

Isocyanate Free Water Repellent Top Coat For Offshore Corrosion Protection

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ABSTRACT

To obtain long term corrosion protection in demanding offshore environments the coating system needs to protect the structure from water to prevent corrosion. We have developed a durable isocyanate free top coat that can actively repel water to provide outstanding protection for offshore steel structures from corrosion.

In this paper, the development of a water repellent, isocyanate free top coat is described and the effect of this top coat is compared to conventional coatings. The top coat is tested in a single coating system, applied directly to metal (DTM) and in a two coat system with a zinc rich primer.

In order to evaluate performance of the coating systems, a range of anticorrosive and mechanical tests are carried out for the top coat both in one coat and two coat systems. Salt Spray (ISO 9227¹), Blister Box (ISO 6270-1²) and Ageing Cycling Resistance (ISO 12944-9³) tests are conducted to compare the water permeation and corrosion resistances of the coating systems. Adhesion of the top coat to steel and the zinc rich primer is evaluated by Pull Off Adhesion test (ISO 4624⁴). Mechanical properties of the coatings are evaluated by Mandrel Flexibility (NACE Standard TM0304 Section 12⁵), Impact (ISO 6272-2⁶), and Thermal Cycling Resistance (NACE standards TM0304-2004 and TM0404-2004 Section 9, but using different type of panels⁷) tests.

The one coat system with the water repellent top coat (DTM application) have shown remarkable corrosion creep and adhesion retainment results after 1440 hours exposure in Salt Spray test (ISO 9227). Blister Box test (ISO 6270-1) results indicate robust water permeation resistance in humid conditions. Ageing Cycling Resistance (ISO 12944-9) test results have shown that two coat system with activated zinc rich primer and the water repellent top coat possesses robust anticorrosive properties and outperforms conventional three coat system. The preliminary test results show how incorporation of active water repellence into the top coat greatly enhances the ability of the coating systems to reduce corrosion in an offshore environment.

Key words: Water repellent top coat, Isocyanate free, Anti-corrosive properties

INTRODUCTION

In the coating industry it is common to assume that main goal of top coats is to provide color, UV-light protection and aesthetic characteristics to coating systems, especially if the coating systems are

designed for harsh environments. In those environments polyurethane (PU) chemistry is the most commonly used chemistry in the top coat finishes, polysiloxane chemistry is the most common for isocyanate free chemistry.

In the recent years, Health and Safety regulations started to restrict usage of PU top coats. Conventional PU top coats applied via spraying mechanism send toxic isocyanates in the air — exposing workers to the dangers of toxic isocyanates. Strict and costly health and safety measures have to be implemented in the manufacture and application of conventional polyurethane due to the toxicity of isocyanates. Many diisocyanates are classified as skin and respiratory sensitizers and are thought to be the trigger for a high number of cases of occupational asthma reported across all European Union (EU) Member States. Regulatory bodies around the world are now looking toward phasing out the use of isocyanates. Many diisocyanates are classified as skin and respiratory sensitizers and are thought to be the trigger for a high number of cases of occupational asthma reported across all EU Member States.⁸ Thus, it is expected that the market will navigate towards substitution of the PU top coats, alternative chemistries will emerge into the top coat market.

As it was mentioned earlier, the protective properties of the top coats are often overlooked. Indeed, due to certain characteristics of polymers used in top coats, the water penetrates through the top coat layer easily or top coats tend to be brittle when cured. Therefore, generally there is always a layer or two of protective coatings underneath the top coat to provide corrosion protection. Addition of each coating layer adds up in time, costs and environmental impact of the coating system application process. Normally, in aggressive environments like offshore, a coating system would comprise of a zinc rich primer applied on top of the steel, an epoxy intermediate adding some barrier properties to the coating system and a top coat to provide aesthetic properties and UV light protection. Zinc rich epoxy primer provides galvanic corrosion protection and will ensure proper adhesion to the substrate. The intermediate epoxy layer plays an auxiliary role in corrosion protection and it can be eliminated if the top coat would be able to prevent water from penetrating and collecting in the interface with zinc rich epoxy. One of the ways to decrease water permittivity of the top coat is to make it hydrophobic or water repellent. The interest in superhydrophobic or water repellent coatings has increased during the last years, driven by the potential industrial applications of these surfaces in different areas. Several techniques have been employed to create superhydrophobic coatings, and the majority rely on the generation of a coating surface profile or chemically modifying the coating's surface⁹⁻¹³. However, when these surfaces are damaged, the superhydrophobicity is usually lost and consequently their inherent water repellent properties. Therefore, a volumetric superhydrophobic / water repellent coating could represent a breakthrough technology in the coatings industry.

In this paper, the development of a water repellent, isocyanate free top coat will be described and the effect of this top coat is compared to conventional coatings. Salt Spray test, Blister box and Ageing Resistance tests were conducted to compare the corrosion resistance of the different coatings. Adhesive and mechanical properties of the coatings are evaluated by Mandrel Flexibility, Impact test, Pull Off Adhesion and Thermal Cycling Resistance tests.

Salt Spray and Blister Box tests were performed to compare the corrosion resistance of the water repellent polyurethane coating and the corresponding standard. The isocyanate free water repellent top coat has shown excellent anti-corrosive properties and outstanding mechanical performance, robustness and durability.

EXPERIMENTAL PROCEDURE

Formulations Preparation

The systems to be tested are shown in **Table 1** and **Table 2**. Tests have been carried out for both one coat and two coat systems. Water repellent PU is an isocyanate containing water repellent top coat and water repellent NISO top coat is an isocyanate free water repellent topcoat.

Table 1: One coat samples prepared for testing.

Standard 1	Standard 2	Prototype 1
Conventional polysiloxane	Water repellent PU	Water repellent NISO (non-isocyanate top coat

Table 2: Two coat samples prepared for testing.

Standard 3	Standard 4	Standard 5	Prototype 2
Zinc primer 1 - Conventional polysiloxane	Zinc primer 1 - Water repellent PU	Zinc primer 2 - Epoxy intermediate - PU topcoat	Zinc primer 1 - Water repellent NISO top coat

Substrate and Surface preparation

Mild steel panels of rust grade A (ISO 8501-1¹⁴) were abrasive blasted with iron grit (G070 acc. ISO 11124¹⁵) to a cleanliness degree equivalent to Sa 2.5 (ISO 8501-1). The surface roughness of the panels had a Rz between 40 and 55 µm.

Testing

Salt spray tests were conducted according to ISO 9227 for the prototypes 1 and 2 and standards 1, 2, 3, 4 directly applied to metal. One coat systems were tested for 1440 hours and two coat systems were tested for period of 2200 hours. After exposure, the degree of blistering, rust, cracking and flaking were assessed on both panel and around the scribe. Pull off adhesion was evaluated 24h after the end of the exposure. The corrosion creep from the scribe was measured at least at nine points and the average width, M, was calculated according to Equation 1, where C is the average of the measurements and W is the original width of the scribe.

$$M = \frac{C-W}{2} \quad (1)$$

Ageing Resistance test was performed for two coat systems, the test was performed for 4400 hours. Thermal cycling crack resistance was conducted under the same conditions as NACE standard TM0404-2004, Section 9, but using internal test Hempel method, that was empirically proven to replicate NACE standard TM0404-2004 test results. Paints are applied by blades with different thicknesses of application gaps on top of steel panels (for information related to substrate and surface preparation please refer to respective section). When paint is applied uniform paint stripes of different thicknesses are formed on steel panels. The steel panels with applied coatings were post cured at 60°C for one week and then subjected to upper and lower temperatures of 60°C to -30°C, within a two hour period of time, for three weeks. After the test period, all the samples were examined for cracks under a microscope.

For the Mandrel Flexibility tests, one side of the steel panels was coated with the Standards 1 and 2, and Prototype 1, and cured for 2 weeks. Then the respective flexure strain was measured using a fixed-radii mandrel bending machine. The Flexure Strain, F_{strain} , of the coating systems material were calculated using the equation:

$$F_{\text{strain}} = \frac{\frac{t+c}{2} + \frac{t}{R}}{\frac{t}{R} + \frac{t+c}{2}} \quad (2)$$

t = steel panel thickness; c = coating system thickness; R = Mandrel radius (mm). The deformed coatings were evaluated visually and microscopically for signs of cracking.

RESULTS