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A STUDY ON THE ADHESION CHARACTERISTICS OF THE PROTECTIVE COATINGS BY IMMERSION FOR NUCLEAR POWER PLANTS

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ABSTRACT

The surface of the liner plate in containment is applied with the protective coatings to control corrosion and radioactive contamination levels, and to protect surfaces from wear. So, the protective coatings should be capable of withstanding the high temperature, humidity, pressure, and radioactivity caused at the simulated design basis accident and operating conditions. For this reason, they are classified into the safety related items and produced under the strict quality control.

When Reg-Guide 1.54(Rev.0) was issued in 1973, it was expected that the protective coatings that met this guide would keep the function for the designed durability period. But, examining the operation history of N.P.P.s, we can find many kinds of deteriorations like unexpected cracks and delamination from substrata in the qualified protective coatings. Therefore, it is very important to understand the adhesion characteristics of the coatings. Adhesive performance of film to a substrate is a very important property, and even the best coating material has no value as coating materials if the adhesion is not good.

Especially, in the protective coatings of containment, the most important performance is adhesive strength. However, adhesive mechanism of the coating materials has not become clear and there might be an error since it has been explained on the basis of construction experience.

In this work, we conducted the accelerated deterioration experiment by immersion. The three types of test specimens were manufactured according to the ASTM D5139 standard. They were made in the construction site with a poor working condition in humid rainy season and cured in normal temperature for about 3 years. They were immersed into the distilled water at 25±1°C, 50±1°C and 75±1°C and investigated for 180 days. Adhesion test was performed according to ASTM D4541 with Elcometer Adhesion Tester. Epoxy Adhesive was used as a bonding agent of Dolly and we measured the adhesive strength after drying and hardening at room temperature for more than 3 days. Contact angle measurements were used to determine the effect of immersion on the surface energetics of epoxy coating system, including surface free energy and water penetration.

From this experiment, the quantitative adhesion characteristics of the protective coatings (Inorganic zinc and Epoxy systems) according to the history of immersion environment were comprehended. Furthermore, methods to improve durability and quality of the protective coatings were suggested.

Keyword: Protective coating, Adhesion, Immersion, Deterioration, Adhesive strength, Accelerated deterioration test, Nuclear Power Plant.

1. INTRODUCTION

The managing safety aspects of nuclear power plant ageing or accident mean ensuring the availability of required safety functions throughout the plant life that occur by external stimulation, such as chemical and physical attack. These require addressing both physical and material ageing, resulting in deterioration of physical and performance characteristics of systems, structure and components, and non-physical ageing, resulting in the plant systems being out of date in comparison with current safety concepts, standard, and technology. Ageing or accident can lead to simultaneous degradation of physical barriers and redundant components, resulting in an increased probability of common cause failures. It is thus possible that degradation does not reveal during normal operation and testing could lead to failure, or even to multiple common cause failures, of redundant components under high loading and environmental stresses associated with an operational upset or accident.

In general, current testing adequately verifies the availability of plant components at the time of observation, but may not provide sufficient information for predicting future performance. In particular, there is a need to improve the correlation between measured condition indicators and future performance under postulated accident and post-accident conditions for many types of components. In nuclear application, epoxy resins are largely coated on the liner plate in the containment structure. These epoxy resins coated on the liner plate should ensure their roles to cover the surface during a predetermined operating period and they should also sustain at the ageing and emergency state, such as, unexpected accident conditions.

In this work, we conducted the accelerated deterioration experiment by immersion. The three types of test specimens were manufactured according to the ASTM D5139 standard. They were made in the construction site with a poor working condition in humid rainy season and cured in normal temperature for about 3 years. They were immersed into the distilled water at 25±1°C, 50±1°C and 75±1°C and investigated for 180 days. Adhesion test was performed according to ASTM D4541 with Elcometer Adhesion Tester. Epoxy Adhesive was used as a bonding agent of Dolly and we measured the adhesive strength after drying and hardening at room temperature for more than 3 days. Contact angle measurements were used to determine the effect of immersion on the surface energetics of epoxy coating system, including surface free energy and work of adhesion.

From this experiment, the quantitative adhesion characteristics and surface free energy of the protective coatings according to the history of immersion environment were comprehended. Furthermore, methods to improve durability and quality of the protective coatings were suggested.

2. EXPERIMENTAL PROCEDURE

TEST SPECIMENS PREPARATION

The test specimens used in this study were manufactured according to the ASTM D5139 standard. They were made in the construction site with a poor working condition in humid rainy season and cured in normal temperature for about 3 years. There was 5 days drying time between the 1st and 2nd applications of the coating. And, the final drying time was 14 days. The test specimens were manufactured in three systems.

Coating System Code 1

Inorganic zinc was used as the material for the primer, and epoxy paint was used as the material for the top coat. (Inorganic / Epoxy). We made the test specimen from ASTM A36 carbon steel after the pre-treatment of the coating surface considering testing conditions according to the methods and thickness in the CP-A3 specification and the ASTM/ANSI standard. Table 1 shows the specification of coating system code 1.

Coating System Code 2

At first, Inorganic zinc was coated on steel plates and then double-coated by Inorganic zinc and epoxy paint for the topcoat. (Inorganic / Inorganic / Epoxy coating system). This system has twice thicker inorganic zinc for primer than code 1. All coating sequences and processes of manufacturing were same as the coating system Code 1. Table 2 shows the specification of coating system code 2.

Coating System Code 3

The suggested coating system with two epoxy layers was used in this study. At first, Epoxy paint coated on steel plates and then double-coated (Epoxy / Epoxy coating system). The epoxy paints were directly applied to the surface without any primers.

We used the epoxy primer and the epoxy topcoat. All coating processes were conducted as same as the coating system Code 1. Table 3 shows the specification of coating system code 3.

ACCELERATED DETERIORATION TEST

Immersion Conditions

To study the effect of adhesion characteristics of the coatings in immersion deterioration, we carried out the standard experimental deterioration tests about the environmental conditions such as possible temperature, immersion. Immersion processes stated at ASTM D 3912-95 were applied to the test specimens. They were immersed into the distilled water at 25±1°C, 50±1°C and 75±1°C and investigated adhesion for 15days, 30days, 60days, 90days, 120days, and 180 days.

EVALUATION TEST

Adhesive Strength

Adhesive performance of film to a substrate is a very important property because even good coating materials cannot maximize its coating potentials if adhesion is low. Especially, in the protective coating materials of containment, the most important performance is adhesion. However, the mechanism of adhesion has not become clear since it has been explained on the basis of construction experience.

Adhesion test was performed to the specimens exposed to deterioration environment with Elcometer Adhesion Tester according to ASTM D4541. We used a small tester, because we expected that the adhesion would not be great before the test. However, the same type of large tester was used with the small one since adhesion of some parts of test specimens were more than 1000 1b/in^2. Epoxy adhesive was used as a bonding agent of Dolly and we measured the adhesive strength after curing at room temperature for more than 3 days. After the adhesive had cured, a testing apparatus was attached to the loading fixture and aligned to apply tensile force normal to the test surface. The force applied to the loading fixture was then gradually increased and monitored until joint failure occurred. For each test, three replicate samples were employed, and the average value quoted.

Contact Angle

Contact angle was measured using the sessile drop method (Adamson, 1990) on a Rame-Hart goniometer. About 5 of wetting liquids is used for each measurement at 20℃. Readings within 5 s of drop formation were taken for the critical surface tension (Chen-Yang et al., 2004, Kim et al., 1998). For this work, the total surface free energies and their London dispersive and specific (or polar) components for the wetting liquids are shown in Table 2.

3. EXPERIMENTAL RESULTS AND DISCUSSION

INFLUENCE BY TEMPERATURE

To understand how temperature influences on the adhesion of test specimens, the adhesive strengths compared in Fig1, Fig2, Fig3 and Fig 4.

Coating System Code 1

The adhesive strengths have declined except for 25℃, which increased steadily. The decline in adhesion is believed to be caused by the after 90days deterioration environment period, with high temperature immersion affecting on it negatively.

Coating System Code 2

The adhesive strengths have decreased except for 25℃. The reason of low adhesion is that Code 2 specimens were manufactured in a relatively thick inorganic zinc layer.

Coating System Code 3

The adhesive strength improved more than the coating system code 2 and code 3. However the adhesive strengths have decrease except for 25℃.

INFLUENCE ACCORDING TO COATING SYSTEM

Regardless of experiment condition for manufacturing and curing, the adhesive strength of coating system Code 3 is of best adhesion. The normal system (Code 1) with inorganic zinc primer and epoxy top is of the next performance, and the repair systems (Code 2) with inorganic zinc primer and epoxy top are of inferior performance.

The repair systems with poor adhesive strength have twice thicker inorganic zinc for primer than the normal system. It suggests that the thickness of inorganic zinc used for primer has a direct influence on lowing of adhesion. Therefore, it is not desirable to use inorganic zinc as a protective coating system except when this kind of system is specially used for preventing steel from corroding. If the system is used inevitably, however, we need a special construction management to make sure that the inorganic zinc is not thicker than the one in the specification. In addition, replacing the currently employed zinc primer to epoxy primer is advantageous to improve the adhesion of repair coating system. The adhesive performance depends on the initial curing condition more than on deterioration environment. It suggests that the initial curing condition is an important factor to secure the durability of protection coating materials in construction.

Therefore, the most important factor for improvement in durability of protective coating materials and better quality is selecting the coating system most suitable for the use and to provide a working environment where the initial curing condition can be performed thoroughly.

SURFACE PROPERTIES

Generally, the contact angle always decreased with time due to factors such as evaporation of the liquid. Consequently, to standardize the procedure, all measurements were done after 60 s. Fig. 5 shows the contact angles of treated epoxy coating system as a function of deposition time. The test results show that the water deposited samples give the best wetting characteristics with increasing the deposition time. Conversely, the untreated sample substrate displays the highest contact angle, with limited spreading.

Several methods are available for calculation of the surface energy of a solid, the particular method adopted depends on the surface to be examined and the selected test liquids. In this study, Owens-Wendt (Owens et al., 1969) methods were used to evaluate the wettability of the differently treated surfaces that used the previous equation to derive a relation for the work of adhesion (WA):

$$WA = WAL + WASP \tag{1}$$

Where, WAL derived from the London dispersion forces and WASP derived from the non-dispersive, i.e., acid-base interaction.

When there are only dispersion forces involved, the work of adhesion can be expressed by the geometric mean of the dispersion component:

$$W_A^L = 2\sqrt{(\gamma_S^L \cdot \gamma_L^L)} \tag{2}$$

Similarly, the non-dispersion contribution (deriving from electrostatic, metallic, hydrogen bonding, and dipole-dipole interactions) to the equation of the work of adhesion can be defined as the geometric mean of polar contributions. The results can be shown in the following equation: (Fox et al., 1950, Comyn, 1992)

$$\gamma_{LV}(1+\cos\theta) = 2\sqrt{(\gamma_S^{SP} \cdot \gamma_L^{SP})} + 2\sqrt{(\gamma_S^L \cdot \gamma_L^L)} \tag{3}$$

For use on a large variety of polar solids, it is at least needed to two-unidentical liquids with a polar surface energy, if the values of γLL and γLSP are known, such as water, diiodomethane, ethylene glycol, and glycerol (Park 1999, Wu 1982, Park et al., 2003). However, recent studies (Fabretto et al., 2004, Krasovskyy et al., 2004, Elmoursi et al., 2004) have shown that using the two liquids according to geometric mean unsatisfactorily gives a significant variety of energetic results when testing liquids were varied in a pair of two liquids used, such as water-diiodomethane, water-ethylene glycol, diiodomethane-ethylene glycol and etc.

In the early, Owens and Wendt (Owens, 1969) and Kaelble (Kaelble, 1970) introduced the concept of a linear first order function for the determination of the surface free energy and its London dispersive component and γSSP of a solid. Therefore, we may rewrite the equations (2) and (3), if the contact angles for several nonpolar and polar testing liquids are measured, such as

$$\frac{\gamma_L(1+\cos\theta)}{2\sqrt{\gamma_L^L}} = \sqrt{\gamma_S^{SP}}\left(\frac{\sqrt{\gamma_L^{SP}}}{\sqrt{\gamma_L^L}}\right) + \sqrt{\gamma_S^L} \tag{4}$$

From the equation (4), we can calculate the surface energetics of a solid, γSL and γSSP (Park, 1999).

The dispersion and polar components of the surface energies calculated from the equation (4) are shown in Fig. 6. As expected, the untreated epoxy coating sample has the lowest surface energy with a very low polar value. The surface free energy values increased for the treated samples. For such surfaces, probe liquids exhibit tendency to spread and, consequently, the hot water easily penetrate epoxy film. The results show that the polar component of the surface free energy of epoxy coating system is increased considerably by the water deposition treatment. No significant difference is observed between the dispersion components of the degreased and treated epoxy coating system, which indicates that the polar component is responsible for the increase in total surface energy due to the thermal treatment. The increase in surface free energy is an indication of the increase in water permeates epoxy coating system.

4. CONCLUSION

1) Concerning the adhesion of coating systems, the coating system that top and the primer coat are composed of

epoxy layers has the highest adhesion, the normal coating system intermediate, and the repair system has the lowest.

2) The repair system with double the inorganic zinc has the lowest adhesion, indicating adhesion drop is directly related to the thickness of inorganic zinc.
3) Adhesion for all the specimens largely depends on the initial curing condition and thickness rather than the deterioration of the environment, suggesting that the initial curing condition is an important factor for the durability of protective coating materials.
4) Epoxy Paint shows the strong initial adhesion even though it decreases when it is immersion.
5) Adhesion of Inorganic Zinc becomes increasing in proportion to a time under immersion conditions at room temperature.
6) We have to concentrate more on the quality control in real field operation in the Inorganic Zinc product. Because it is affected by the operation condition with surface preparation and film thickness.
7) The immersion in hot water can make increased surface free energy and the water easily permeates through the epoxy coating film.
8) In the future, research should be carried out in terms of the effect of the aging upon radiation and adhesion of protective coating materials. This will deliver a better and more systematical method for the evaluation of deterioration characteristics.

5. REFERENCES

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6. ATTACHMENT

Table 1. Spec. of the coating system Code 1

No.	The Front Side Name of Product / Thickness
1st	Inorganic Zinc Primer CZ 11SG (3-5)
2nd	Epoxy Topcoat ET 562 (3-5)
Total	(6-10)

Table 3. Spec. of the coating system Code 3

No.	The Front Side Name of Product / Thickness
1st	Epoxy Primer ET 562 (3-5)
2nd	Epoxy Topcoat ET 562 (3-5)
Total	(6-10)

Table 2. Spec. of the coating system Code 2

No.	The Front Side Name of Product / Thickness
1st	Inorganic Zinc Primer CZ 11SG (3-5)
2nd	Inorganic Zinc Touch-up CZ 11SG (3-5)
3rd	Epoxy Topcoat ET 562 (3-5)
Total	(9-15)

Table 4. *Surface Tension Components and Parameters*
London dispersive (γ_L^L), and specific (γ_L^{SP}) components of surface free energy (γ_L) of wetting liquids (subscript: L), measured at 20℃

Wetting liquids	γ_L [mJ·m^{-2}]	γ_L^L [mJ·m^{-2}]	γ_L^{SP} [mJ·m^{-2}]
Water	72.8	21.8	51.0
Diiodomethane	50.8	50.42	0.38
Ethylene glycol	47.7	31.0	16.7
Glycerol	63.7	33.9	29.8

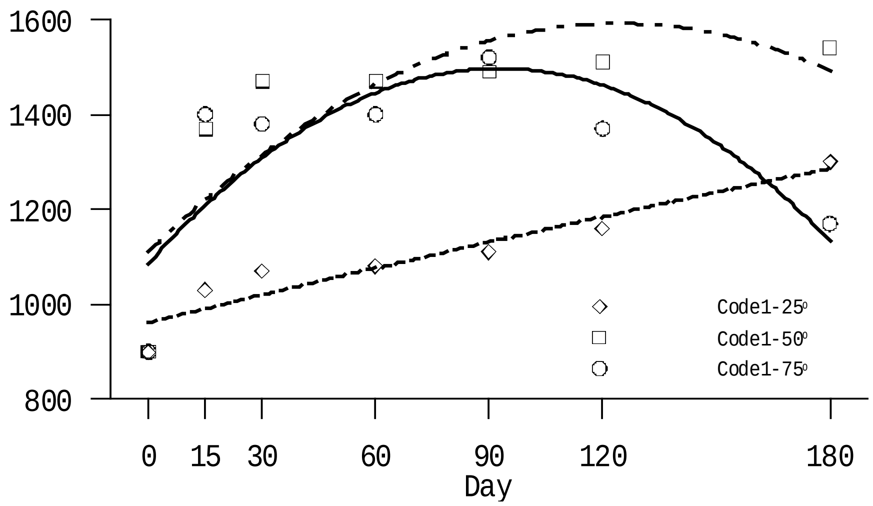

Fig 1. Adhesive Strength of Code 1

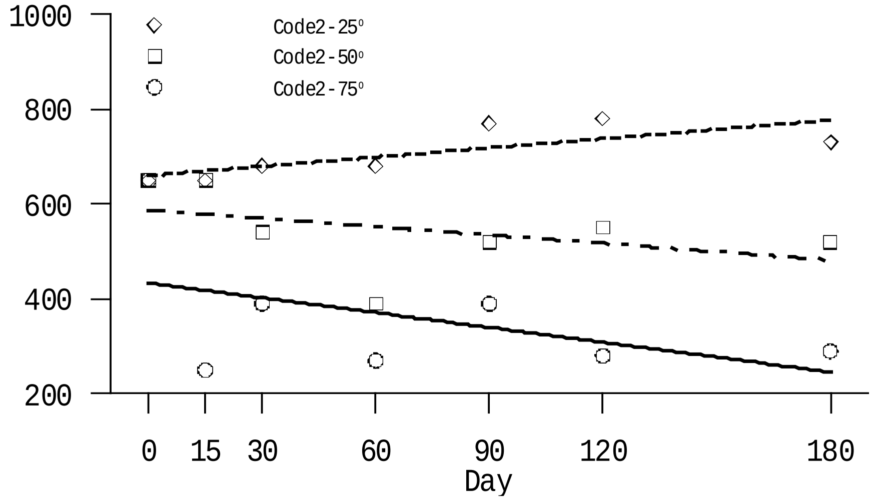

Fig 2. Adhesive Strength of Code 2

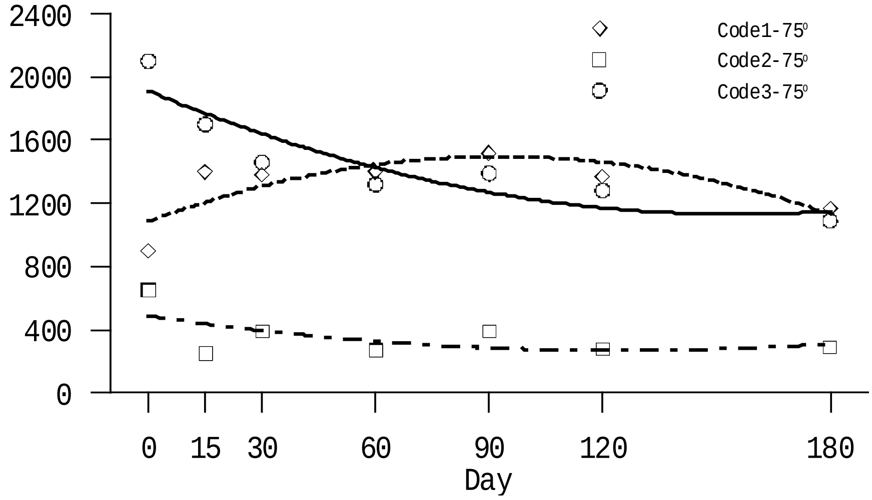

Fig 3. Adhesive Strength at 75℃

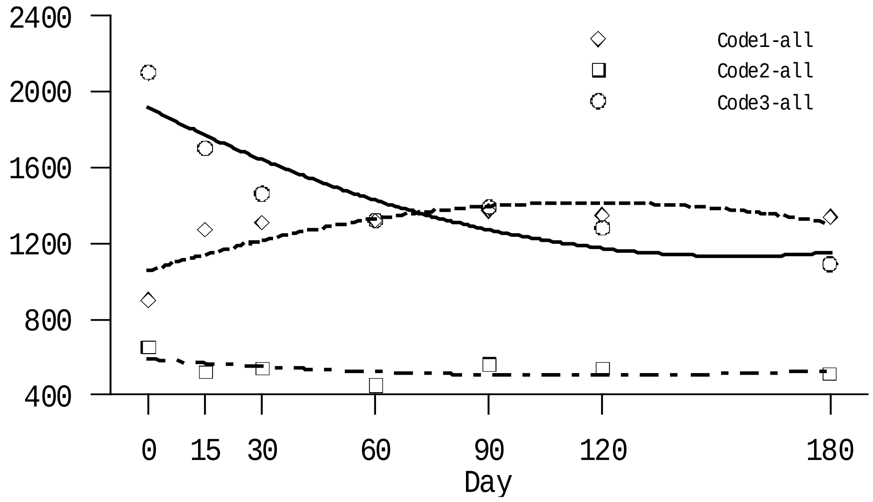

Fig 4. Average Adhesive Strength of Code 1, 2, 3

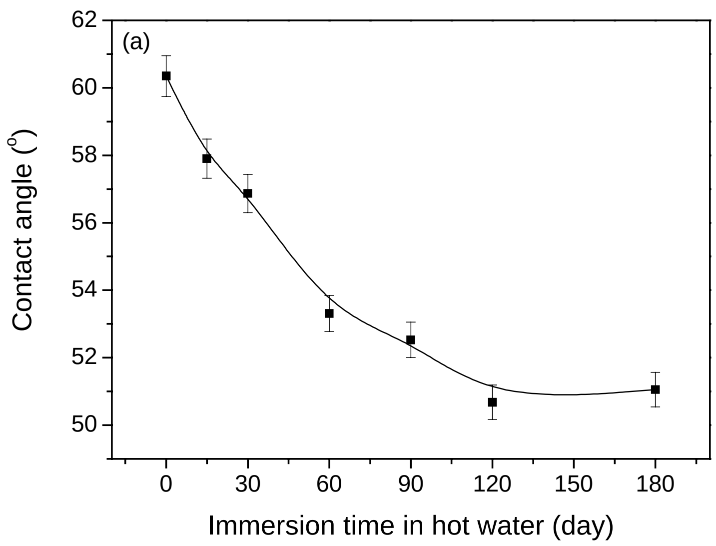

Fig 5. Contact Angle for Immersion Condition.

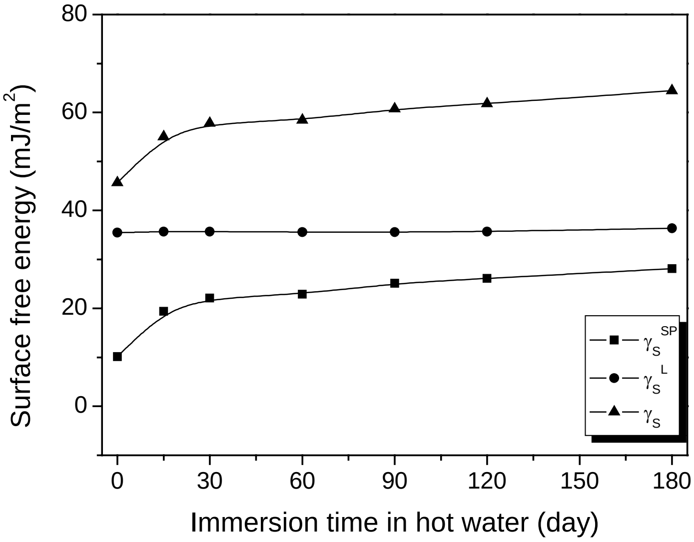

Fig 6. Surface Free energy for Immersion Condition