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Third Generation Polysiloxane Coatings for CUI Mitigation

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ABSTRACT

Polysiloxane is an inorganic compound with tremendous advantages of stability vs. organic compounds such as epoxy and urethane. Third generation, pure inorganic formulation, elevated temperature polysiloxane coatings for CUI mitigation offer significant advantages over earlier versions, including true air dry, weather resistance without baking, and an ultra-high-build spray-on insulation material suitable for cyclic service to 750 °F.

Keywords: Polysiloxane, CUI, insulation, third generation

INTRODUCTION

Corrosion Under Insulation (CUI) is a well-known industrial problem that has been plaguing asset owners for decades. CUI presents one of the costliest corrosion factors for Oil and Gas, petrochemical and general processing industries and can result in unplanned shutdowns, maintenance repairs or even explosions on live plants. Due to the risk factors present, many methods to prevent CUI have been adopted, with the intention to find best practices to minimise the risk of potentially catastrophic issues surrounding CUI.

The CUI concept is composed of a three-component system:

1. Steel – substrate for processing chemicals (constant or in cyclic temperature operation)
2. Insulation – provides thermal efficiency
3. Cladding – protection for insulation and steel from atmospheric elements

In practice the cladding system is not truly sealed from the atmospheric elements and rain, deluge water, steam or cooling towers is often is able to penetrate the system through an ingress point in the cladding material, generally where complex structures pose huge difficultly in building a watertight system. Additionally, due to the permeable insulation (open cell) types used being moisture sensitive, condensation build is a frequent CUI contributor. Once water has penetrated the system via an ingress point such as breaks, seams, gaps, unsealed valve sections it is absorbed in to the open cell insulation causing saturation or highly concentrate and able to cause corrosion to the steel. Potential contaminates like acid or high salt content rain or leaching chemicals (chlorides /sulphides) from insulation systems that can form acidic compounds accelerating the corrosion rate.

Most predominate materials used for industrial processing are carbon and stainless (austenitic or duplex) steels (CS) and (SS) respectively. Both steel types are susceptible to CUI via multiple corrosion mechanisms. Temperatures where high CUI (either in cyclic or constant operation) is present in CS is between -4 to 175 °C (-25 to 350 °F). In SS, the temperatures where CUI is likely to occur is between 50 to 175 °C (120 to 350 °F). The rate of corrosion is directly related to the CUI system, suitability of CUI coating, insulation type and cladding installation quality.

Specifiers and asset owners have a wide selection of materials to choose from a variety of suppliers when designing, building plants and during maintenance. To aid this process, the main universal guidance document available is NACE SP0198 – 2017[1] *Control of Corrosion Under Thermal Insulation and Fireproofing Materials – A Systems Approach*" which lists suitable material selections in cladding, insulation and coatings. Listing coating selection as per operating temperature and chemistry allows classifications and easier for coating selection.

CURRENT COATING MITIGATION TECHNOLOGIES AND STANDARDS

Generally, usage and specification of CUI coatings is dependent on operating temperatures of processing equipment. NACE SP0198 -2017 is an industry standard for CUI coating classification which highlights and tabulates substrate (carbon or austenitic/duplex stainless steels) material, temperature ranges, recommended surface preparation, surface profile (R_z) and coating dry film thicknesses of CUI protective coating systems.

From the beginning of 1970's inorganic zinc (IOZ) coatings were used as a CUI prevention method however, due to the sacrificial properties of IOZ coatings the zinc is rapidly consumed under insulation (cyclic wet/dry) environments providing inadequate corrosion protection. Due to this mechanism, IOZ coatings are no longer specified for sole use under insulation, instead if used, must be overcoated with a suitable CUI resistant finish coat. Epoxy type coatings are predominately used for lower temperatures in CUI, epoxy novolacs range from -45 to 150 °C (-50 to 300 °F) and epoxy phenolics range from -45 to 205 °C (-50 to 400 °F). Other coatings include metallization processes, fusion-bonded epoxies and thin film petroleum wax primers. NACE has introduced within the last 15 years inorganic copolymer (IC) and inert multipolymeric matrix (IMM) coatings for the recommended full temperature range regarding industrial CUI mitigation ranging from -45 to 650 °C (-50 to 1200 °F), various versions of IMM are available on the market and are now at second generation status by some suppliers. From a chemical perspective, IC and IMM type coatings are classed as polysiloxane coatings.

Table 1
Under Insulation Coatings (NACE SP0198-2017 classification) for Carbon Steel

System	Chemistry	Temperature range ºC (ºF)
CS1	Epoxy	-45 to 60 ºC (-50 to 140 ºF)
CS2	Fusion bonded epoxy	-45 to 60 ºC (-50 to 140 ºF)
CS3	Epoxy Novolac	-45 to 150 ºC (-50 to 300 ºF)
CS4	Epoxy Phenolic	-45 to 205 ºC (-50 to 400 ºF)
CS5	TSA	-45 to 595 ºC (-50 to 1100 ºF)
CS6	Inorganic copolymer (IC) / Inert multipolymeric matrix (IMM)	-45 to 650 ºC (-50 to 1200 ºF)

Coating requirements for under insulation service include temperature stability and thermal cycling, corrosion resistance, hot saline water immersion (HWI) properties, chemical resistance, mechanical properties. The coating properties must be present from application conditions and not require stoving or curing at elevated temperatures. Issues have been identified in the field with products requiring heating before providing full corrosion and mechanical properties and therefore, resistance to CUI environments. What must also be highlighted is if the need for heat curing is present, specification and use below the curing temperature should be highly avoided as CUI protection will be limited.

Although an official coating classification is certainly a huge benefit for specifiers and asset owners in coating selection for under insulation corrosion prevention, the NACE SP0198 - 2017 does not provide insight, guidance or test methods for establishing coating performance. To date multiple laboratory protocols have been developed by manufacturers and asset owners, most of the methods documented are used universally for CUI coating testing. Even so, the testing standards/methods are still a relatively vague area with formulators, specifiers and asset owners often confused or undecided on which test(s) should be adopted to demonstrate product suitability and to distinguish performance levels between alike products.

TESTING PROTOCOL FOR CUI COATINGS

For CUI coatings, a diverse testing program must (see Table 2 for suggested tests) be adopted to demonstrate resistance to the multi-aggressive environment, which the coating is likely to be subjected to during its service life. Taking in to account the environments from immediately after application to in service and therefore, performance levels at ambient, after heating exposure and in cyclic fashion.

Table 2
CUI Coating Testing Program

All testing was run after coatings had been cured for 168 hours at 23 °C and 50% humidity.

Laboratory Test	Method	Standard
Cyclic CUI Program	1. **16 hours @ 204 °C** 2. **Thermal shock (water, 23 °C)** 3. **8 hours in HWI (5% NaCl) at 95 °C** Repeat 80 cycles	N/A
Adhesion	Dolly pull-off testing. PosiTest AT-A Automatic Adhesion Tester	ISO 4624 ASTM D4541
Salt Spray	Q-FOG cyclic corrosion chamber C5 (1440 hours)	ISO 12944-6 ASTM B117
Hot Water Immersion (HWI)	Immersion at 90 °C (5% NaCl solution) (4000 hours)	ISO 2812-2 ASTM D870-15
Impact Resistance	TQC Direct impact tester	ISO 6272-1 ASTM D2794
Flexibility	TQC Cylindrical bend test 100mm (SP1820) 0.75mm panels	ISO 1519 ASTM D522
Pencil Hardness	TQC Pencil Hardness Test (750g) VF2377	ISO 15184 ASTM D3363
Thermal Stability	Heat to 650 °C - Allow to cool to ambient temperature Repeat 30 cycles	N/A
Cryogenic Cyclic Program	1. **Heating at 200 °C for 30mins** 2. **Cooling to 23 °C for 30mins** 3. **Immersing in liquid nitrogen at -196 °C for 30mins** 4. **Directly returned to the oven at 200 °C** Repeat cycle 5 times	N/A
Abrasion Resistance	Taber Abraser (Abrader) – Model 5135	ISO 7784-3 ASTM D4060
Chemical Resistance	Using 10% HCL & H_2SO_4, Diesel & Benzene (hydrocarbons) (720 hours)	ISO 2812-4 (method A) ASTM D6943-15 (method A)
QUV Weathering	QUV weathering testing (3000 hours)	ISO 11507 ASTM D4329
Solvent-wipe (rub test)	MEK/Xylene solvent rub test	ISO 13523-11 ASTM D5402 - 15

The resulting test program allows demonstration of combined and individual properties of coating systems. One universal CUI protocol does not cover the full scope of subjected circumstances during a coatings service life for CUI use. Therefore, as a guide such a program gives beneficial insight to a performance level of a CUI coating.

As indicated within table 3 from application to service there are many potentially catastrophic elements which can attack and jeopardise the integrity of the coating system resulting in compromised service life. It is vitally important to consider the main necessary coating parameters and demonstrate the required performance levels of the protective coating. Such a test program can provide valuable evidence of a coatings suitability for CUI usage.

Table 3
Relation from Laboratory to Expected Service Environments for CUI Coatings

Test Type	Description	Exposure in Practice
CUI Cyclic Test Program	To simulate a typical CUI environment of which the coating can demonstrate long-term durability in cyclic fashion in such an aggressive scenario.	The subjected coating will be in a CUI environment throughout its required service life.
Thermal Resistance	Demonstrates that the coating can endure high temperatures without any degradation occurring.	Substrate temperatures are likely to be cryogenic or elevated and cyclic throughout service life.
Salt Spray	The product is able to provide high levels of anti-corrosive protection to the substrate.	Waiting for service, during transit and during service.
Hot Water Immersion (HWI)	Immersion is a part of CUI hence; the coating must be able to endure heated immersion to prevent any corrosion of the substrate.	During a CUI environment e.g. cyclic wet/dry environments.
Adhesion	To demonstrate the coating is capable of adhering to the required substrate which sufficient strength to provide long-term service life.	Continuous throughout service life.
Chemical Resistance	High performance against acidic & hydrocarbon chemical environments demonstrates the coating can perform without degrading from corrosive foreign contaminates.	During service from leaching insulation, waiting for service & during transit or spillages on-site.
Impact Resistance & Cylindrical Mandrel Testing	Demonstrates the coating is flexible and hard and it can endure stresses applied to the coating in service.	During service, maintenance procedures & during transit.
Pencil Hardness	Demonstrates the coatings film hardness & the physical state of the polymer in question.	During transit and service life.
Abrasion Testing	Abrasion testing will show the levels of; film hardness, cohesive and adhesive strength of the coating system.	During transit and service life.
QUV Weathering	Cyclic weathering testing demonstrates UV and condensation cyclic resistance.	During storage and transit.
Solvent-wipe	Demonstrates a cure state of TGPS.	Field testing shows indication of cured state.

POLYSILOXANE CHEMISTRY AND SUITABILITY FOR CUI

Careful material selection is vital for providing the protection in the multi-aggressive environments such as CUI service. Polysiloxane polymers demonstrate particular characteristics including hot water immersion, high temperature, chemical & UV resistance allowing to withstand the harsh circumstances of CUI, from shop application through to enduse the polymer and resulting coating will provide protection to the substrate via the inherent inorganic polymeric based backbone.

A polysiloxane polymer is based upon $[\text{-Si-O-Si-}]_n$ backbone, the silicon – oxygen bonding is very resistant to heat & UV degradation due to its higher bond dissociation energy (452 kj/mol) and being already oxidised. This fares highly against the traditional congeners like carbon – carbon bonding of organic based polymers that have lower bond dissociation energy (346 kj/mol) and the potential to oxidise further, making the organic type polymers more susceptible for degradation. This bonding strength difference is related to organic polymers (generally) having lower temperature tolerances and considerably faster UV deterioration when compared to siloxane based coatings. Hence, when the requirement for heat and UV resistance (either individually or combined) are present polysiloxane chemistry demonstrates a greater degree of suitability over organic based polymers.

POLYSILOXANE COATING SEGREGATION

- **First Generation Polysiloxane (FGPS)**

In the mid 1990's a polysiloxane hybrid coating was introduced that composed of an epoxy-siloxane hybrid. Developed for use as an elevated temperature coating, exposed or under insulation and was usable to 1100 °F. The polysiloxane hybrid chemistry still contained a densely cross-linked organic polymeric structure. In cyclic ambient-hot-ambient service on small diameter piping or convoluted small shapes, FGPS tended to crack and disbond from the substrate due to internal stresses caused by the inherent two component highly cross-linked hybrid chemistry. In the intervening two decades, first generation polysiloxane has continued in ambient temperature service but is rarely used on high-heat equipment.

- **Second Generation Polysiloxane (SGPS)**

During the last 15 years, IMM (1st /2nd generation) or IC coatings have been widely used for CUI mitigation purposes. These coatings fall in to the category of second-generation polysiloxanes (SGPS). For such coating chemistries, the temperature limits are normally in the region of 1200 °F. The higher level of temperature tolerance is mostly due to the elimination of organic counterparts, high concentration of inorganic siloxane based polymers and higher flexibility.

The introduction of these coatings were a step forward in providing protection to under insulation substrates. However, there usage has indicated issues in the field such as soft film before heating, typically >150 °C (300 °F), the results of the necessary heating step not only affects the mechanical properties of the coating but also corrosion, UV, chemical and adhesion properties all of which are required to ensure maximum CUI protection. Hence, multiple failures have been identified in the field either before service above >150 °C (300 °F) or with use below curing temperatures.

- **Third Generation Polysiloxane (TGPS)**

Now available is a 3rd generation polysiloxane introduced for CUI mitigation purposes. The new coating was developed and launched in 2015 and tested under multiple laboratory and field test protocols. The characteristics of this coating are a single component, fully ambient curing inorganic polysiloxane that demonstrates elimination of field issues seen with SGPS coatings. The removal of the necessary heating as seen with SGPS allows for full protection from ambient application temperatures as low as 10 ^{o}C (50 ^{o}F) and specification across temperature range from -196 to 650 ^{o}C (-320 to 1200 ^{o}F) without heating to obtain properties required for CUI protection.

Table 4
Polysiloxane Evolution

Chemistry	Component	Curing mechanism
First Generation Polysiloxanes (FGPS)	Two	Ambient
Second Generation Polysiloxanes (SGPS)	One / two	Thermal (150 – 180 ^{o}C)
Third Generation Polysiloxanes (TGPS)	One	Ambient

POLYSILOXANE CUI TESTING PERFORMANCE

The following comprehensive testing program was designed to evaluate CUI coatings in a variety of environments and physical states. One of the most universally known CUI tests is the cyclic test as described in table 5, Corrosion Under Insulation (CUI) test, as a wet/dry, heat cyclic test it provides useful insight to CUI resistance and allows ease of simulation for manufacturers. However, due to heating step at 204 ^{o}C (400 ^{o}F) it masks the properties of a heat curing coating system. Accordingly, to demonstrate properties prior to heating other testing must be adopted allowing coating performance to be identified at lower temperatures <150 ^{o}C (300 ^{o}F) and at elevated temperatures >150 ^{o}C (300 ^{o}F). The coating system must demonstrate it can provide corrosion, HWI, mechanical, UV and chemical resistance from ambient application without heating. Whether this is due to low temperature operating service <150 ^{o}C (300 ^{o}F) under insulation, transportation, exterior exposed storage or general weathering conditions good performance is essential to longevity of the coating before, during and after installation.

Table 5
Testing Results for Second and Third Generation Polysiloxane CUI Coatings

All testing was run after coatings had been cured for 168 hours at 23 °C and 50% humidity.

Test Type	Test Procedure	SGPS - A (IMM)	SGPS - B (IC)	TGPS
Corrosion Under Insulation (CUI)	1. **16 hours @ 204 °C.** 2. **Thermal shock (water, 23 °C).** 3. **8 hours in HWI 5% NaCl (95 °C).** Repeat 80 cycles.	No cracking, delamination or blistering. Heavy rusting under film.	Blistering & cracking present with corrosion spots across film.	No cracking, delamination, blistering or corrosion.
Adhesion: Cross-cut & Pull-off	PosiTest AT-A Automatic Adhesion Tester.	4A – 5A – cross cut (X-Cut) 2.5 MPa 100% adhesion failure	3A – Cross cut (X-Cut) 1.5 MPa 100% adhesion failure	5A – cross cut (X-Cut). 5 MPa 100% cohesive – dolly.
Salt Spray	Q-FOG cyclic corrosion chamber. 1440h, C5	Unmeasurable corrosion creep & heavy corrosion build up.	High corrosion creep, blistering & corrosion build up.	Max 1mm corrosion creep & no blistering.
Hot Water Immersion (HWI)	Immersion for 4000h @ 90 °C (5% NaCl solution).	Blistering & delamination from substrate. Heavy corrosion under film.	Cracking, blistering & corrosion build up on coating film.	No cracking or blistering or adhesion loss. 99% corrosion free.
Impact Resistance	TQC Direct impact tester.	25cm	<5cm	25 cm
Cylindrical Mandrel (bend)	TQC Cylindrical bend test 100mm (SP1820). 0.75mm panels	32 cm – cracking	32mm – cracking / delamination	32 mm – Microcracking
Pencil Hardness	TQC Pencil Hardness Test (750g) VF2377.	2B (ambient cured 7 days).	<9B (ambient cured 7 days).	7H (ambient cured 7 days).
Thermal Resistance	Heat to 650 °C. Allow to cool to ambient temperature.	No cracking blistering or adhesion loss.	400 °C heating, No cracking blistering or adhesion loss.	No cracking, blistering or adhesion loss.
Cryogenic Testing	1. **Heating at 200 °C for 30mins** 2. **Cooling to 23 °C for 30mins** 3. **Immersing in liquid nitrogen at -196 °C for 30mins** 4. **Directly returned to the oven at 200 °C** Repeat cycle 5 times	Not tested	Not tested	No cracking, delamination or blistering. Full corrosive and mechanical properties remain
Abrasion Resistance	Taber Abraser (Abrader) – Model 5135.	Fails 500 cycles Ambient – to the substrate	Passes 500 cycles Ambient - 100µm film loss (soft film caused difficulties measuring accurately)	Passes 500 cycles Ambient - 110µm film loss
Chemical Resistance	Using 10% HCL & H_2SO_4, Diesel & Benzene (hydrocarbons)	24 hours' immersion HCl – coating failure & corrosion H_2SO_4 – coating failure & corrosion Hydrocarbon – coating soft & removed to the substrate.	24 hours' immersion HCl – coating failure & corrosion H_2SO_4 – coating failure & corrosion Hydrocarbons – coating soft & easily removed to the substrate.	720 hours – acid resistance + 1 year – hydrocarbon resistance No removal of coating or blistering. Discolouration from chemical. Film remains hard with 100% integrity.
QUV Weathering	Cyclic UV / condensation 3000h	Excessive colour change and chalking	Colour change	No change
Solvent-wipe	Using MEK or xylene 50 rubs using solvent soaked cheesecloth or equivalent.	Fails to substrate	Fails to substrate	Passes, no removal of coating

Laboratory testing of TGPS and associated advancements over current technologies has supported field application findings for hardness development, mechanical damage resistance (transportation) and corrosion resistance prior to service and now is the coating of choice for CUI mitigation within multiple Oil and chemical Majors, figure 1 shows some applications on asset structures being protected by a TGPS coating.

Figure 1: TGPS CUI mitigation coating - shop application prior to transport and installation.

LIQUID APPLIED INSULATION COATINGS

Thermal Insulations Coatings (TIC) coatings have been used for over 10 years in a range of different applications including thermal insulation and personnel protection either partly or completely replacing traditional insulation cladding systems and wire cages for both hot and cold processing temperatures. The overview is the resulting low thermal conductivity (λ) properties of the coatings allow reduction of hot or cold temperatures of processing equipment such as pipe, ductwork or tanks to within safe to touch limits (personnel protection), maintain temperatures in storage units and or provide thermal insulation properties.

For personnel protection purposes TIC coatings can be used as replacement for traditional systems or wire cages presenting less labour intensity, safer, minimise space requirement and faster application to complex structures and provide thin film protection for workers where the outer coating surface is contactable with causing burns. Additionally, the removal of the traditional insulation and cladding system results in the CUI concept being eradicated and if any corrosion (from mechanical or other sources) is occurring, it is visible and easily rectified during a maintenance program. The TIC coating technologies can be applied at ambient or elevated temperatures for in-service applications and adhere to a range of anti-corrosion primers giving a high performance coating system providing corrosion and insulation properties. This monolithic coating approach to insulation certainly demonstrates it benefits predominately in personnel protection scenarios.

To date the TIC coatings have been formulated from predominately organic based polymers (acrylics or epoxies) and filled with ceramic/glass microspheres or silica based insulation media, the specific media heavily influence the resulting low thermal conductivities of TIC coatings. There are two major (current) draw backs of the organic based TIC coatings. Firstly, they have relatively low film build capabilities between 500 to 1000µm (20 – 40 mils), it can take up to 10 or more coats to get to the required thickness for providing insulation properties. Lastly, a limited temperature resistance to -40 to 180 °C (-40 to 356 °F) is set by the use of organic based polymers.

A new addition to liquid applied insulation is now available and has been commercialised in early 2017 to the market. The chemistry is a third generation polysiloxane resulting in a waterbased (low VOC) single component, ambient curing polysiloxane TIC coating. Designed for ultra-high-build (UHB) in excess of 20000 microns (800 mils) Dry Film thicknesses (DFT) and temperature tolerance range from -60 to 400 ºC (-76 to 752 ºF) which allows to exceed current boundaries of thermal insulation coatings set at approximately 180 ºC (356 ºF). The polysiloxane TIC coating can be applied over a TGPS CUI primer as a system for high temperature exposure, personnel protection and thermal insulation purposes.

Additionally, the use of a polysiloxane polymer results in high weathering resistance and thermal cycling properties in ultra-high film thicknesses beyond 20000 micron (800 mils) DFT’s, eliminating necessary cladding as with traditional insulation systems and providing film thickness capabilities needed for efficient thermal insulation and personnel protection properties.

Table 6
Thermal Insulation Coating Overview

TIC coating	Temperature range ºC (ºF)	λ value (W/mK)	Film build capabilities µm (mils) per coat
Acrylic	-40 to 180 (-40 to 356)	0.05 – 0.09	500 – 1000 (20 – 40)
Epoxy	0 to 150 (32 to 302)	?	5000 – 19000 (200 – 748)
Polysiloxane	-60 to 400 (-76 to 752)	0.05 – 0.07	20000 (800)

TGPS CUI MITIGATION SYSTEM

As of 2017 with the new developments in polysiloxane coatings both in anti-corrosion and insulation products, it is now possible to protect assets for thermal insulation, anti-corrosion and personnel protection purposes via a two coat system.

1. TGPS CUI primer – high temperature, anti-corrosion primer
2. TGPS TIC coating – low λ, UHB and high temperature resistant >180 ^oC (356 ^oF) properties

This system allows coating use for providing replacing traditional coating/insulation systems which are prone to excessive corrosion build up from CUI environments. By using a coating, system which doesn't need a protective cladding, asset owners can remove the hidden corrosion aspect of CUI. Therefore, offering easier corrosion monitoring and maintenance programs from visually assessable inspection programs without dismantling/destruction requirements. Figure 2 shows a site application of the TGPS CUI mitigation system. Applied on-site (in service) at an elevated temperature of 200 ^oC (392 ^oF) between 4.5 – 5mm total DFT with a surface temperature reduction of approx. 160 ^oC (320 ^oF) measured with a surface contact probe.

Figure 2: TGPS CUI mitigation system.

CONCLUSIONS

Minimizing CUI and its related degradative, potentially life threatening and economic consequences is a top priority for asset owners within the Oil and Gas and petrochemical industries. Forwarding new technologies, which offer more efficient alternatives in diagnosis, maintenance and prevention methods is essential in the combat against CUI.

Presented and highlighted throughout this paper are new developments in prevention methods for CUI environments. TGPS CUI coatings demonstrate an advancement in properties and allow facilitation across full operating temperature range. TGPS TIC coatings and mitigation systems in combination with TGPS CUI primers allow performance expansion in to areas where such existing TIC coating limits were present, UHB and higher temperature capabilities thus forwarding the technology and gaining progress in the combat against CUI elimination.

Further improvement to the coatings industry:

1. Devise a set testing standard for universal use within CUI and high temperature coatings. Which demonstrates before, during and after installation coating performance.
2. Update NACE SP0198-2017 and other coating standards to include TGPS CUI and TGPS TIC coatings.

REFERENCES

1. NACE SP0198-2017 (and previous versions), “Control of Corrosion Under Thermal Insulation and Fireproofing Materials --- A Systems Approach”