

Electro-chemical Impedance Spectrometry testing of **Ecospeed®**
English translation

Principle

The technique of Electro-chemical Impedance Spectrometry (EIS) is effected by applying an Alternating Current (ac) to the sample material. The electro-chemical effect of that material is then measured whilst remaining immersed in solution. The measurement of this voltage will provide information on the impedance of this material. The difference in voltage (and thus impedance) is equal to the chemical changes within that material.

By choosing a very low amplitude, the return signal for all frequencies will be virtually linear. Thus the measured voltage will be sinusoidal at the same frequency as the input, but with a distinct phase shift. The degree of the phase shift depends on the characteristics of the sample material. This test procedure allows study of the anticipated electro-chemical reaction (via measurement of the impedance changes) over a wide range of frequencies.

The impedance changes are analyzed by comparison checking against similar impedance as that of the sample material through an electrical circuit made up of resistances, capacitances and inductances. From the measurement of the changes in impedances, it can be seen that the impedance spectrum of the sample can be accurately determined. The equivalent electrical network simulates a metal covered with a coating, where R1 and C1 characterize the coating and R2 and C2 characterize the corrosion reaction.

Set up

The exposure area for all of the experiments is no greater than 33 cm². The ac is applied and then its potential (of the study material) is measured utilizing a highly accurate and calibrated Calomel electrode. The ac signal, (measured by the frequency response analyzer) allows the impedance of the sample material to be accurately determined via calculation.

Samples

In order to produce an accurate and un-biased result, all samples were designated with anonymous numbers and not by their commercial names. Experiments were conducted on four different samples (CO54, CC65, M9, M15) all samples were steel from various ships hulls coated with different coatings.

CO54	metal coated with a normal glass flake	
CC65	metal coated with an epoxy material	
M9	metal coated with a polyester material	(Ecospeed)
M15	metal coated with a polyester material	(Ecospeed coated)

By impedance measurements of a system metal/organic coating/electrolyte, the coating offers itself as a capacitor (C1 and a resistance R1). These two component effectively act as a dielectric between the two conductors. The value of the capacitance is determined using the formula for a flat plate capacitor. ($C_v = \frac{\epsilon \cdot A}{d}$)

The size order of C1 is a few nano-Farads per/cm². The resistance behavior depends on the porosity of the layer and is a measurement of chlorine ions, which have permeated the material of the study samples.

With a newly applied layer, immersed in a corrosive solution, only the capacitance of the layer will be measured. The electrical resistance of a totally intact coating is extremely high, thus initially the capacitance is the correct measurement to study. However this will also fall and will go below the value that can be accurately measured by the apparatus. Due to the extremely low value of the paint capacitance the electrolyte resistance can only be measured at high frequencies (at this point the capacitance is outside the range of the apparatus). The changes in behavior of the capacitance manifests itself as a phase shift of 90° and results in a perfectly linear reaction between log (Z) EIS (Electrochemical Impedance Spectrometry) and log (F). If the coating has been badly applied or has skin defects, this will become immediately apparent within the impedance spectrum. The values of C1 and R1 are directly proportional to the increase of capacitance in the electrolyte (H₂O with O₂, Cl) once immersed. The capacitance increases because the porosity of the coating

increases (as in CO54 and CC65). Thus it can be seen that for a small amount of water absorption, capacitance (C1) will increase proportionally. The resistance decreases until measurable values are obtained due to the increasing porosity of the coating and therefore also the amount of conductive paths to the substrate; initiating the corrosion process. This process can be fully observed and proven with EIS(Electro-chemical Impedance Spectrometry).

Note: C1 is the capacity of the coating layer and increases by diffusion (absorption) of water. R1 is the resistance of the coating and it will decrease by diffusion of a solution into the layer. CT R2 and C2 act as second time constant and they show the reaction (corrosion) of the substrate.

Report on coating porosity

A & B

Samples M9 and M15 (subsequently known commercially as Ecospeed®)

The resistance is so high that the equipment continues to measure 'infinity' at all times throughout the experiment. The capacity of C1 does not vary at all. The coating can be considered as intact and totally impervious to seawater.

C

Sample CO54 (A product from a well known and established international paint manufacturer)

The resistance R1 decreases drastically over a short period of time. The capacity C1 varies slightly towards the positive side. There is some infusion of seawater into the coating, but no reaction with the metal is yet present. The coating is porous and the absorption rate will increase over time, reach the steel and thus corrosion will occur.

D

Sample CC65 (A product from a well known and established international paint manufacturer)

The capacity C1 varies slightly towards the positive potential. The resistance R1 decreases rapidly over a short period of time. After one week a visible reaction of the metal surface to seawater was seen where the protection capacity of the coating was lost. (Shown by C2 and R2)

Conclusion

After a period of one month of immersion in seawater we can conclude that study materials CC65 and CO54 provide insufficient protection against aggressive corrosive elements such as salt water or acidic solutions. The steel of sample CC65 had actually started to corrode. Whilst the water had penetrated the coating on sample CO54, there are no signs of corrosion on the actual substrate. However, this would not be the case after a longer period of time as the absorption rate of this sample was increasing with time. Our long and intricate experience with impedance measurements informs us that samples M9 and M15 are of an extremely high quality. There is absolutely no diffusion of watery solutions (in which we also conclude the very aggressive chlorine ions) in the coating whatsoever.

References: Free University of Brussels: **Professor J. Vereecken**
Department of Metallurgy, Electro-chemistry and Material Engineering
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