

**Abstract**

Coatings control corrosion by providing a barrier against oxygen and water. Although coatings are extremely effective, all organic coatings are semi-permeable to O<sub>2</sub> and water. The water permeability coefficient of fusion bonded epoxies, one of the best coating systems, is approximately 10<sup>-6</sup> gms/mil/24 hours, but minimum concentration of oxygen and water that can start the corrosion process is 10<sup>-28</sup> M. In this paper, Nernst equation is used to calculate these concentrations. Cathodic Protection, CP, on the other hand controls corrosion by providing excess electrons to the pipe surface. This system is based on the electrical circuit, where the negative terminal of electrical source is connected to the pipe and the positive terminal to the anode that is placed in the soil. Both systems have limitations in providing the absolute protection single handedly. A combination of CP and coating is the best solution for this complex problem. In the CP-Coating System, coating undertakes the major role to provide the needed protection and CP assumes the secondary role. However, in all cases where the coating fails to provide protection, CP becomes critically important and should provide the necessary protection. Therefore, the limitations of each system should be evaluated and their properties must be adjusted so that they will work in union. In this paper, the properties of coatings that are critical in making the coating a part of the CP-Coating Combination System are discussed. Adhesive Strength and Cohesive Strength are two important and two distinctively different properties. Adhesive Strength is a total sum of several components. Mechanical adhesion, polar-polar adhesion and chemical adhesion are three major components of Adhesive Strength of the coating. The role of these (adhesion and cohesion) properties in providing long-term protection are explained. Along with the chemistry of the coating, the application parameters have a major role in the final Adhesive Strength of the coating. In this paper, the important parameters that control the adhesive strength and how they depend on some of the application parameters are also explained.

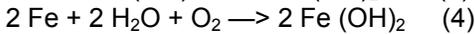
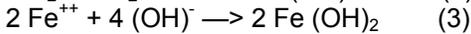
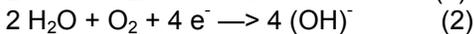
**Introduction**

Coating is one of the corrosion control systems for underground pipelines. It is a highly efficient system, provided care is taken during material selection and application of the coating. There are some key parameters that dictate the success of the coating system which are to be clearly understood by corrosion engineers.

Coatings control corrosion by providing a barrier against oxygen and water and also by insulating the metal surface. Although many coatings are excellent barriers, all organic coatings are semi-permeable to oxygen and water. Therefore, it is important to understand the minimum concentrations of oxygen and water, which can start the corrosion process in order to devise efficient corrosion protection coatings.

**Minimum Concentrations of Oxygen and Water to Start Corrosion**

Corrosion is an electrochemical process. Metal iron (Fe<sup>0</sup>), oxygen, water, electrons and ferrous hydroxide are involved in this process. The corrosion process can be represented by the following equations.



Nernst equation can be used to calculate the minimum concentration of oxygen and water to start the corrosion process.

The Nernst equation for any electrochemical reaction is given below:

$$E = E^0 - \frac{RT}{nf} \log \frac{[\text{Products}]}{[\text{Reactants}]} \quad (5)$$

For corrosion, the reactants are Fe<sup>0</sup>, O<sub>2</sub>, H<sub>2</sub>O and the product is Fe (OH)<sub>2</sub> (equ.- 4). Assume at certain levels of O<sub>2</sub> and H<sub>2</sub>O, there is no corrosion. This means, E = 0.

Rewriting the above equation for no corrosion.

$$0 = 1.255 - 0.059 \log [(\text{FeOH})_2]^2$$

$$4 \quad [\text{Fe}^{\circ}]^2[\text{O}_2] [\text{H}_2\text{O}]^2 \quad (6)$$

or

$$[\text{Fe}(\text{OH})_2]^2 \text{ and } [\text{Fe}^{\circ}]^2 \text{ are } 1$$

$$\text{then } 1.255 = \frac{0.059 \log \quad 1}{4 \quad [\text{O}_2] [\text{H}_2\text{O}]^2}$$

Solving this equation, the concentrations of O<sub>2</sub> and water are 10<sup>-28.4</sup> M. A detailed study on this is given by G.D. Mills<sup>1</sup>. It had been reported that the water permeability of the best organic coatings are in the ranges of 10<sup>-6</sup> gms./mil/24 hours.

Therefore, it is impossible to stop corrosion by organic coatings alone.

From equation (1), it is evident that if the pipe surface has excess electrons, Fe<sup>(0)</sup> will not become Fe<sup>++</sup>. Cathodic Protection, (CP) is based on this principle.

For most underground pipelines, CP is provided by impressed current system. The negative terminal of the rectifier is connected to the pipe and the positive terminal to the anode. The effectiveness of this system depends on its ability to provide sufficient electrons where they are needed. Any obstacle such as rocks, loose coatings which prevent the electrons from reacting the areas where they are required, can result in serious corrosion and pipeline failures<sup>5</sup>.

Both coating and CP have limitations, in providing total corrosion protection when used alone. However, both systems have unique properties. When used in combination, CP-coating can provide excellent, cost-efficient corrosion control for underground pipelines. In the CP-Coating combination system, coating undertakes the primary role and CP the secondary role. However, in all cases where coating fails to provide protection, CP should assume the primary role.

Protective coatings should have corrosion-resistant properties to provide long-term corrosion protection. It also should have mechanical properties to sustain environmental conditions and pipeline construction activities. It is desirable to have a single product with the maximum values for all these properties. However, because of the opposing nature of some of these properties, it is impossible to formulate such a coating. Some of these properties, although highly desirable, may have to be sacrificed to some extent to make the CP-coating combination system to work in union<sup>2</sup>. Therefore, it is highly important to the corrosion engineers to understand the critical properties of the coating that will work with or against the CP system.

Adhesive strength and cohesive strength of the coating are two important properties that are to be understood properly in this context. Adhesive strength is the strength needed to pull the coating from the substrate without tearing it.

Cohesive strength is the force needed to tear the coating, meaning it is a measure of the film's strength. (The adhesion property is an integral to the coating's corrosion prevention properties.) Cohesive strength dictates the coating's ability to resist mechanical damages. Both cohesive strength and adhesive strength are extremely important and the higher these values, the better the system is. However, if one has to sacrifice any portion of one of them, to make a choice, a clear understanding of both properties and their relationship to one another and to the CP system is needed to make the right decision.

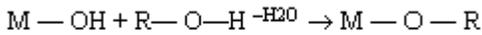
### **Adhesion, Cohesion and CP**

#### **Adhesive strength**

Adhesive strength is the sum of several components. The major portion comes from mechanical adhesion, polar-polar adhesion and chemical adhesion. By definition, mechanical adhesion is the gripping force of the coating onto the substrate. The polar-polar adhesion is the force of attraction between the positive and negative poles of the substrate and the coating. The polar-polar adhesion can be represented as follows:



Where M represents the metal substrate and R-O-H the coating. Chemical adhesion is due to the chemical bonds that are established between the substrate and the coating through chemical reaction. This can be represented as follows:



Although mechanical, polar-polar and chemical adhesion all play a significant role in the total adhesive strength, the absolute values of each are quite different. It is claimed that a chemical bond is 20 to 1000 times stronger than a polar-polar bond. Therefore, the coating which can establish the greatest number of chemical bonds with the metal substrate will have the highest adhesive strength.

### Influence of surface preparation and coating application on adhesive strength

Surface preparation and application temperature greatly influence coating's adhesion to the pipe surface. Most of the high performance powder coating systems require an extremely clean surface. For FBE, the minimum required cleanliness is Sa 2.5 per ISO 8501-1/SIF or NACE level-2. The importance of this requirement can be easily understood by reviewing the role of adhesion in the coating's performance. The two important components of adhesion, polar-polar and chemical, are directly linked to the number of hydroxyls of the substrate surface.

The absence of these hydroxyl groups can adversely affect the overall adhesive strength of the coating. An improperly cleaned surface can limit the number of hydroxyls available for bonding.

Another important step is the removal of water-soluble salts and organic contaminants. If left on the surface, salts, especially chlorides and sulfates, can initiate water absorption by osmosis that lead to coating blisters. It has been reported that chloride contamination will seriously affect adhesion and cathodic disbondment properties<sup>4</sup>.

International standard organizations such as NACE and CSA address this issue in their FBE application specifications. The standard procedure to remove soluble salts, (such as chloride), involves washing the pipe with phosphoric acid followed by deionized water. The maximum allowable chloride concentration is 2.0 mg/m<sup>2</sup>, according to NACE standards.

Proper initial adhesion and the powder coating's ability to provide adequate adhesion throughout the design life of the pipeline are the key factors in providing adequate corrosion protection. Profile is a key factor in deciding the total adhesive strength of the powder coating. The required profile for FBE application is 2.5 to 4.5 mils (62-112 microns). As stated earlier, the major adhesion components are mechanical, polar-polar and chemical. All of these are greatly influenced by the shape, peak heights and density of the anchor profile<sup>4</sup>. By increasing the depth and density of the profile, the available bonding area is increased.

Powder coatings control corrosion by separating the cathode and anode. This can only be achieved if the coating can wet out the surface completely on the micro level. To have excellent wetting properties, the powder coating should have low viscosity. Because FBE is solid, the melt viscosity has to be low enough to fill the profile without leaving any air pockets. Low viscosity can be achieved by using proper resin systems. However, the viscosity depends to a greater extent on the pipe surface temperature. A higher temperature will result in a lower melt viscosity, allowing the powder coating to wet out the surface completely.

FBE systems require high energy to achieve cross-linking between the epoxy molecules and the curing agent. Improper energy levels can leave powder coating components un-reacted. This will adversely affect the applied film properties. One of the properties that will be seriously affected is flexibility, since under-cured coatings will crack during field bending of the coated pipe. Another property that will be affected is adhesion. For chemical adhesion, an excited metal surface is needed. By increasing the application temperature, the chance for excitation of iron molecules on the substrate will be increased. This will

lead to more chemical adhesion sites and increased adhesive strength of the applied coating.

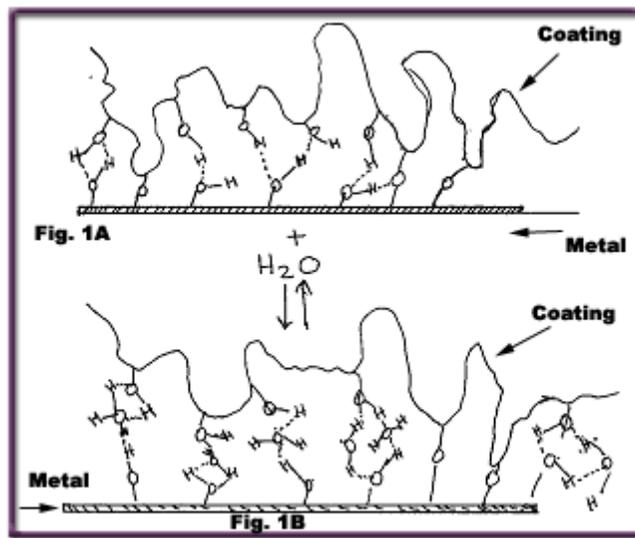
### Adhesion of Coating In Wet Condition

Maintaining proper adhesion throughout the service life of the pipeline is one of the key factors in the success of the coating. But the initial adhesive strength can diminish during the service life due to several reasons. Degradation of the organic components in the coating is one of the reasons.

Permeation of foreign molecules which can destroy adhesion is another reason. A good example for this is the permeation water molecules through the coating to the metal-coating interface.

Water, once reaches the interface can destroy polar-polar bonds between the coating and the substrate by establishing hydrogen bonds with them separately.

This is illustrated in the following figure:



(Fig. 1 Polar-Polar adhesion) (A. Dry and B. Wet)

Destruction of the polar-polar bonds by the presence of water molecules will reduce the overall adhesive strength of the coating. However, this is not a serious concern since a reduction in adhesion does not necessarily mean a loss of adhesion.

As long as the forces causing coating disbondment on the pipe is lower than the total adhesive strength, (eventhough it goes considerably lower than the initial value) the coating will adhere to the pipe. It should be pointed out that the wet coating will regain the lost polar-polar bonds once the wet section is allowed to dry.

### Cohesive strength

Cohesive strength of the coating is a measure of the force of attraction between the molecules, or the force required to tear the coating apart. This property is dependent on the coating's constituents, especially the base resins. Coatings, both thermoplastic and thermoset, come in a wide range of cohesive strengths.

Cohesive strength of the coating is a temperature-dependent property. Usually it will decrease with an increase in temperature.

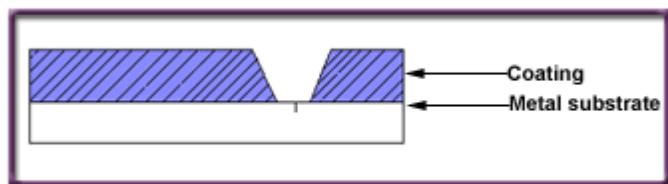
Sometimes a reduction in cohesive strength can be mistakenly identified as adhesion failure. Above the glass transition temperature (T<sub>g</sub>) FBE changes to an amorphous, soft material with lower cohesive strength. If adhesion tests are performed at

a temperature above the  $T_g$ , the coating will tear easily. This behavior can be mistaken for adhesion failure and can cause concern. Although it is not a serious problem in the plants during pipe coating application (due to the strict guidelines on the adhesion test temperature), it may become a serious problem in the field during the girth-weld coating application, where curious inspectors from other disciplines are also involved.

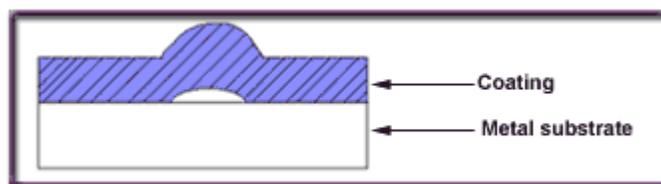
### **Influence of Adhesive Strength and Cohesive Strength on CP Performance for Underground Pipelines**

A coating with better cohesive strength is desirable to ensure minimal damage during transportation and pipeline construction. But in some cases, this highly desirable property can be an obstacle in the performance of the CP-Coating combination system, if it exceeds the adhesive strength of the coating. This can be easily understood by comparing the CP performance on impact-damaged areas of two coating systems; one with higher adhesive strength than cohesive strength and the other vice versa. In the CP-Coating combination system, the CP is designed as a supplementary system to provide protection if coating fails. However, if coating fails, even though CP is only meant as a secondary protection system, it becomes the primary protection system and its performance becomes extremely critical. The area where the coating failed must be protected by CP alone. For this, there should not be any obstacle in the electrical path between the CP source and the damaged area. With this understanding, consider the performance of the CP system in both cases where coated joints were impacted. Impact damages can be minor bruises, damaging only the outer layer of the coating. But if the impact is high enough, the coating can break or delaminate, depending on the cohesive and adhesive strengths of the coating. The coating with higher adhesive strength than cohesive strength, will break before it disbonds from the pipe surface. But the coating whose adhesive strength is lower than its cohesive strength, will delaminate without any break.

These two cases are represented in Figures # 2 and # 3.



**Fig 2. Ruptured Coating**



**Fig 3. Delaminated Coating**

The first one, where the coating has ruptured, is an obvious damage. However, the second one (delamination without any visible rupture) is also a damage even though the area appears to be damage free. In both cases, the coating damages are serious and the metal underneath can corrode if not protected by the supplementary system, CP. In the first case where coating has ruptured due to impact, the electrical resistance is non-existent and the electrons from the CP system can reach the pipe surface. But in the second case where the coating has only delaminated without any break, electrons cannot reach the surface due to the high resistance of the coating. In this case, the CP system cannot protect the area.

### **Conclusions**

Some of the important properties that dictate the coating's ability to control corrosion are water and oxygen permeability, wetting, adhesion, cohesion, cathodic disbondment and CP compatibility. Most of these properties are somewhat interrelated. For example, adhesion and wetting properties will affect the cathodic disbondment values. Similarly, poor wetting will affect adhesion.

For the success of the CP-Coating Corrosion Control System, the coating should work in union with CP. The system will fail if any of the properties of the coating become an obstacle to the performance of the CP system. Out of several properties only a few may be critical for the CP-Coating combination system.

Although the coating with the highest values of all important properties is the first choice, it may not be the best for the combination system. Quite often, coatings with lower values of some of the properties may have to be selected to make the

coating an integral part of the combination system. Identifying the optimum values of the essential properties is the most important step in the coating selection process.

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