

**POLYMER COMPOSITE COATING PERFORMANCE
EVALUATION ON CARBON STEEL IN MIXED BRINE
SOLUTION**

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POLYMER COMPOSITE COATING PERFORMANCE EVALUATION ON CARBON STEEL IN MIXED BRINE SOLUTION

This report is submitted in accordance with requirement of the University Teknikal
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(Engineering Materials) (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Materials) (Hons). The members of the supervisory committee are as follow:

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.....
(Dr. Mohd Sukor Bin Salleh)

ABSTRAK

Kebuk tekanan merupakan salah satu peralatan yang penting dalam industri petrokimia disebabkan oleh keperluannya untuk menyimpan bahan kimia, mencampur aduk dan banyak lagi. Memandangkan kebanyakan kebuk tekanan dibuat daripada besi versi karbon *ASTM* A516 gred 70, salutan Belzona 4341 dan 4311 dipilih untuk melindungi saluran daripada terhakis. Objektif kajian ini adalah untuk mengenal pasti kesan pH terhadap salutan Belzona 4341 dan 4311 mekanikal, kekerasan dan prestasi elektrokimia dalam air garam NaOH dan untuk menganggar penurunan gred bagi hayat salutan. Sampel salutan menjalani ujian mengikut ASTM D6943 untuk menguji cecair meresap air rendaman dan formasi hakisan. Tingkah laku kakisan telah dijalankan keatas salutan menurut kepada ASTM G-99 dengan menggunakan ukuran pin-on disk sebelum dan selepas rendaman dalam rumusan NaOH dengan berbagai nilai pH. Akhir sekali, ujian kekerasan dan ujian elektrokimia telah dilakukan kepada sampel salutan selepas 4,8,12 dan 16 hari rendaman. Daripada keputusan yang diperolehi, salutan Belzona 4341 dan 4311 mempunyai cecair ingresi yang amat minimum semasa ujian rendaman. Cecair yang termasuk didalam permukaan salutan mempengaruhi prestasi dengan mengurangkan ketahanan wear dan dengan itu menurunkan hayat salutan. Rendaman untuk masa yang lama akan meningkatkan ketumpatan semasa, dengan ketahanan rendah, sampel terdedah kepada hakisan. Belzona 4341 menunjukkan lebih baik dari segi mekanikal dan mempunyai masa hidup yang lebih tinggi berbanding Belzona 4311.

ABSTRACT

Pressure vessel is one of the important equipment in petrochemical industries due to its requirement to store chemical, mixing and many more. Since, most of pressure vessel is made up of carbon steel ASTM A516 Gr. 70, Belzona 4341 and 4311 coating are selected as to protect the vessel from corrode and erode. The objectives of this study are to determine the effect of pH on Belzona 4341 and 4311 coating in mechanical wear, hardness and electrochemical performance and to estimate the degradation of the coating life. The coating samples are undergo immersion test under controlled temperature as per ASTM D6943 as to evaluate solution ingress and corrosion formation. The wear behavior is done on the coating according to ASTM G-99 using pin-on disk measurement before and after immersion in NaOH solution with various pH value. Last but not least, hardness and electrochemical test is done to the coating samples after 4,8,12 and 16 days of immersion. From the results, Belzona coating 4341 and 4311 have very minimal solution ingress during the immersion test. Solution that ingress inside the coating surface affect the performance by reduced the wear resistance and thus decreased the life of the coating. Longer the immersion time will increased the current density, with low resistance the samples are susceptible to corrode. Belzona 4341 shows better mechanical performance and have higher estimate life compared to Belzona 4311.

DEDICATION

To everyone that contributes to this research and my friend that has helping me all along

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURES

ASTM	-	American Society for Testing and Material
Ag/AgCl/KCl	-	Silver-Silver Chloride
Fe	-	Iron
FBE	-	Fusion Bonded Epoxy
Gr.	-	Grade
H ₂ SO ₄	-	Hydrochloric acid
H ₂ O	-	Water
Imm	-	immersion
ID	-	Internal Diameter
KOH	-	Caustic Potash
NaOH	-	Sodium Hydroxide
N	-	Newton
NaCl	-	Sodium Chloride
OM	-	Optical Microscope
PTS	-	Petronas Technical Standard
wt. %	-	weight percentage
°C	-	Degree celcius
HV	-	Hardness Vickers

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, oil and gas industry in Malaysia has become one of most important economic sector as it has contributes the largest government income. Petroleum and natural gas becomes primary energy sources and heavy dependence to sustain its economic growth compared to others energy sources such as coal, biomass and hydroelectricity (Macrae.G, 2011)

The use of vessel is very common in petrochemical industries due to its operational requirement to store materials, mixing chemicals and many more. The vessel is usually made of carbon steel such ASTM A516 grade 70, is susceptible to corrosion and erosion when exposed to chemicals. For example, sour crude storage tanks with their saline solutions, aqueous bacterial sludges, and soluble sulfur materials, produce low pH environments that are particularly corrosive in the water phase beneath stored hydrocarbons (low concentration use of treatment chemicals can also initiate the formation of sulfuric and hypochlorous acid) (O'donoghue, 2003). In order to prevent corrosion and erosion to the vessel, various type of corrosion protection methods are applied such as sacrificial anode, coatings, and corrosion inhibitor injection. However, it is impossible to evaluate the coatings performance directly in the operating vessel due to its criticality. For example, if the vessel is the heart of the process, any failure that occurred will affect the whole operation.

In this study, the coating performance will be evaluated using mechanical testing and electrochemical testing as per followed ASTM standard testing method. It will include

Immersion test (ASTM D6943), Pin-on-disk test (ASTM G-99), Micro-Vickers hardness (ASTM E384-16) and electrochemical testing. Figure 1.1 shows the example of caustic corrosion occurred in pressure vessel.



Figure 1.1: Caustic Corrosion (Lesley.B, 2016)

1.2 Problem Statement

As per recommended by PETRONAS technical standard (PTS), the coating supposed to be lasting for at least 10 years services. However, in case of using Ceilcote 652, fiberglass reinforce with vinyl ester coating, the coating failed approximately 14 months during services due to caustic corrosion in which the damages is due to concentration of alkaline salt (API 571, 2003). In addition, the coating is total damaged results exposed the bare surface metal. The new Belzona 4341 and 4311 coating are suggested to be used but coating performance yet to be studied and it is impossible to predict the lifetime of the coating inside operating pressure vessel or field testing where the coating is directly applied and put inside an operating vessel. This is because any failure & damages occurred will affect whole petrochemical operations. Hence, it is very crucial to predict the performance of the coating before applied it. The mechanical testing will be conducted to the sample after immersion test. There are various type of mechanical testing related to evaluate the mechanical performance of the coating but still the specific condition is unknown.

1.3 Objectives

The aims of this research are:

- i. To determine the effect of pH on Belzona 4341 and Belzona 4311 coating on mechanical wear, hardness and electrochemical performance in sodium hydroxide (NaOH) mixed with sulphuric acid (H₂SO₄).
- ii. To estimate the degradation of the coating life using wear rate and initial coating wear after pin on disk test.

1.4 Scope

The sample is undergoing the pH testing by immersed the coating sample through, sodium hydroxide (NaOH) at constant temperature of 45 ± 2 °C. The immersion days take from 96hours to 384 hours which equivalent to 16 days with adjusted pH from alkaline to acidic using (H₂SO₄). Then, coating performance will be evaluated using ASTM standard testing method, including, Pin on disk test, hardness test and electrochemical testing in order to determine the mechanical and electrochemical performance in that NaOH brine. The surface morphology of the coating samples will be analyzed using Optical Microscope (OM). At the end of this research, researcher responsible to decide whether the Belzona coating could be replacement coating as for corrosion protection for the pressure vessel based on the overall performance. In this study, the suitability of the Belzona coating as the replacement for the pressure vessel will be studied.

CHAPTER 2

LITERATURE REVIEW

2.1 Protection method for internal vessel

In general, pressure vessel is used to store and transmit liquids, vapors and gases. Each vessel has physical interaction between metal and its environment, which may result in change of metal properties and lead to functional impairment of the metal, the environment or the technical system of which they form a part. These phenomenon will lead failure and thus affect the whole operation. Hence, protection method should be applied to the surface of substrate as to protect and improve appearance, corrosion resistance, wear resistance and etc.

Cathodic protection is one of the common methods used to prevent metal from corrosion. In practice, this method mainly uses to protect steel in soil or immersed in water it also suitable for the interior surfaces application especially for water storage tank and water circulating systems. In addition, this method has also been suitable to be applied for steel, which embedded in concrete, copper based alloy and lead sheathed cables as this method can be carefully controlled. Basically, cathodic protection prevents corrosion by converting all the anodic (active) sites on the metal surface to cathodic (passive) by supplying electric current or free electron from an alternate source (Baxter.R, 2013)

Other method that commonly used is surface modification. This method includes all types of surface treatments and coatings that resulting in change of composition and microstructure of the surface layer. There are several methods for modifying the surfaces of

structural alloys, dictated by the performance requirements of the alloy in its service environment. (Krastev, 2012)

Another method is corrosion inhibitor. This method use chemical as medium to retard or slow down the corrosion process that possibly damaging a given metal exposed to a specific environment with a resulting reduction of the overall corrosion rate of that system. By adding small amounts of acids, cooling water, steam and many environments, either irregular or continuously as to reduce the corrosivity. In addition, some of the inhibitor retard corrosion by absorption to form a thin, invisible film for molecules thick, which coat the metal and protect it from attack. There are two general categories of corrosion inhibitors which are immersion inhibitor and atmospheric inhibitors. Some of the direct benefits of using corrosion inhibitors are it could extend the life of equipment, prevent shutdown, avoid product contamination and prevent accident resulting from brittle (catastrophic) failure. However, this method is seldom used in practice due to limitation such as cost, toxicity, availability and environmental friendliness which are normally considerable important (Camila, G 2014).

2.2 Painting & Coating

Painting and coating is most the commonly method used as to protect the surface from corrosion and specifically formulated to adhere especially for internal vessel.

A coating, layer of material is deposited onto a substrate to protect the surface from corrosion and thus increase the wear properties. There are several factors that affecting choice of a coating, service environment, life expectancy, substrate material compatibility, component shape and size and last but not least cost. (TWI, 2015)

Previously, coat systems have been replaced from five to six coat to three coats only, and the latest formulations have focused on application with decreasing number of coats but increasing individual film thickness. Usually, paint systems consists of primer, undercoats and finish coat which each of layers has specific function.

2.2.1 Composition of paints

Paint may be broadly classified into decorative paints and industrial coating which are applied to decorate, protect and prolong the life of natural or synthetic material and acts as a barrier against environment condition. Paint consists of 3 main components which are pigments, binders and solvent where every component have their own functions.

2.2.1.1 The pigments

The pigments give color and finish to the paint. It also provide protection the surface that underneath from corrosion and weathering as well as to hold the paint together. The substances that have been used in pigments are inorganic and organic. Both inorganic and organic pigments have their own uses and strength based on their chemical and physical properties.

Organic pigment contains carbon in molecular structure and metallic element that help to stabilize the properties but it more prone to fading or may be destroyed by exposure to sunlight and harsh chemicals. Organic compound gives transparent properties and generate brighter and higher color strength. Commonly, organic pigments are applied in a single layer, which make it incapable of generating a surface coat that will completely hide the undercoat. (Pylam D, 2016). Diazo, benzimidazolone, metal complex, naphthol, triarylcarbonium, thioindigo are the examples of organic pigments.

Inorganic pigment is made up from chemical compound that not based on carbon and usually metallic salts precipitated from solution. It has larger average particle size that between 400 and 800nm that make inorganic pigment tend to be more opaque. In addition, inorganic pigments are more stable in the presence of organic solvent and gives better heat stability compared to organic pigments. There are several example of in organic pigments such as titanium dioxide whitem iron oxide, cadmium, mixed meta oxide, manganese oxide, phthalo chrome green and lead chromate (BASF, 2016).

2.2.1.2 The Binder

The binder also known as resins that ability to form a dense, tight film and thus increase adhesive force between the substrate. Binder plays major roles in composition of the paint. Binders that have the highest molecular weight will form films by evaporation while binder with smaller molecular weight reacted in situ. Binders can be classified based on their chemical reaction. There are oxygen reactive binders, lacquers, heat conversion binders, co-reactive binders, condensation binders, coalescent binders, and inorganic binders. Examples of common binders used are:

a) Alkyds

Alkyds are form by reacting alcohols with acids like pthalic anhydride or malein acids such as soya oils and linseed. Advantages of these binders are user friendly, surface tolerant, expand and contracts with substrate but it required high amounts of solvent and slow drying. Figure 2.1 shows the molecular structure of alkyd

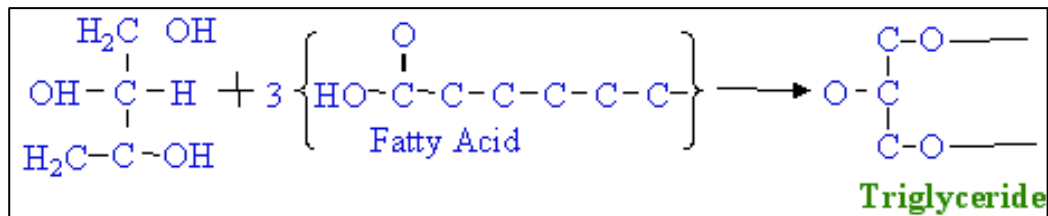


Figure 2.1: Molecular structure of alkyd (britannica, n.d)

b) Epoxy esters

Epoxy ester is formulated from epoxy and drying oil. The properties of epoxy ester are hard, give adhesion and flexibility and improve water and hydrocarbon resistance. Epoxy ester is commonly used for primers & coating for metal surface, floor finishes, coil coating and electrical insulating coating. Figure 2.2 shows molecular structure of epoxy ester.