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Paints and varnishes — Electrochemical noise measurement for assessing the protection of metal afforded by organic coatings

~~DTR stage~~

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Contents

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This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

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Introduction

There are several test methods for assessing the ~~assessment of~~ protection~~ being~~ afforded by organic coatings on metal, particularly on low carbon steel, using the available electrochemical measurements. The most commonly used technique is electrochemical impedance spectroscopy (EIS~~)~~), which is detailed in the ISO 16773 ~~(all parts)~~,series, and~~ this~~ is well suited for laboratory use. However, there is a strong need for a non-intrusive technique that can be used on site to monitor or for quality control that is quick and is relatively simple to use and interpret.

This document gives the current state of the art for such a technique, ~~this being~~which is electrochemical noise measurement (EN). The developments described in this document suggest that electrochemical noise measurement ~~might~~can be used as an alternative to and ~~maybe~~potentially even as the preferred process for field or on-site use.~~ But it needs more people to use it.~~

For further information, a detailed description of the EN methodology when applied to bare metal~~,~~ can be found in ISO 17093~~ which contains a brief appendix about organic coatings~~. The differences associated with using the technique for organic coatings are described in this document~~ and~~, which is intended to complement ISO 17093. ~~Similarly, ISO/TR 16208 on making EIS measurements on bare metal compliments the standard ISO 16773, the making of EIS measurements on coated substrates.~~

The EN approach has been directly compared with methodologies such as EIS and DC resistance, with good agreement.[3]~~,~~ ~~[]~~[4]

Furthermore, electrochemical noise applied to assess coatings has been ~~recently~~ reviewed~~,~~ in References [5] and [6], showing the potential for this technique.~~[5],[6]~~

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Electrochemical noise measurement for assessing the protection of metal afforded by organic coatings

1 Scope

This document describes the principle of electrochemical noise measurement (EN), specifically focusing on the application of the technique to indicate the level of protection provided by an organic coating to the underlying metal. It discusses the principles behind the measurement method but also the type of electrochemical apparatus, the experimental set-up and electrodes configurations, the presentation of measured data, and analysis of results that have been used in the work done so far and reported in the references. This work has mainly been done in the laboratory, and there are some examples of work conducted in the field.

NOTE Electrochemical noise measurement for coatings is only used in few academical groups. A general application of the method cannot be guaranteed.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 16773-~~-~~1, *Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens — Part 1: Terms and definitions*

ISO 17093, *Corrosion of metals and alloys — Guidelines for corrosion test by electrochemical noise measurements*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 16773-~~-~~1, ISO 17093 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at ~~https://www.iso.org/obp~~https://www.iso.org/obp

— IEC Electropedia: available at ~~https://www.electropedia.org/~~https://www.electropedia.org/

3.1
electrochemical noise
EN
fluctuation typically at low frequencies (≤1 Hz) and low amplitude in current and potential, generated by electrochemical reactions and other processes on the surface, for example, bubble evolution

3.2

electrochemical potential noise

EPN

fluctuation in potential of an electrode relative to a reference electrode or fluctuation in potential between two similar electrodes

Note 1 to entry: The electrochemical potential noise is expressed in microvolts (µV) or millivolts (mV).

3.3

electrochemical current noise

ECN

fluctuation in current to one electrode or between two electrodes

Note 1 to entry: The electrochemical current noise is normally expressed in nanoamperes (nA).

3.4

electrochemical noise resistance

R_n

resistance obtained by dividing the standard deviation of potential noise by the standard deviation of current noise from the time record

3.5

working electrode (coated)

WE

coated metal in contact with the electrolyte, made out of the investigated material(s)

3.6

pseudo-working electrode

PWE

working electrode (3.5) other than coated metal

Note 1 to entry: A silver/silver chloride electrode (Ag/AgCl) in laboratory work or a noble metal like silver, platinum or gold can be used as part of a sensing probe in field work. PWEs are needed for configurations other than the standard bridge.

3.7

pseudo- reference electrode

P_{Ref}

electrode used as a reference electrode in field work

Note 1 to entry: Examples are theEXAMPLE The metal itself (for single substrate configuration), platinum wire or sheet, copper, and silver.

3.8

electrode configuration

arrangement by which the electrodes are connected to the measuring device, i.e. bridge (Bridge), single Substrate (SS), no connection to the substrate (NOCS)

Note 1 to entry: The configuration used depends on the particular circumstances of the measurement.

3.9

zero resistance amperemeter

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ZRA
electronic circuit which measures current but has itself no significant impedance

Note 1 to entry: For coatings, a ZRA capable of measuring low levels of current down to picoamperes (pA) is usually needed.

4 Principles

4.1 Organically coated metal exposed to a corrosive environment – how a resistance measurement can indicate protection

Water and oxygen penetrate through an organic coating leading to electrochemical reactions occurring at the interface between the metal and the coating [7]. In aqueous corrosion, discrete anodic and cathodic areas arise, and these allow corrosion to proceed whenever there is an ionically conductive pathway between the substrate and the surrounding environment. However, if a high ionic resistance is introduced into the circuit between anodes and cathodes, e.g. by the coating, the rate of corrosion will decrease to a low value. This is one accepted mechanism by which the coatings can operate to prevent corrosion. Another mechanism, which can take place concurrently, is interface reactions when aided by an oxidizing agent, e.g. oxygen, hydrogen peroxide or chemicals within the coating. These can result in the formation of a passive coherent, protective, chemically stable oxide layer which slows the corrosion rate. For this "passivity" to pertain for any length of time, the coating acts to prevent the arrival of incoming aggressive ions. In both mechanism routes, a high resistance (R) between the anodes and cathodes prevent aggressive ions arriving at the interface and the rate of the corrosion process is largely determined by the through film ionic resistivity of the coating system. Overall, the resistance whether measured by a DC technique as R_{dc}, by EIS as $R_{0,1Hz}$, or by electrochemical noise resistance as R_n, is believed to provide a quantitative measure for the extent to which the coating is protecting the underlying metal. However, the influence of e.g. binder type on coating resistance is not fully understood, therefore the above statement on coating resistance is not fully justified.

4.2 Generation of electrochemical noise from bare and coated metal

A metal in contact with any solution generates both current noise and potential or voltage noise, due to small random fluctuations which arise stochastically during electrochemical processes [8]. The voltage noise can be easily measured with respect to a stable reference electrode. In the case of current noise, it is ~~necessary~~important to simulate the situation within the metal by using two identical but separated metal specimens and measuring the current in between using a zero resistance amperemeter (ZRA). The current noise is the level of fluctuation on the current value. It has been theoretically shown [5] that the standard deviation of the voltage values, i.e. voltage noise, divided by the standard deviation of the current values, i.e. current noise, gives rise to a parameter called electrochemical noise resistance ~~noise~~ (R_n). In the case of bare metal, R_n has been shown to be equivalent to the resistance obtained using the linear ~~polarisation~~polarization technique.

When a coating is present, R_n can be attenuated in the case of current noise and amplified in the case of potential noise, through the coating. The level of both potential and current noise that is sensed by the instrument can be converted to R_n. The largest value of resistance R_n is very likely the resistance of the coating system to the movement of ions (R_{paint}) and this in turn has a direct bearing on the rate of corrosion, as described in 4.1. An exception would be when the coating has broken down and corrosion is occurring, and in that case a low measured value will be indicative of failure.

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