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Study of Cresol-Novolac Epoxy Systems on Fusion Bonded Epoxy Coatings for Pipeline Protection

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Fusion Bonded Epoxy(FBE) systems have been widely used to protect pipelines for over 30 years. Numerous attempts have so far been made to improve the properties of FBE coatings such as chemical resistance, adhesion, water resistance, cathodic disbondment resistance, impact resistance, and flexibility to protect pipelines at a wet and a high temperature condition. But these attempts have not been successful in reducing some weakness, for instance, in pipeline operating at high temperature due to poor hot water resistance and cathodic protection. The purpose here is to build a basis for getting better corrosion resistance of FBE systems. Cresol-novolac epoxy coating systems were studied compared to bisphenol A type epoxy systems. After the immersion of the film in water at a high temperature for a long period, good adhesion to metal substrate and excellent cathodic disbond resistance were observed in the cresol-novolac epoxy resin systems. It is well known that the adhesion of organic coatings to metal substrate might be decreased due to the disruption of a chemical bond across the film and metal interface induced by water molecules. A high crosslinking density might decrease water permeability and improve cathodic disbonding protection in the coatings. Other factors are studied to understand anti-corrosion mechanism of Cresol-novolac epoxy coatings. In addition, the water absorption rate and the effect of cure temperature on the adhesion and cathodic disbonding resistance of the films were studied in different epoxy coatings and the effect of substrate was evaluated.

The results of field application are proved that the Cresol-novolac epoxy coating system developed recently is one of the most suitable coatings for protection of pipelines.

Keywords *: Fusion Bonded Epoxy(FBE), cresol - novolac epoxy, Cathodic Protection(CP).*

1. Introduction

The main point of this paper is to assess the external circumstantial (water, ion, bacteria) caused the corrosion of pipeline in applying fusion bonded epoxy coating which is cresol-novolac based thermosetting powder and accordingly to study excellent anti-corrosion material under the moisture and high temperature.

Fusion Bonded Epoxy(FBE) coatings have been revolutionized the pipe coating industry.

The coatings provide corrosion protection for pipeline systems used in the production, transportation, and distribution of oil, gas, water, and petroleum products. FBE is used the interior and exterior of pipe and field-weld joint, as well as the interior of tubing and fittings.

Anti-corrosion methods and materials have been gradually developed along with pipeline construction for 50 years.

The first generation : Coal tar/ Enamel have been used in pipeline protection.

The second generation : Thermoplastic sheet and tape have been used in pipeline protection from 1960.

Third generation : Fusion bonded epoxy have been used pipeline industry protection from 1960 and it is now most popular due to the continuous improvement of quality and coating facility.

Fourth generation : 3-layer coating system and field application in pipeline corrosion protection

3-Layer coating which unite Fusion bonded epoxy with thermoplastic PE(PP) has been widely used from the late 1980.

Fifth generation : Dual Epoxy coating system

It is designed for high temperature and wet condition and it has been widely used in middle east countries.

Briefly we touched the change of anti-corrosion material and the application for pipeline.

It is natural that the need for long durable anti-corrosion in the construction of pipeline is required.

Accordingly the study for the limit of application temperature(max ; 110℃) in cresol-novolac based Fusion bonded epoxy for last 30 years and the deterioration of adhesion due to the water absorption in wet condition is the main point of this report.

2. Experimental

The required properties in anti-corrosion material for pipe are closely related with the durability of pipeline.

The demand for new excellent anti-corrosion coating material has been continuously required according to the change of external circumstance for pipeline.

About 20,000 mile of pipeline ever year is newly constructed and rehabilitated world widely.

But new pipeline requires more excellent anti-corrosion coating material than required in NACE or the specification of Oil and Gas company.

Given values in specification is the minimum property required. There is a difference in properties between given specification and real one required according to the external circumstance mentioned previously.

There are important standards in International specification.

ⓐ National standard of Canada CAN/CSA Z245.20-98- External fusion bonded Epoxy coating for Steel pipe

ⓑ German Institute for standardization - DIN 30670, DIN30678,DIN30671

ⓒ NACE Standard RP0394-94 - Application, Performance, and Quality Control of Plant-Applied, Fusion Bonded Epoxy external pipe coating.

2.1 Properties of FBE coating in pipeline

Fusion Bonded Epoxy (FBE) has been most widely used as anti-corrosion material for pipeline application company and customer.

The main reason is that FBE coatings has good chemical and mechanical properties and that following properties is important factors, which is cathodic disbondment property, water diffusion protection, high elongation, impact resistance, dielectronic properties etc.

2.2 Service life of coatings

The durability of layed pipeline is very important. Also a series of study to extend the durability has been continuing and this report is an achievement of research and development to extend the service life under high temperature.

Table 1. Minimum expect serive life

Operating temperature (℃)	Minimum expect service life(years)
23	50
60	50
80	30
90	15
100	8

DIN 30678 -1992 "Polypropylene coatings for steel pipe"

3. Cresol novolac based FBE powder properties

The performance and assessment of novolac epoxy based fusion bonded epoxy powder are made in lab and field application. The test items are long term adhesion on steel surface and cathodic disbondment protection, low water absorption and high temperature resistance.

3.1 Powder production

Solid raw materials such as epoxy resins, hardeners, pigments, extender, and additives are weighing and premixing in room temperature.

Dry premixed raw materials were hot melt blending in an extruder at a temperature of about 90 ℃ to 130 ℃. The extruderate is then cooled through squeezing roll and is ground to a fine particle size, for example to a powder with a maximum particle size40 to 60 microns.

3.2 Experimental test sample panels

Samples used in the test programs were laboratory prepared panels (CAN/CSA Z245.20-98) No chemical surface treatment was used. The steel was blasted to SSPC 5, near white metal, and pre-heated steel.

Application of the powder can be by electrostatic spraying or by the use of a fluidized bed. The test articles consisted of resin coated pipe sections and steel sheets measuring $100 \times 100 \times 6$ mm. They were heated by gas burners or convection oven to the desired surface temperature (230 ℃) ±10 ℃, after which the powdered coating composition was electrostatically applied and hardened.

The following tests were carried out using test articles of sheet steel measuring $100 \times 100 \times 6$ mm coated with a 300 micron thick epoxy resin composition prepared.

3.3 Fusion bonded epoxy powder characteristics of different epoxy based powder.

Characteristics of fusion bonded epoxy powder are shown in Table 2.

Table 2. Fusioon bonded powder characteristics of different epoxy based powder

	BPA EPOXY	Phenol novolac epoxy	Cresol novolac epoxy
Heat distortion Temp (DSC method)	90~100℃	100~110℃	105~120℃
Elongation	6~10%	5~7%	6~8%
mpact resistance	160 in.lbs	160 in.lbs	160 in.lbs
Adhesion-Shear	6,000 psi	6,000 psi	6,000 psi
Volume resistance	1015 ohm-cm	1015ohm-cm	1015 ohm-cm
Dielectric strength	1200 volts/mil	1200 volts/mil	1200 volts/mil

* At 230℃ cured free film
Film thickness : 12~14 mils

3.4 Hot water immersion resistance

This is one of the most important tests conducted on pipe coatings. The coated panels were immersed in hot water

Bath at 95 ±3 ℃(203°F) for a period of time ranging from one to 3 months and also

At 50 ℃(122°F) for six months. Results showed that after three months there are no blisters.

Adhesion was excellent: (Note : Samples were left for one hour to cool to room temperature before testing the adhesion of coating. / CAN/CSA Z245.20-98.)

The following table shows the hot water immersion test results.

Table 3. Results of hot water immersion test

Temperature	Duration	Rating	Test methods
95℃(203°F)	1 day	1	CAN/CSA Z245.20
95℃(203°F)	90 days	1~2	CAN/CSA Z245.20
50℃(122°F)	1 day	1	CAN/CSA Z245.20
50℃(122°F)	180 days	1~2	CAN/CSA Z245.20

*Rating 1 : Coating can not be removed cleanly
*Rating 2 : Less then 50% of the coating can be re moved
*Rating 3 : More then 50% of the coating can be removed, but the coating demonstrates a definite resistance to the levering action
*Rating 4 : the coating can be easily removed in strips or large chips
*Rating 5 : the coating can be completely removed as a single piece

3.5 Cathodic Disbondment

The test was conducted according to the ASTM specification(ASTM G-8, ASTM G-42) and NACE specification.

Additional tests involved modification of voltage and temperature.

Table 4. Results of cathodic disbondment test

At room temperature(20℃)   initial hole diameter 3 mm

	Voltage	Duration	Test results	Acceptance criteria
Lab panels	-1.5 V	28 days	2.0 mm R	8.0 mm R
Pipe sample	-1.5 V	28 days	2.0 mm R	8.0 mm R
Third party Evaluation	-1.5 V	28 days	2.0 mm R	8.0 mm R

At 65℃   initial hole diameter 3 mm

	Voltage	Duration	Test results	Acceptance criteria
Lab panels	-1.5 V	48 days	0.5 mm R	8.0 mm R
Pipe sample	-1.5 V	48 days	0.5 mm R	8.0 mm R
Third party Evaluation	-1.5 V	48 days	0.5 mm R	8.0 mm R

At 95℃   initial hole diameter 3 mm

	Voltage	Duration	Test results	Acceptance criteria
Lab panels	-1.5 V	48 days	1.0 mm R	8.0 mm R
Pipe sample	-1.5 V	48 days	1.0 mm R	8.0 mm R
Third party Evaluation	-1.5 V	48 days	1.0 mm R	8.0 mm R

* disbondment was measured from the edge of the intentional hole

Cathodic disbondment test was the most important property decided to select the pipeline coating material.

Applied cathodic potentials results in activation of the cathodic reaction immediately at the holiday and at the coating/metal surface.

Mechanism of cathodic disbonding

[1] $H_2O + 1/2O_2 + 2e^- \rightarrow 2OH^-$: The oxygen reduction reaction

[2] $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$: The hydrogen evolution reaction

3.6 Other mechanical properties

3.6.1 Impact resistance

The impact test and evaluation criteria were conducted according to modified ASTM G14 on cold rolled steel

Table 5. The results of impact resistance test

Inch-Pounds	BPA epoxy	Phenol novolac epoxy	Cresol novolac epoxy
180	Fail	Fail	Pass
120	Fail	Pass	Pass
60	Pass	Pass	Pass

panels. (3/16 × 3 × 6 inch)

Typical FBE recommended thickness of 14 mils(350 microns) nominal.

3.6.2 Abrasion resistance

Panels were tested per ASTM D4060 at 5,000 cycles with a 1,000 grams weight and CS-17 wheel.

Table 6. The results of abrasion resistance test

	BPA epoxy	Phenol novolac epoxy	Cresol novolac epoxy
Loss weight	0.158 grams	0.120 grams	0.098 grams

3.6.3 Flexibility

Coating flexibility was evaluated by bending laboratory and commercially applied coating bars.

Samples were bent on a fixed radius apparatus after being in the freezer for 1 hour at the following temperature.

25 ℃	6.0 ° /PD	No crack, No holiday
0 ℃	4.5 ° /PD	No crack, No holiday
-30 ℃	3.5 ° /PD	No crack, No holiday

3.7 Water absorption

The Cresol novolac epoxy based FBE coating was developed to be the coating choice today pipeline corrosion protection. Cresol novolac epoxy has increased cross- linking density in coating films, and has protected water absorption. All coatings, without exception, allow the passage of some water through the film. Amounts vary according to film thickness, temperature and natural permeability of the coating. The water diffused mechanism of adhesion and the influence of water.

The results are reduced adhesion and in some case blistering. The local water volumes grow laterally along the metal/polymer interface. The increase in the water volume exerts a peeling force in the contract area between the polymer and the metal. The magnitude of this force is determined by the mechanical properties of the coating film.

The pipeline industry is in need of a good coating that can adhere to the substrate and perform well after being immersed in water at high temperature for long periods of time.

Table 7. The results of water absorption test

Free film@12~16mils Temperature 50 ℃

Duration	BPA epoxy	Phenol novolac epoxy	Cresol novolac epoxy
Duration	100 days	100 days	100 days
Weight gain	2.58%	1.45%	1.25%

* Test methods : ASTM D570

Cresol novolac epoxy based powder free film was very lower water absorption than other epoxy resin. They have higher epoxy functionality and the structures of these resins have give very rigid polymers extremely high cross link density. Such as, heat, chemical, and solvent resistance are substantially elevated compared to low and high molecular weight bi-functional systems of bisphenol A epoxy and bisphenol F type epoxy.

3.8 Field application

This FBE coatings relates in particular to the coatings of large pipes, for example such pipes having an internal diameter of more than 100 mm and more usually pipes having diameter of 300 to 1600 mm. Such pipes are often used for transporting petrochemicals and other gaseous and liquid chemicals at various temperatures and are laid above or below ground or under water. They may be made of various metals, but especially from iron and its alloys.

We have found that a coating thickness of 100 to 2000 microns in generally adequate. However thicker coatings may also be applied.

4. Conclusions

Various kinds of specific polymer materials- polyethylene, polypropylenes, and epoxy resins-have been studied and discussed for external pipeline coatings.

Cresol-novolac epoxy coating systems were better mechanical properties compared to bisphenol A type epoxy systems. After the immersion of the film in water at a hightemperature for a long period, good adhesion to metal substrate and excellent cathodic disbondment resistance were observed in the cresol-novolac epoxy resin systems.

It is well known that the adhesion of organic coatings to metal substrate might be decreased due to the disruption of a chemical bond across the film and metal interface induced by water molecules. A high cross-linking density might decrease water permeability and improve cathodic disbondment protection in the coatings.

Other factors are understanded anti-corrosion mechanism of Cresol-novolac epoxy coatings.

In addition, the water absorption rate and the effect of cure temperature on the adhesion and cathodic disbondment resistance of the coated films have been established for different epoxy coatings and the effect of substrate is evaluated.

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