environments would protect valuable assets and increase mission readiness via reduced asset down-time. Further, beyond the scope of this project, PPG is supporting training video production which will enlighten the defense community on these advantages and hopefully increase usage where applicable.

The project team also explored alternative coating chemistries that would potentially push polyurea performance even further in terms of elongation and strength. In particular, polyurea systems modified with polyacetoacetate functional co-reactants were explored since the cure kinetics is comparable to that of the standard isocyanate-amine systems. We found that while cure speed was equivalent for these modified systems increases in elongation were offset by significant reductions in Young's modulus. While an isocyanate free coating with properties approaching polyurea may be desirable from and worker safety perspective, this particular approach failed to match polyurea resistance to breaking.

Lastly, the standard polyurea coating stack includes the use of approved pretreatment and primer layers prior to polyurea application. This combination of coatings provides outstanding adhesion, corrosion resistance and protection from impacts/abrasions. It can also be time consuming to apply each layer and wait for sufficient cure before applying the subsequent layers. To address this the project team investigated and made significant progress toward direct to metal polyurea systems which would eliminate the pretreatment and primer layers. While such a system is not anticipated by MIL-PRF-32440 it's worth considering in future revisions of that spec. Final formulations of direct to metal polyurea were demonstrating good performance for adhesion and corrosion resistance while maintaining the desirable rapid cure response.