Water Absorption in Organic Coatings For Metal Substrate: A Review

Amna Akhtar, Tahir Jamil.

Faculty of Engineering and Technology, University of the Punjab, Lahore, Pakistan

Abstract

Organic coatings are widely used for corrosion control of steel structures. The presence of moisture in the coating can activate corrosion process. For organic coatings to serve their intended purpose they must maintain a good adhesion with the substrate. Proper adhesion of the coating is related to the effective surface preparation. The surface preparation techniques for steel substrate include mechanical and chemical pretreatments. The surface characterization tests are carried out and roughness parameters are measured using surface profilometer. After surface preparation/characterization, organic coatings are applied to the substrate by different methods depending upon the purpose of application, types of coatings, size and geometry of the object to be coated, and site of application. The most commonly used techniques that have been applied to provide information on water uptake phenomena in coatings applied to substrate is electrochemical impedance spectroscopy (EIS) and Fourier Transform Infrared Spectroscopy (FTIR). EIS and FTIR determine the dielectric properties and structure of the material respectively.

Introduction

Organic coatings are applied to many industrial steel structures for corrosion control. Organic coatings act as a barrier layer to decrease diffusion of the aggressive species such as oxygen ions and salts towards the interface between the substrate and coating [1-4]. There is usually a good adhesion to prevent the coating delamination from the substrate due to corrosion. The metallic structural equipments are prone to be attacked by aggressive species in natural environment among which water is the most common. The presence of moisture in the coating can activate corrosion process and can cause loss of adhesion and formation of blister [6-8]. For organic coatings to serve their intended purpose, surface pretreatment of the steel substrate is extremely important. This pretreatment could be mechanical or chemical in nature. The mechanical pretreatment includes processes like brushing, grinding and blasting thereby resulting in cleaning and roughening of steel surface for better and enhance micromechanical interlocking. The chemical pre-treatment comprises the use of primers as coupling agents that form a chemical bridge between the steel substrate and organic coatings [9].

After surface pretreatment, surface is evaluated with the help of surface profilometer.Then organic coatings are applied to the substrate by different methods such as brushing, dip coating, conventional air spraying, airless spraying and electrostatic spraying. The most commonly used technique that has been applied to provide information on water uptake phenomena in coatings applied to substrate is gravimetric analysis (GA).The main drawback of gravimetric technique is that it don’t discern the water accumulated at the coating/substrate interface from the sorbed into the bulk of coatings. If water is absorbed at the coating/substrate interface it would incorrectly estimate the rate of water transport in a coating applied to substrate. Hence coating capacitance (C_c) is very important source of information concerning the water barrier properties of an organic coating. The capacitance of organic coatings is determined with the help of EIS which then gives the volume fraction of water in coating and coefficient of diffusion [12-13]. Fourier transform infrared spectroscopy (FTIR) is used to study the interaction of water molecules with polymeric structures and degradation of organic coatings [11].

Surface Preparation

Surface preparation is the most important factor in determining the success of organic coatings. Effective surface preparation ensures that the substrate is uniform, showing that a sufficiently large number of potentially reactive sites on the steel will be available for binding with the coating. It also ensures that the mechanism by which the coating system protects the steel is not hindered by the presence of water-soluble oxides and hydroxides beneath the film.

If the coating system has an improper foundation it will fail sooner than expected or can fail catastrophically within its first year of application. The ultimate objective of surface preparation is to create proper adhesion of a coating with the substrate. Proper surface preparation is vital to the service life and overall effectiveness of a coating. The purpose of surface preparation is two fold: Firstly to roughen the surface, providing an increased surface area for mechanical bonding of the coating with the substrate. This roughening is commonly referred to as anchor pattern or profile and is essentially a pattern of peaks and valleys etched into the surface. This pattern is most commonly attained by abrasive blast cleaning although it can also be obtained by the use of certain power tools which simultaneously clean and roughen the surface.

Secondly, to clean the surface for chemical adhesion of coating to the substrate because coating applied over soluble salts, rust, dirt or oil bonds poorly to the substrate. Early coating failures usually take place if the substrate is not free from these contaminants [19].

Methods of surface preparation

A variety of surface preparation methods exist which can be broadly classified into mechanical and chemical pretreatments.

Mechanical pretreatment

It includes the following techniques:

Hand tool cleaning (SSPC-SP 2): It is a method of preparing the substrate by the use of non-power hand tools to remove all mill scale, rust, paint and other detrimental foreign matter. Hand-tool cleaning is slow and tedious, it is not intended for preparation of large surfaces and it will not generate the surface roughness required for most of the industrial protective coatings. Common hand tools include wire brushes, non-woven abrasive pads, scrapers, chisels, knives, and chipping hammers.

Power tool cleaning (SSPC-SP 3): Power-tool cleaning removes all adherent rust, paint, mill scale, etc. using pneumatic and/or electrically operated tools rather than hand tools. The three common categories of power tools are impact cleaning tools, rotary cleaning tools, and rotary impact cleaning tools. Through careful selection and use, many cleaning operations can be accomplished quickly to produce satisfactory surface cleanliness.

Fig 1.1 Brush and Wheel cleaning

Water jetting (Low & High Pressure): Low pressure (1,000 to 3,000 psi) water jetting can be used with or without detergents to remove grease, oil, or other foreign matter from the surface. The application is best suited for general overall cleaning operations on various substrates. High pressure (5,000 to 10,000 psi) water jetting will effectively remove many tightly adherent materials. This method is perhaps the most common use of water jetting.

Abrasive blast cleaning: Abrasive blast cleaning is perhaps the most productive method of surface preparation for coatings that requires both an anchor pattern and a high degree of surface cleanliness. Conventional blast cleaning generally falls into five categories: open nozzle, water blast with abrasive injection, open nozzle with a water collar, automated blast cleaning, and vacuum blast cleaning. Perhaps the most common method of abrasive blast cleaning is the use of an "open nozzle".

Fig 1.2 Abrasive blast cleaning

Water abrasive blast cleaning: Water abrasive blast cleaning involves the incorporation of water into a dry abrasive blast-cleaning operation. Water abrasive blast cleaning uses high-pressure water and abrasive to provide a cleaned and roughened surface. The advantages of this technique include the control of dust emissions and aid in the removal of chemical contamination by the introduction of water.

Chemical Pretreatment

It involves the following techniques:

Solvent cleaning (SSPC-SP 1): Solvent cleaning is a form of surface preparation used specifically for the removal of oil and grease, soil, and other contaminants from steel surfaces by the use of solvents, emulsions, and cleaning compounds. The bonding of the coating to the steel will be inhibited if a thin film of oil remains on the surface. However it does not remove rust and mill scale from the surface. Solvents which are commonly used include benzol, methyl ethyl ketone, acetone, and naphtha.

Chemical Stripping: Chemical stripping involves the application of an alkali, acid, or methylene chloride solution to a coated surface by spray, brush, or trowel. The solution remains on the surface for a few hours or overnight to allow the chemical reaction to take place and soften the coating. Before the advent of blast cleaning as an effective method for a thorough cleaning of structural steelwork, the removal of rust and scale by immersion in dilute acid was employed. But the acid treatment requires addition of some inhibitors to stop acid attack on steel and save its unnecessary use.

Surface Characterization

After surface preparation, following tests are used for its characterization:-

Surface cleanliness test

In order to check the cleanliness of the surface, copper displacement test is carried out using solution of $CuSO_4/H_2SO_4$ (15 g/liter of $CuSO_4$, 0.9 g/liter of H_2SO_4). With the help of a dropper, 2 to 3 drops of above solution are placed on the surface. Appearance of reddish brown color, owing to the copper deposit on the surface, establishes the cleanliness of the surface [14].

Surface energy test

The conditions for good wetting are always fulfilled whenever the surface tension of the substrate is higher than that of coating materials. Such a requirement can easily be fulfilled when coating metals are of high surface tension. Viscosity of the coating material has to be sufficiently low in order to give functional groups, capable of bonding, an opportunity for orientation towards the substrate. Materials, which meet these requirements, can be formulated if the surface tension of the solid is known. It can only be measured indirectly by introducing droplets of liquids of known surface tensions (e.g. 34 mN/m, 38 mN/m, 44 mN/m, and 46 mN/m). Surface tension of the treated substrate is greater than the surface tension of the liquid which spread on the surface after a while and less than the liquid which retains the spherical shape of the drop for considerable time until environmental effects such as temperature, humidity etc starts affecting it.

Surface Profilometery

Surface profilometer is used to measure and record surface roughness parameters. The Profilometer has a diamond stylus traveling along a straight line over the surface. The distance that the stylus travels is called cut-off length. To highlight roughness, profilometer traces are recorded on an exaggerated vertical scale. A record of surface profile is made by mechanical and electronic means. Some of the parameters measured by this device are maximum peak to valley height, maximum peak height, peak counts and sampling length [15].

Coating Application

Organic coatings can be applied to the substrate by different methods. The applications mainly depend upon the purpose of application, types of coatings, size and geometry of the object to be coated and site of application. Some of the important techniques used for coating are brushing; dip coating, conventional air spraying, airless spraying, and electrostatic spraying. The followings give a brief description of these techniques:

Application Techniques

- *Brushing* gives better penetration of paint into pores, cracks and crevices. It involves very low wastage. But it is less suitable for very fast drying products.

- *Dip coating* is a simple, cheap and quick method. The quality depends upon time of withdrawal, viscosity, and mixing of coating.

- *Conventional air spraying* is a much faster application technique. The layers obtained are uniform in thickness. The critical parameters for spraying are distance, pressure, and nozzle type. The disadvantage of this technique is the larger waste.

- *Airless spraying* is suitable for coating application at higher viscosity, resulting in higher film thickness. It involves lower loss of solvents and is suitable with more volatile solvents. But it is unsuitable for spraying on small objects.

- *Electrostatic spraying* is an economical process because of the low waste but it is restricted to coat the objects only on the outside [16].

Measurement of Film Thickness

A range of instruments is available for the measurement of film thickness. Provided they are regularly and correctly calibrated and used properly, they will provide reasonably accurate measurements of thickness. The instruments are divided into three broad types: magnetic pull–off, fixed probe and electronic induction. Generally there are two types of film thickness; wet film thickness and dry film thickness. Wet film thickness is most commonly measured with a small comb gauge. This has a number of projections similar to a comb. The two at the end are of the same length and those in between progressively vary in height. Many instruments have been developed for the measurement of dry film thickness. The most commonly non-destructive methods used depend upon measuring magnetic flux between the instrument probe and the substrate. The weaker the flux, the bigger the gap and therefore the thicker is the apparent coating. The relationship between dry film thickness and wet film thickness is given as follows [16]:

Dry film thickness = wet film thickness x % solids (vol) /100.

Fig 1.4 Combgauge

Fig 1.5 Electrometer 456-Dry film thickness gauge

Adhesion Test

Adhesion testing is performed for quality control purposes. Testing of adhesion is of prime importance for the characterization of organic coatings. The pull- off adhesion testing is a measure of the resistance of a coating to separate from a steel substrate when perpendicular tensile force is applied. The pull-off strength of coatings with varying bond strengths on steel substrate can be measured with the help of hand –held as well as desktop adhesion tester [18].

Methods of Coating Characterization

The techniques which are most commonly used to characterize the corrosion protection performance of organic coatings are EIS and FTIR.

Electrochemical impedance spectroscopy (EIS)

EIS has been used extensively as a laboratory-based research tool for studying the performance and deterioration of polymeric protective coatings [20-24]. In recent years, the EIS technique has been used in routine laboratory testing of coatings [23-24]. The EIS data can be used to predict film porosity, solution absorption into the coatings and film delamination properties. EIS also provides a technique to optimize coatings while reducing the time of coating evaluation and gives insight into the chemical and physical properties of the coatings. [25]

The impedance of a coating determined by EIS is the electrical resistance of the coating, as measured by AC (alternating current) signal. Coating impedance can be regarded as a measure of barrier properties, or conversely, a measure of permeability to water, dissolved gases like oxygen, and corrosive species like chloride ions. Impedance measurements are most applicable for coating systems used in water immersion or in environments with high humidity. High performance coatings with excellent barrier properties have high impedance (i.e. low permeability to water) and vice versa. If a coating is subjected to an aggressive aqueous environment, its impedance decreases as a function of time. The resulting loss of barrier properties and influx of water promotes disbandment and the onset of under film corrosion.

Impedance measurements make possible to arrive at lifetime predictions of coatings after relatively short exposure times. EIS helps to study delamination of coatings as well as initiation of corrosion underneath the coating systems. EIS can also be used to measure and characterize defects in coating because a defect will also have a specific impedance response.

While all polymeric coatings are permeable to species such as oxygen, water and ions, water molecules at the metal/coating interface may drastically affect coating adhesion and thus promote corrosion and blister formation at the coating-substrate interface**.** All these processes influence the impedance response of the coating-substrate system under the application of a small ac signal and thus useful information concerning them can be extracted from the analysis of the EIS spectra. For example corrosion performance of epoxy-polyamide, alkyd, and polyester polymeric coatings has been successfully investigated by EIS spectra.

The results of impedance measurements of the coatings have shown that the entering water not only affects the dielectric properties but also results in swelling of the coating polymer. Using EIS, for the long-term immersion of the coating, it has been reported that the start of the corrosion process under high impedance barrier type coatings can be detected by changes of the dielectric properties of the coating [26-31].

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR is the most useful technique for characterization of coatings and is an efficient mean of gathering the structural information. Almost all components of a coating can be identified by using FTIR which can monitor changes such as drying, curing, and degradation. Quality control of raw/virgin materials and process monitoring during coating synthesis and formulation can also be accomplished with the help of FTIR.

It is often possible to analyze a coating with minimal preparation. At other times, it is worth the extra effort to separate a coating into its components. The polymers and resins can be separated from the inorganic components, such as pigments and extenders, on the basis of solubility. Proper solvent must be chosen that can dissolve the organic components. After dissolution, filtration or centrifugation can be used to separate the inorganic pigments and fillers from the dissolved polymers or An IR spectrum is an almost unique fingerprint of a particular molecule or of a coating formulation, characterized by the number, shape, and intensity of absorption bands. This pattern can be compared to a collection of known patterns, either manually or with a computer. An IR spectrum contains significant structural information besides being a unique fingerprint. IR absorption bands can be divided into characteristic bands and fingerprint bands. The latter are unique to a particular molecule. Characteristic bands or group frequencies are caused by a particular functional group, such as an ester or an amide. These group frequencies are almost independent of the rest of the molecule in which they occur, and they can be used to determine which functional groups are present in a molecule.

An important application of FTIR spectroscopy to coatings is chemical analysis and the determination of the composition of a coating. IR is unique in being able to identify almost the full range of coating components, including volatile solvents, resins and polymers, inorganic and organic pigments, and a wide variety of additives.

FTIR is very useful for studying changes that occur within coatings. Examples include following polymerization reactions that occur during the production of a coating or after its application. The degradation of a coating with time, temperature, or adverse conditions can be monitored. IR spectroscopy can be used to study surface phenomenon associated with coatings. It is useful for interfacial studies like investigations of interactions between coatings and substrates [16]. Most coatings problems can benefit from investigation by FTIR spectroscopy.

Conclusion

The findings of this review article are given below;

- It makes possible to arrive at life time predictions of coatings within relatively short exposure of time.

- It is helpful to study the surface phenomenon associated with coatings e.g. interfacial studies can be conducted
- .It determines the composition of coatings and almost full range of coating components including volatile solvents, resins polymers, inorganic and organic pigments and wide variety of additives can be examined.
- The delamination of coatings and initiation of corrosion underneath the coating system can be investigated.
- Changes occurring during production of a coating or after its application can be monitored in addition many coating problems can be benefitted

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