Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens

Part 4: Examples of spectra of polymer-coated specimens (ISO 16773-4:2009)

ICS 87.040

British Standards

National foreword

This British Standard is the UK implementation of EN ISO 16773-4:2009.

The UK participation in its preparation was entrusted to Technical Committee STI/10, Test methods for paints.

A list of organizations represented on this committee can be obtained on request to its secretary.

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 November 2009.

ISBN 978 0 580 63955 5

Amendments/corrigenda issued since publication

Date	Comments

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN ISO 16773-4

May 2009

ICS 87.040

English Version

Paints and varnishes - Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens - Part 4: Examples of spectra of polymer-coated specimens (ISO 16773-4:2009)

Peintures et vernis - Spectroscopie d'impédance électrochimique (SIE) sur des éprouvettes revêtues de haute impédance - Partie 4: Exemples de spectres d'éprouvettes revêtues de polymères (ISO 16773-4:2009)

Beschichtungsstoffe - Elektrochemische Impedanzspektroskopie (EIS) von beschichteten Proben mit hoher Impedanz - Teil 4: Beispiele für Spektren von polymerbeschichteten Proben (ISO 16773-4:2009)

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Ref. No. EN ISO 16773-4:2009: E

Foreword

This document (EN ISO 16773-4:2009) has been prepared by Technical Committee ISO/TC 35 "Paints and varnishes" in collaboration with Technical Committee CEN/TC 139 “Paints and varnishes” the secretariat of which is held by DIN.

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Foreword

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ISO 16773-4 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

ISO 16773 consists of the following parts, under the general title *Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens*:

— *Part 1: Terms and definitions*

— *Part 2: Collection of data*

— *Part 3: Processing and analysis of data from dummy cells*

— *Part 4: Examples of spectra of polymer-coated specimens*

Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens —

Part 4: Examples of spectra of polymer-coated specimens

1 Scope

This part of ISO 16773 gives some typical examples of impedance spectra of high-impedance coated metal samples. Some guidance on interpretation of such spectra is also given.

2 Theoretical background

2.1 Basic considerations

A basic introduction to electrochemical impedance spectroscopy, especially in connection with corrosion, is given in ASTM G 106.

It is not intended to limit the interpretation of EIS measurements to the models given below. Other interpretations may be valid. The choice of the proper model requires other experimental and theoretical considerations to be taken into account.

2.2 Examples of models

2.2.1 Purely capacitive coating

A metal covered with an undamaged coating generally has a very high impedance. The equivalent circuit for such a situation is shown in Figure 1.

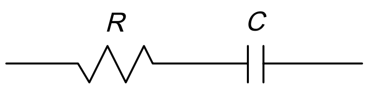
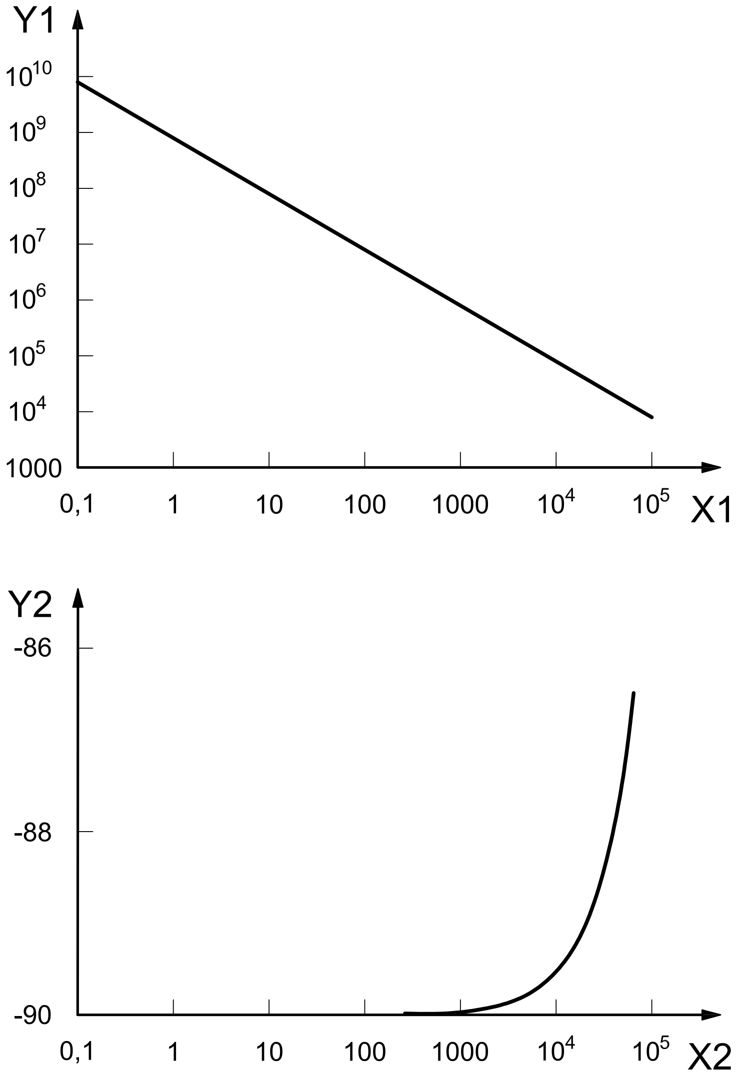


Figure 1 — Equivalent circuit for a purely capacitive coating

The model includes a resistor representing the resistance R of the solution and, connected in series with it, a capacitor representing the capacitance C of the coating.

In practice, the resistance of a perfect coating can often not be seen in the given frequency range. Any deviation from the graph given in the Bode plot in Figure 2 indicates either a modified model or the input limits of the impedance device (see Annex A of ISO 16773-2:2007).



Key

X_1 frequency f, in Hz
Y_1 impedance Z, in Ω
X_2 frequency f, in Hz
Y_2 phase angle φ, in degrees

Figure 2 — Bode plot for a perfect coating

2.2.2 Randles equivalent circuit

The Randles equivalent circuit includes the resistance of the solution R_S, the capacitance of the coating C_C and the ohmic resistance of the coating R_C, as shown in Figure 3.

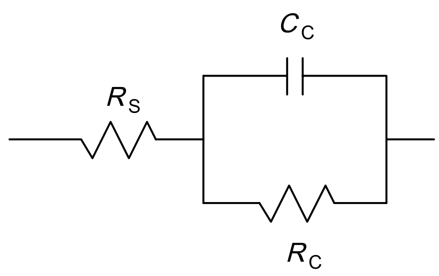
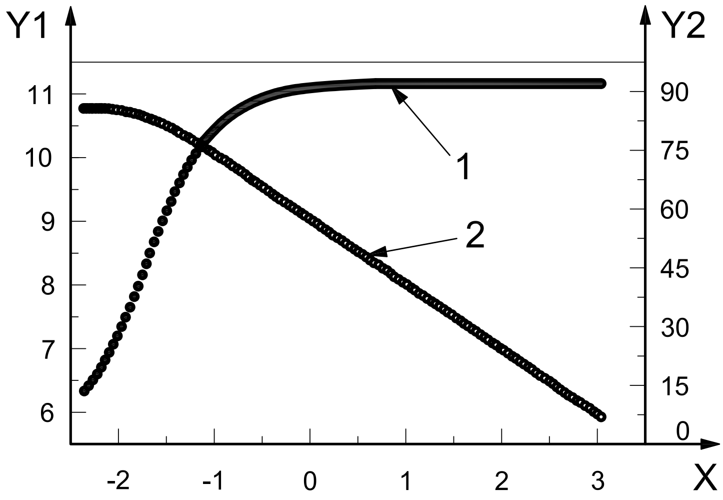


Figure 3 — Randles equivalent circuit

The Bode plot for a Randles equivalent circuit is shown in Figure 4.



Key

X log$f$ (f in Hz)

Y_1 log$|Z|$ (Z in Ω)

Y_2 $|\varphi|$ (degrees)

1 phase angle φ

2 impedance Z

Figure 4 — Bode plot for a Randles equivalent circuit

2.2.3 Extended Randles equivalent circuit

Quite often, fitting experimental data to the model shown in Figure 3 results in systematic errors. In such cases, the literature shows that it is possible to use the model shown in Figure 5 to obtain a better fit.

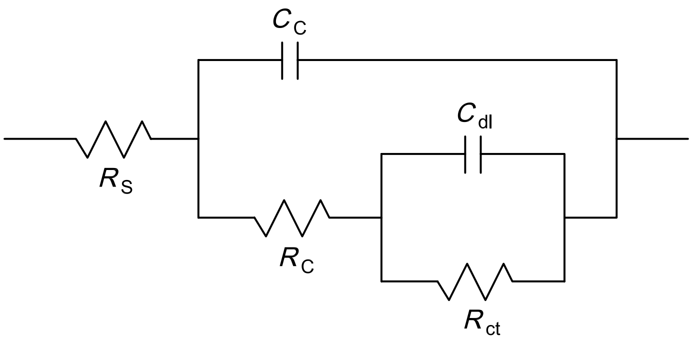
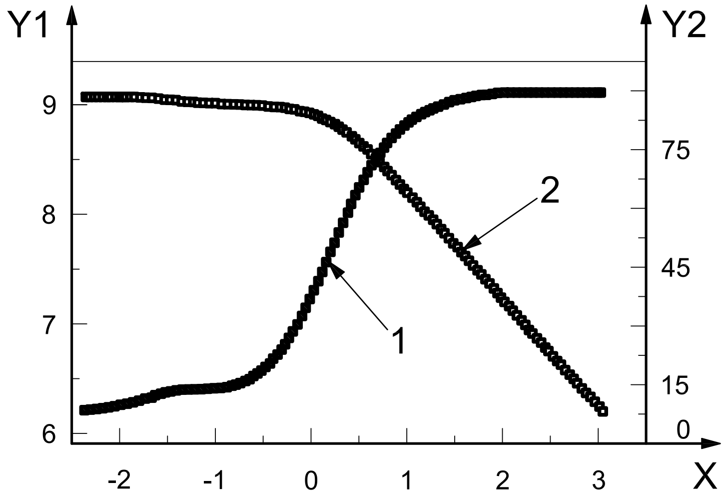


Figure 5 — Extended Randles equivalent circuit

NOTE This model is not necessarily the most appropriate and other models are not excluded.

In the case of high-impedance coatings, the charge-transfer resistance R_{ct} and double-layer capacitance C_{dl} in the extended Randles circuit correspond to properties of the coating rather than to corrosion processes in the underlying metal.

The Bode plot shown in Figure 6 clearly shows the additional contribution of these two added elements. Again, the Bode plot does not go high enough in frequency to measure the solution resistance. In practice this is not a problem, because the solution resistance is a property of the test solution and the test cell geometry, not a property of the coating.



Key

X log$f$ (f in Hz)

Y_1 log|Z| (Z in Ω)

Y_2 |φ| (degrees)

1 phase angle φ

2 impedance Z

Figure 6 — Bode plot for an extended Randles equivalent circuit

Annex A
(informative)

Examples

A.1 General

This annex contains a collection of spectra obtained from materials described briefly in the relevant clause. The examples were obtained from various laboratories using a range of different equipment and materials.

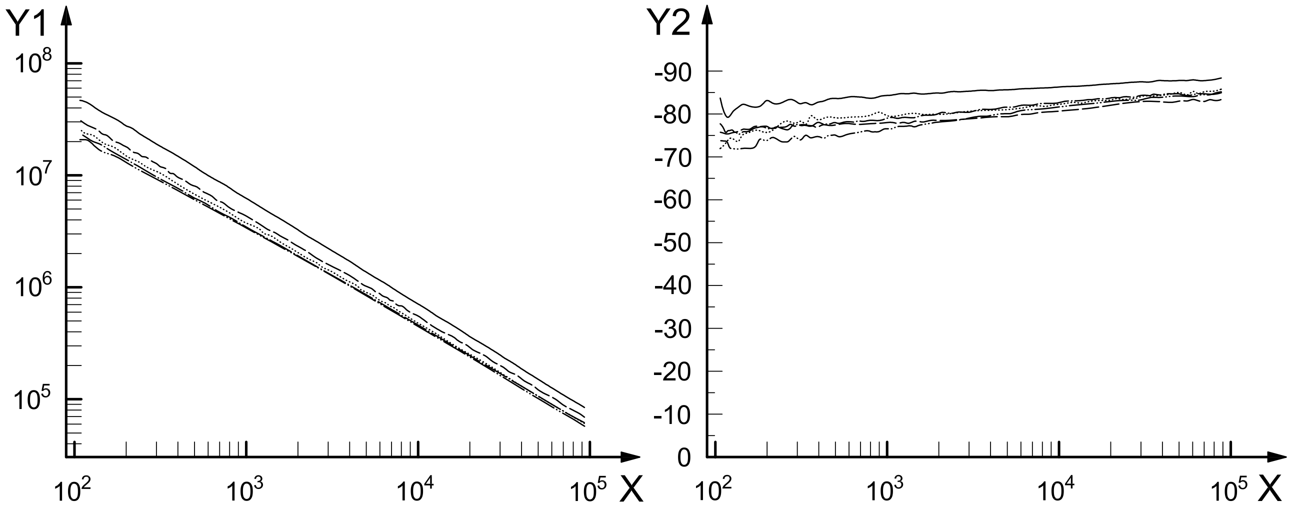
This collection of spectra is not intended to imply that all the materials mentioned necessarily give spectra similar to those shown or that the spectra given here are free of experimental errors. The collection does not represent the complete range of coating materials.

A.2 Example 1

This example shows how a smaller than usual thickness of a high-build coating material can be used to investigate the influence of immersion time on EIS measurements.

Details: Two-component epoxy coating, typically used for (maritime) steel constructions, above and below the water level. Airless spray application. DFT (dry film thickness) recommended by the manufacturer: 1 000 µm to 3 000 µm.

Measurements were performed on one coat on steel, DFT 200 µm, on an area of 10 cm^2 at 21 °C using concentrated artificial rainwater (see Annex B). A vertical three-electrode set-up, with a saturated Ag/AgCl reference electrode, was used. Spectra were recorded after defined periods of immersion.



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in Ω·cm^2

Y_2 phase angle φ, in degrees

———— t = 0 h

– – – – t = 2 h

.... t = 24 h

—·—·— t = 168 h

—··—··— t = 503 h

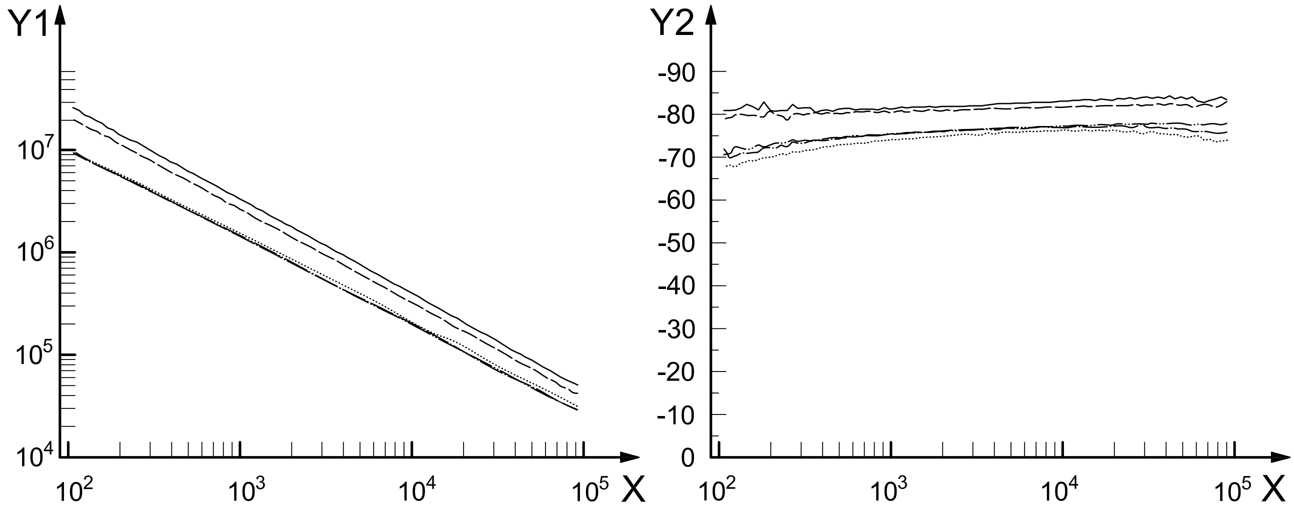
Figure A.1 — Bode plot for a high-build coating material under immersion conditions

A.3 Example 2

This example concerns a surface-tolerant coating material which does not require the same amount of surface pretreatment as that in Example 1. Usually, derusting with mechanical tools is used rather than grit blasting.

Details: Surface-tolerant two-component epoxy coating for (maritime) steel constructions, above and below the water level. Can be applied on corroded steel, grit-blasted steel and old (undamaged) paint coatings. Application by airless spray, conventional spray, brushing or rolling. DFT recommended by the manufacturer: 100 µm to 200 µm.

Measurements were performed on one coat on steel, DFT 250 µm, on an area of 10 cm^2 at 21 °C using concentrated artificial rainwater (see Annex B). A vertical three-electrode set-up, with a saturated Ag/AgCl reference electrode, was used. Spectra were recorded after defined periods of immersion.



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in Ω·cm^2

Y_2 phase angle φ, in degrees

——— t = 0 h

– – – – t = 2 h

·········· t = 24 h

—·—·— t = 168 h

—··—··— t = 502 h

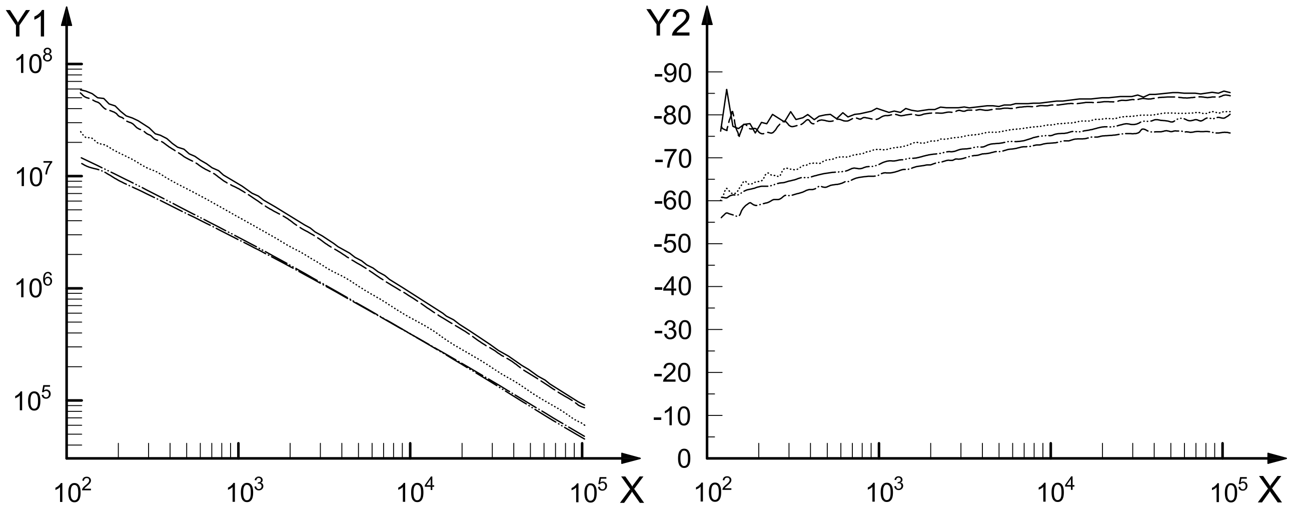
Figure A.2 — Bode plot for a surface-tolerant coating material under immersion conditions

A.4 Example 3

This example represents a high-build, solvent-free coating material with high abrasion resistance, applied as a single coat.

Details: Solvent-free two-component epoxy coating for grit-blasted metals, concrete and fibreglass in aggressive environments. High abrasion resistance and corrosion protection. Application by airless spray or brush. DFT recommended by the manufacturer: 500 µm to 1 000 µm as one coat.

Measurements were performed on one coat on steel, DFT 230 µm, on an area of 10 cm^2 at 21 °C using concentrated artificial rainwater (see Annex B). A vertical three-electrode set-up, with a saturated Ag/AgCl reference electrode, was used. Spectra were recorded after defined periods of immersion.



Key

X frequency *f*, in Hz

Y_1 modulus of the impedance $|Z|$, in $\Omega \cdot cm^2$

Y_2 phase angle φ, in degrees

——— t = 0 h

– – – – t = 2 h

·········· t = 24 h

—·—·— t = 168 h

—··—··— t = 505 h

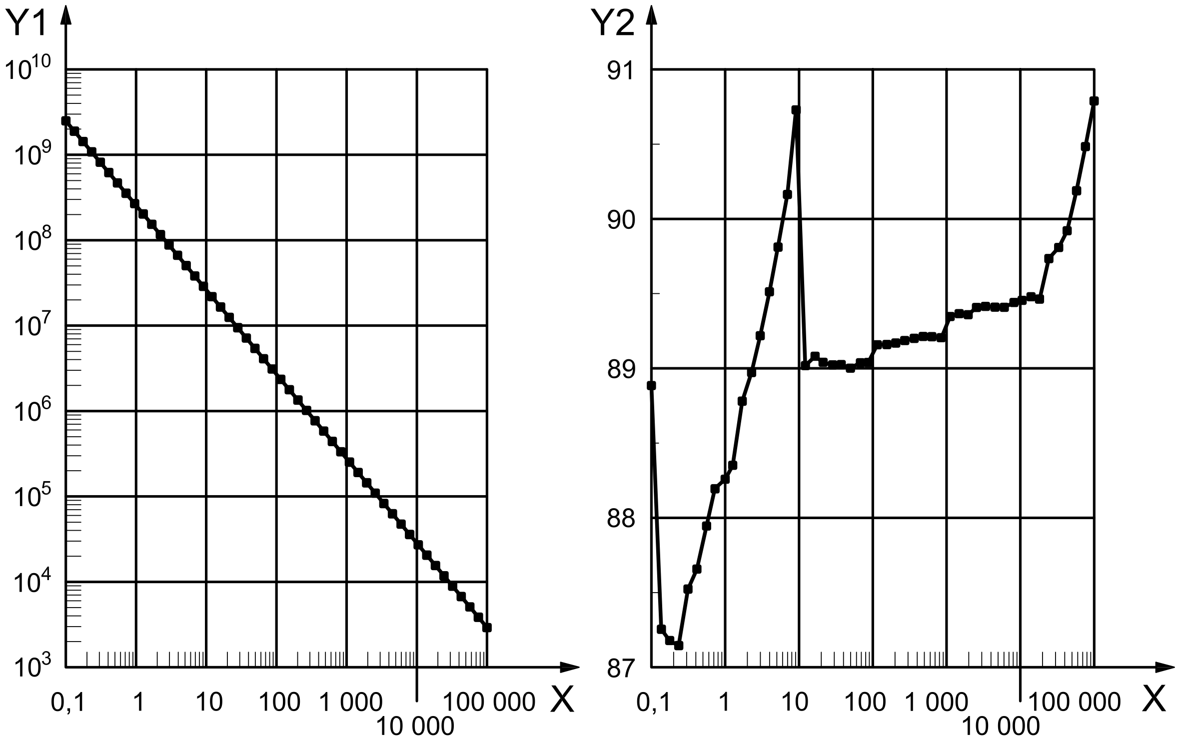
Figure A.3 — Bode plot for a solvent-free coating material under immersion conditions

A.5 Example 4

This example concerns a representative powder coating applied by spray on aluminium. The quite large measurement area of 16,5 cm^2 allowed a three-electrode set-up to be used, but the open-circuit potential was not delivered with the spectra. The discontinuities in the phase-angle plot are due to potentiostat current range changes combined with the low capacitance of the system being examined, indicating incorrect setting of the measurement device.

Details: Polyester powder coating material sprayed on chromatized aluminium frames as a single coat with a DFT of (93 ± 3) µm. No ageing.

Measurements were performed at 25 °C in 3 g/l Na_2SO_4 solution on an area of 16,5 cm^2. A three-electrode set-up, with an Ag/AgCl reference electrode, in a vertical plastic tube was used.



Key

X frequency f, in Hz

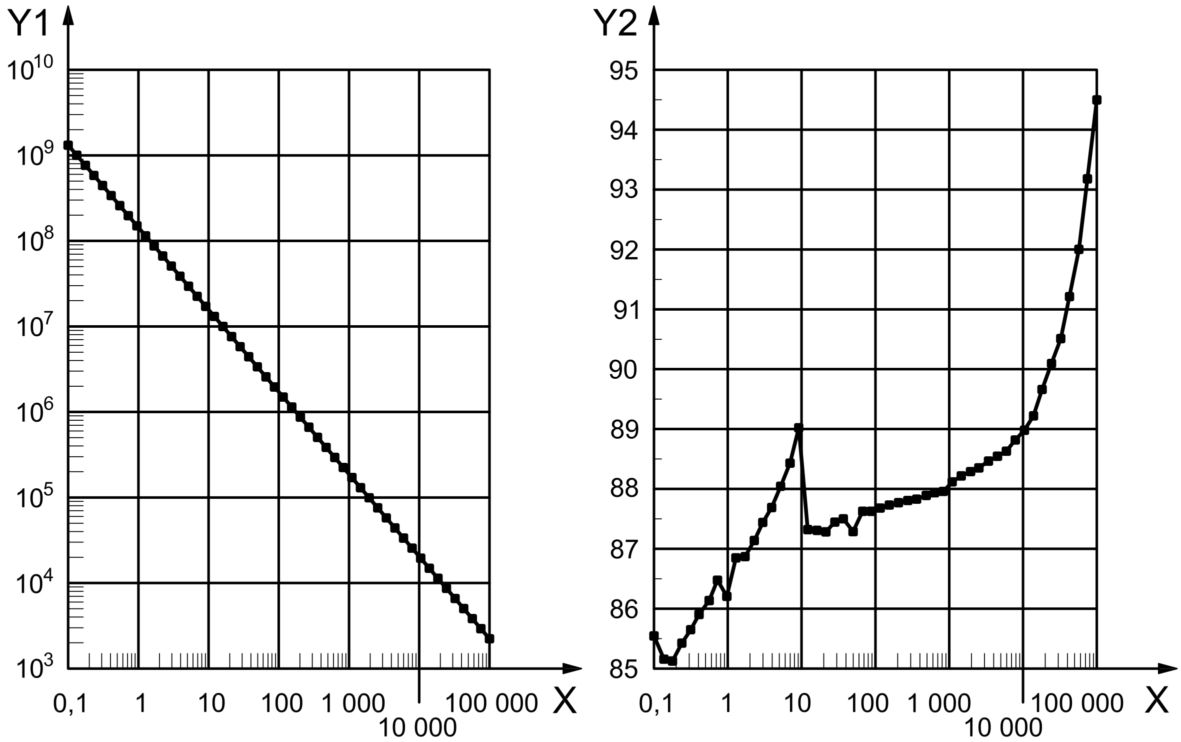
Y_1 modulus of the impedance $|Z|$, in Ω·cm^2

Y_2 phase angle φ, in degrees

Figure A.4 — Bode plot for a powder coating before ageing

The spectra shown in Figure A.5 were obtained after ageing through eight thermal cycles, the coating remaining continuously in contact with the electrolyte.

One cycle consists of heating from 25 °C to 75 °C in 1 h, holding at 75 °C for 4 h and then cooling to room temperature. The time between each cycle was about 24 h. The temperature during the measurements was 25 °C.



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in $\Omega \cdot cm^2$

Y_2 phase angle φ, in degrees

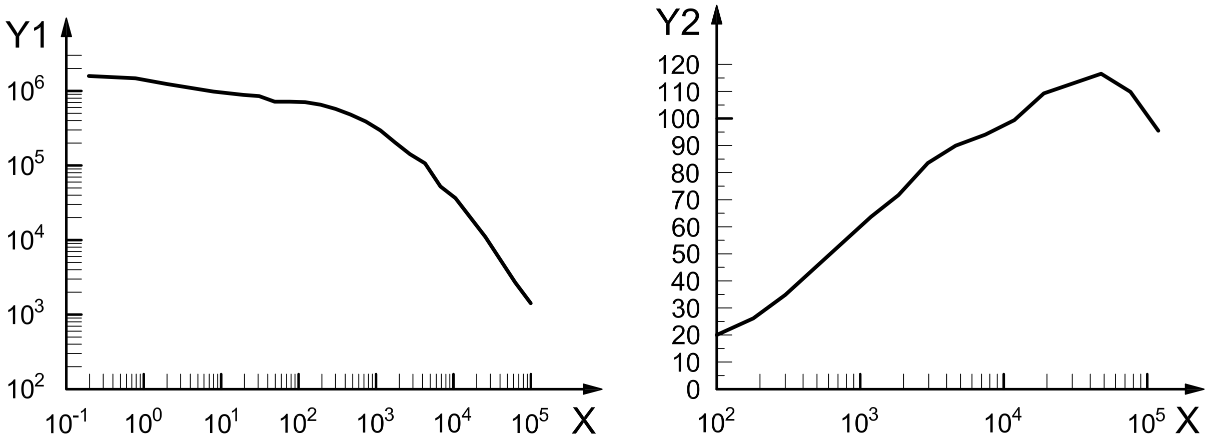
Figure A.5 — Bode plot for a powder coating after ageing

A.6 Example 5

Packaging materials are frequently coated with thin, unpigmented “clear coats”. The spectra of a coating of this type were measured after chemical attack by citric acid and sorbic acid. Such thin coatings do not give high impedance values but they give relatively high capacitance values. The phase angle plot indicates measurement anomalies in the high-frequency range.

Details: Epoxy-phenolic lacquer coating typical of that used for packaging. Two coats applied on tin-plated steel by roller and stoved at 220 °C for 20 min. Total DFT: 7 µm to 8 µm.

Before measurement, the sample was immersed for 2 days at 25 °C in an electrolyte containing 5 g of citric acid per litre and 200 mg of sorbic acid per litre. Measurements were performed on an area of 105 cm^2. A vertical three-electrode set-up, with a calomel reference electrode, was used.



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in $\Omega \cdot cm^2$

Y_2 phase angle φ, in degrees

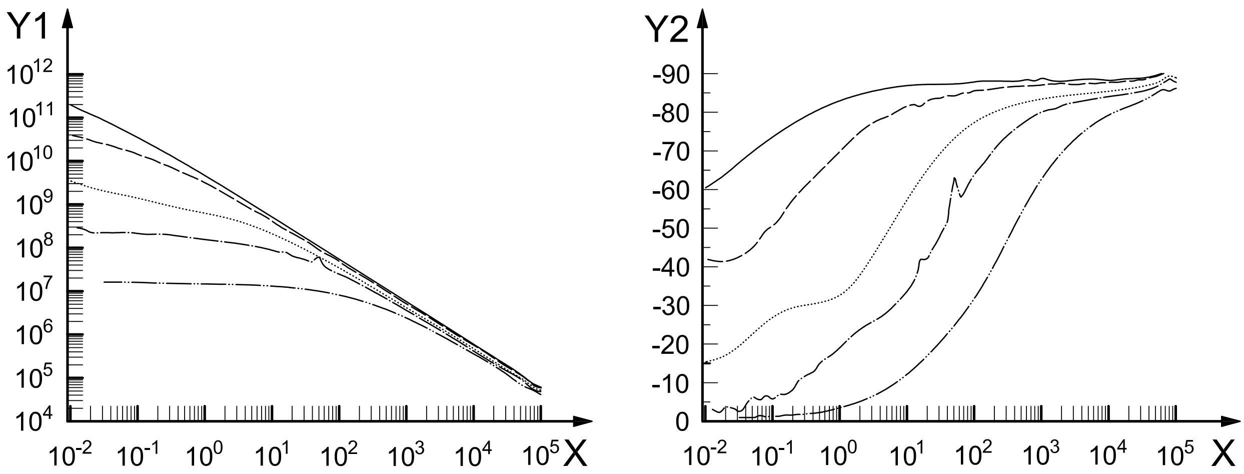
Figure A.6 — Bode plot for a thin lacquer coating, as used in the packaging industry, after chemical ageing

A.7 Example 6

Temperature has an enormous effect on impedance spectra. Figure A.7 shows the temperature dependence of the impedance of a clear coat.

Details: Pure epoxy-vinyl coating without pigments. Same binder as used for marine anti-corrosion primers. Spray application in two coats on sand-blasted steel prepared to surface preparation grade Sa 3 (see ISO 8501-1) (24 h drying between coat 1 and coat 2) followed by one week's curing at 80 °C. Total DFT 170 µm.

The temperature was cycled between 20 °C and 90 °C, each cycle lasting 10 h. Measurements were made at temperatures ranging from 20 °C to 90 °C on an area of 14 cm^2 with the sample immersed in a vertical position in a saline solution containing 30 g of NaCl per litre, using a two-electrode set-up with a Pt counter-electrode.



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in Ω·cm^2

Y_2 phase angle φ, in degrees

———— T = 20 °C

– – – – T = 40 °C

·········· T = 50 °C

—·—·— T = 72 °C

—··—··— T = 89 °C

Figure A.7 — Bode plot for an epoxy coating at various temperatures

A.8 Example 7

This example concerns a combined coating system with a high-solids primer and a waterborne topcoat after immersion for 0,5 h, 300 h and 1 200 h (see Figures A.8, A.9 and A.10). This coating system gives very similar spectra to those given by the dummy cells used in ISO 16773-3.

Details: Coating system made up of high-solids epoxy-polyamine primer and waterborne acrylic urethane topcoat. Used for repair and maintenance of structures, mainly if good surface preparation is not possible.

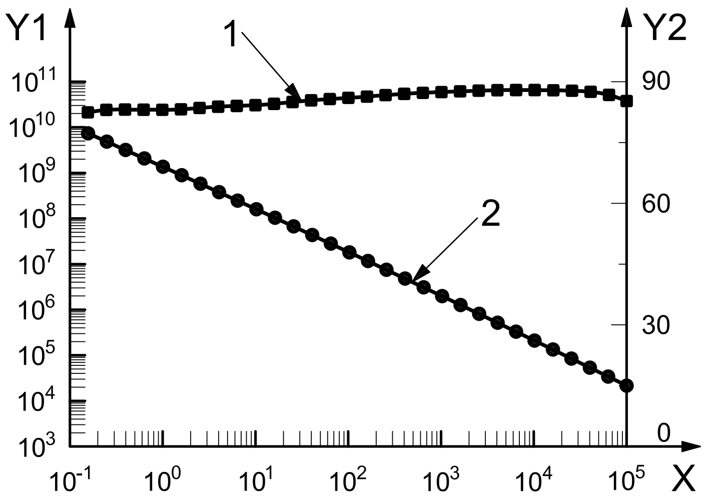
— Primer: 82 % solids content, pigmented with aluminium.

— Topcoat: 82 % solids content, pigmented with micaceous iron oxide.

Two coats applied by brush (primer 70 µm, topcoat 50 µm) on freshly galvanized steel (degreased prior to painting).

Measurements were performed at ambient temperature (about 23 °C) in a 0,5 mol/l Na_2SO_4 solution on an area of 13 cm^2.

A horizontal cell design with a three-electrode set-up, including a saturated calomel electrode (SCE), was used. The electrochemical impedance measurements were performed at the open-circuit potential. The frequency range scanned was from 10^5 Hz down to 10^{-2} Hz and the signal amplitude was 20 mV rms.



Key

X frequency f, in Hz

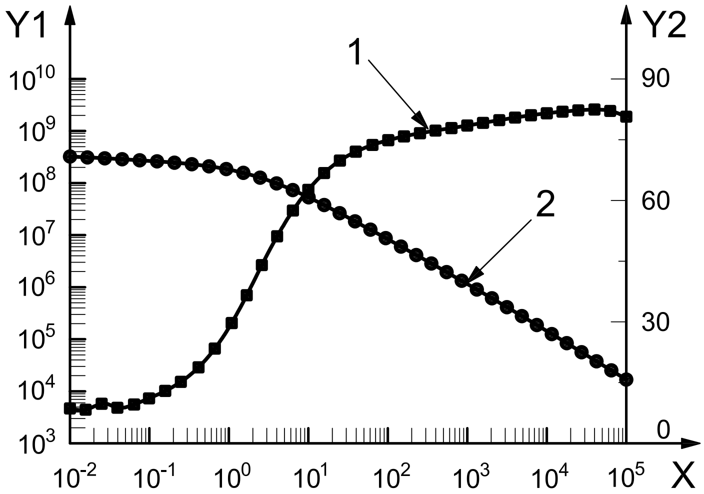
Y_1 modulus of the impedance $|Z|$, in $\Omega \cdot cm^2$

Y_2 phase angle φ, in degrees

1 phase angle φ

2 impedance Z

Figure A.8 — Bode plot for primer/topcoat system in Example 7 after 0,5 h immersion



Key

X frequency f, in Hz

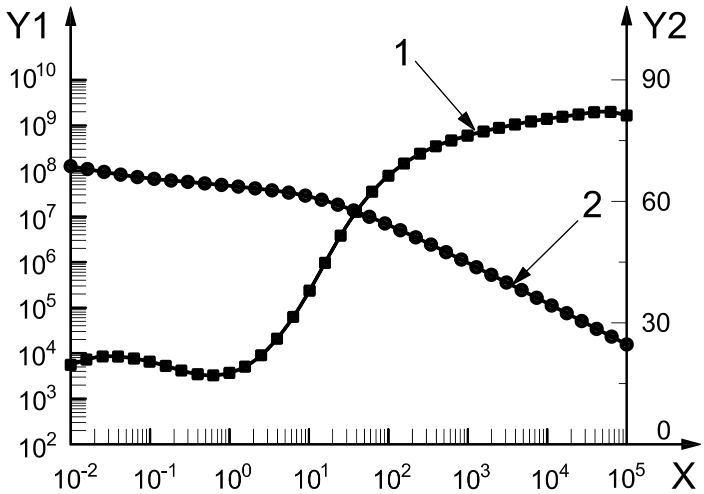
Y_1 modulus of the impedance $|Z|$, in $\Omega \cdot cm^2$

Y_2 phase angle φ, in degrees

1 phase angle φ

2 impedance Z

Figure A.9 — Bode plot for primer/topcoat system in Example 7 after 300 h immersion



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in $\Omega \cdot cm^2$

Y_2 phase angle φ, in degrees

1 phase angle φ

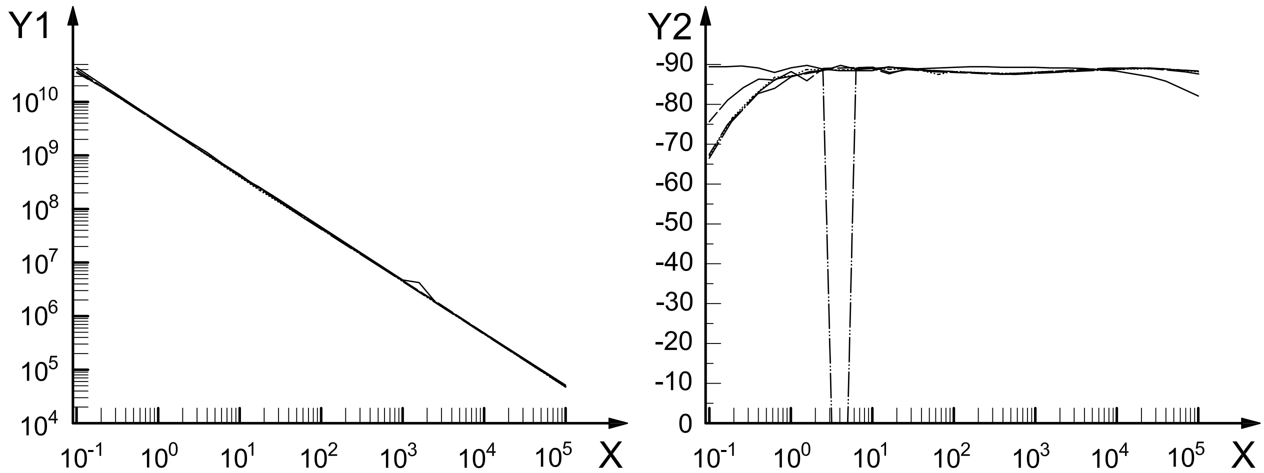
2 impedance Z

Figure A.10 — Bode plot for primer/topcoat system in Example 7 after 1 200 h immersion

A.9 Example 8

Measurements on free films are not as easy to make as those on attached films because the preparation of the free film can cause defects which might be misinterpreted. This example concerns a free film measured at elevated temperatures in deionized water.

Details: A non-commercial epoxy-amine clear coat of DGEBA-MCDEA [diglycidyl ether of bisphenol A cured with 4,4′-methylene-bis(3-chloro-2,6-diethylaniline)] prepared by moulding. Thickness 2 mm. Measurements performed on an area of 12,5 cm^2 of the film in a double cell, with the film in between, during exposure to deionized water at 100 °C. Horizontal cell design with two-electrode set-up.



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in Ω·cm^2

Y_2 phase angle φ, in degrees

——— t = 0 h

– – – – t = 10 h

·········· t = 20 h

—·—·— t = 40 h

—··—··— t = 70 h

Figure A.11 — Bode plot for a free film

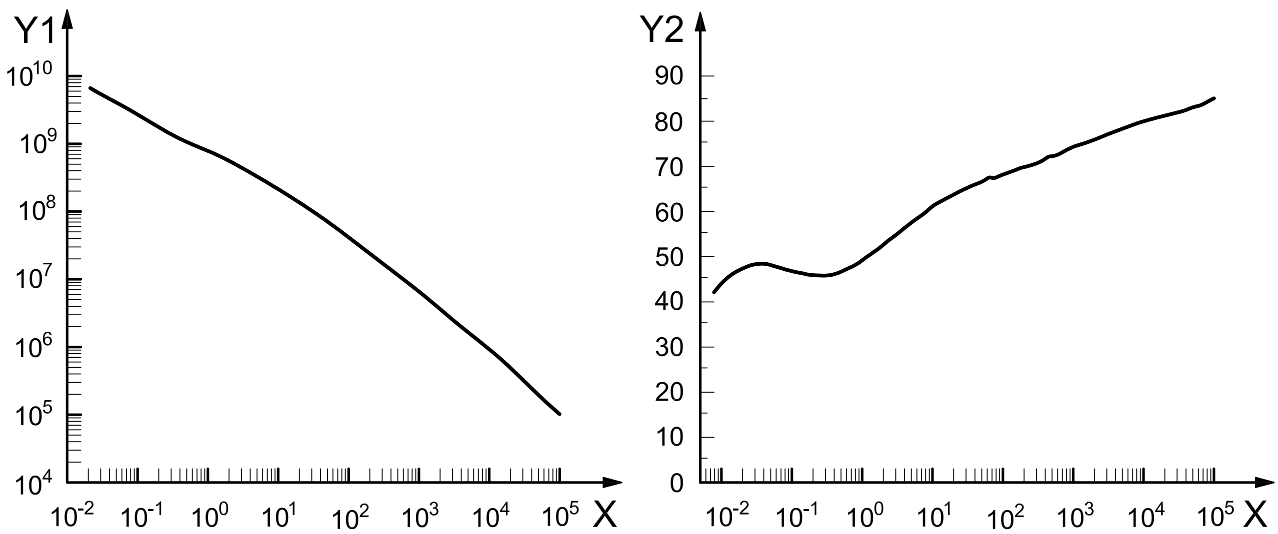
A.10 Example 9

Marine coatings are often associated with cathodic protection which can lead to cathodic disbonding. It is therefore necessary to test coatings for compatibility with cathodic protection over a long period so that any degradation of the coating can be detected.

This example concerns a double coat of epoxy-vinyl containing calcium ferrite pigment. It was sprayed onto sand-blasted steel prepared to surface preparation grade Sa 2½ (see ISO 8501-1). The total DFT was 250 µm.

The coating was aged for 556 days in artificial seawater (prepared in accordance with ASTM D 1141) at a cathodic potential of – 1,53 V (SCE) using an Mg-alloy anode.

The measurements were performed on an area of 64 cm^2 at – 1 V and ambient temperature in artificial seawater using an SCE and a platinized Ti counter-electrode. The frequency range scanned was from 100 kHz down to 10 mHz with a 10 mV rms perturbation-signal amplitude (see ISO 16773-1).



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in Ω·cm^2

Y_2 phase angle φ, in degrees

Figure A.12 — Bode plot for a marine coating aged under immersion conditions with cathodic protection

Annex B
(informative)

Composition of concentrated artificial rain water

The composition of the concentrated artificial rain water given in Table B.1 corresponds to rain at Dutch coastal sites concentrated 50 times.

Table B.1 — Composition of concentrated artificial rain water

Chemical	Concentration mg/l
Ammonium chloride	7,23
Ammonium nitrate	0,85
Ammonium sulfate	15,14
Calcium nitrate	17,71
Iron chloride	0,99
Potassium nitrate	3,03
Copper sulfate	0,05
Magnesium chloride	12,71
Sodium bicarbonate	0,17
Sodium chloride	28,03
Sodium fluoride	0,31
Sodium sulfate	19,20
Nickel chloride	0,02
Nitric acid	3,74

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[1] ISO 8501-1, *Preparation of steel substrates before application of paints and related products — Visual assessment of surface cleanliness — Part 1: Rust grades and preparation grades of uncoated steel substrates and of steel substrates after overall removal of previous coatings*

[2] ISO 16773-1, *Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens — Part 1: Terms and definitions*

[3] ISO 16773-2:2007, *Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens — Part 2: Collection of data*

[4] ISO 16773-3, *Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens — Part 3: Processing and analysis of data from dummy cells*

[5] ASTM G 106, *Standard Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements*

[6] ASTM D 1141, *Standard Practice for the Preparation of Substitute Ocean Water*

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