

# Effect of environmental temperature variations on protective properties of organic coatings

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## Abstract

Natural conditions are characterised by variability of temperature. Therefore, the effect of temperature changes on the durability of coating systems on steel was investigated. Using the impedance spectroscopy technique changes of coating parameters have been determined of coatings submitted to thermal treatment typical for natural exposure, including temperatures below 0 °C. A negative influence of temperature variations on coating barrier properties has been observed.

## 1. Introduction

Organic coatings have been used for a long time to protect metals against corrosion in atmospheric conditions. The fundamental property of natural environment conditions is variability, mainly connected with sun operation and meteorological phenomena, Fig. 1 [1]. Coating systems on metal undergo cyclic thermal loading connected with temperature fluctuations in the 24 -hour cycle (Fig. 1) and seasonal cycle (Fig. 2) [1]. This aspect does not reflect in condition of accelerated weathering or formulation of new coating products. Usually, testing of coating system is carried out at constant temperature or at two levels of temperature in cyclic tests [2,3]. The damaging effects of extreme weather condition are obvious; but constant damage caused by everyday weather conditions which has a cumulative and synergistic effect that in the long run is even more destructive. This approach is based on the concept that degradation is cumulative and that failure is therefore considered to be the result of the accumulation of damage with time [4,5].

Environmental temperature changes affect coated metal in two ways: by inducing thermal stresses in the system and by changing the mechanical properties of the viscoelastic coating. Thermal stresses resulting from mismatch of the coefficients of thermal expansion of the coating and substrate (e.g., for an epoxide resin from  $45$  to  $65 \times 10^{-6} \text{ deg}^{-1}$ , for alkyds  $55$ - $60 \times 10^{-6} \text{ deg}^{-1}$  [6] and for the metal base: steel  $16 \times 10^{-6} \text{ deg}^{-1}$ , zinc  $23 \times 10^{-6} \text{ deg}^{-1}$ , aluminium  $23 \times 10^{-6} \text{ deg}$  [7]). Temperature determines both the stress level and the rate of viscoelastic response of the coating to stress level. In the initial period of exposure the coating material, due to its properties, has the ability to respond to stress by molecular rearrangement. Temperature- and time dependent behaviour of polymeric material systems subjected to thermal changes is known [8,9]. Below glass transition process ( $T_g$ ) in polymer amorphous materials spontaneous changes occur. It is a result of non-equilibrium state, which slowly attempts to reach equilibrium. These processes are ascribed to conformational changes of the polymer backbone and are related to physical ageing. As a result the density, elastic modulus of the polymer increases, impact strength, fracture energy decreases; creep and stress relaxation rates decrease [10]. A number of phenomenological theories have been proposed to describe the time-dependent changes observed in the physical properties [8,10,11]. Loss of

coating ability to relax of formed stress is the result of physical ageing and chemical degradation. In effect mechanical damage to the coating occurs (microcracks) and its delamination from the base [12-14]. Subsequently, during cyclic temperature changes propagation of defects and delamination on the metal/coating interface occur. In this way protective properties of the coating connected with existence of the barrier and adhesion to the substrate deteriorate [15]. Therefore, the lifetime of the coating system in a significant degree is connected with capability to resist the forming and diminishing of stress without mechanical damage to the coating and the coating/metal interface.

On another hand a need exists to rapidly and simply predict the service life of organic coatings on metal [3,16,17]. Successful prediction of long-term weather performance of organic coatings in different conditions requires identification of the critical environmental variables that control degradation rate and determination of the distribution of the values in the given place. For polymeric materials temperature and humidity play an important role [18,19]. These environmental parameters are strongly related to sunlight intensity, Fig. 1. On this way temperature changes may be an indicator of sun load, which is the reason of photo-oxidation also [19-21].

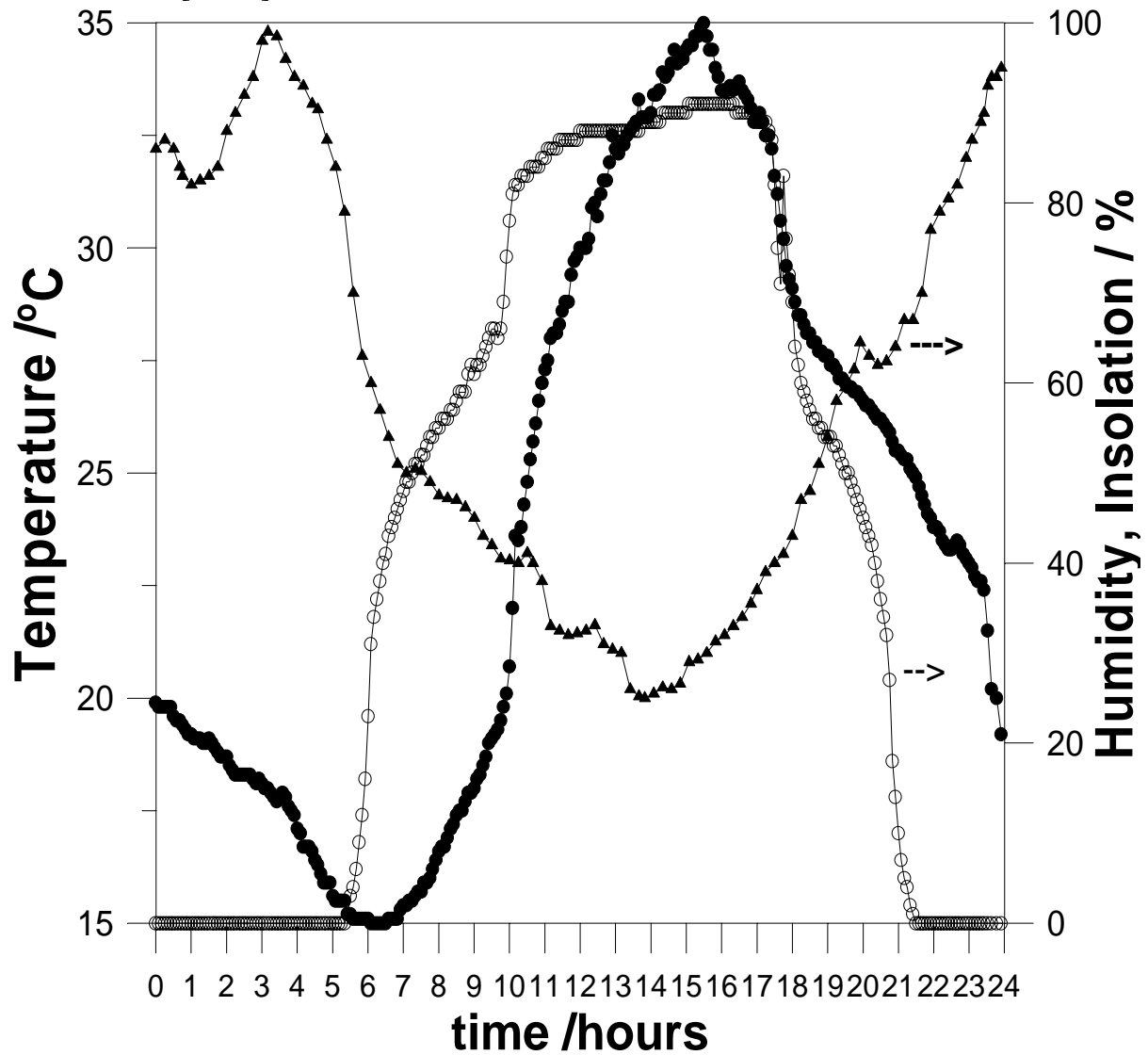


Fig. 1. Examples of temperature (●), humidity (▲) and insolation (○) changes during 24 hours, Warsaw, Poland, 15 May 2000 [1].

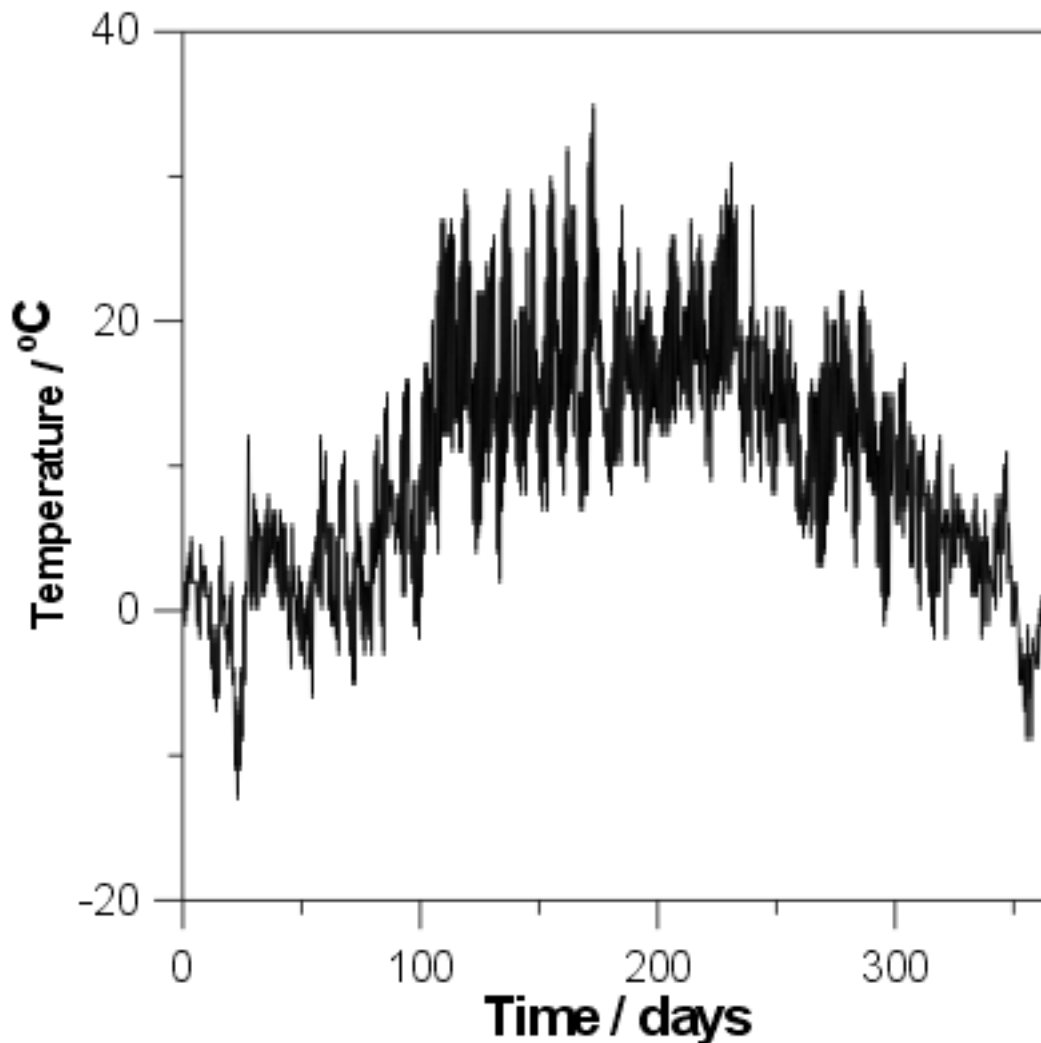


Fig. 2. Temperature changes during the year 2000 in Warsaw, Poland [1].

## 2. Experimental

The different types of commercially available paints were studied:

solvent-borne polyvinyl coating system, 4 layers,  $380 (\pm 40) \mu\text{m}$  thick (supplied by Polish Paint Factory Malchem),

solvent-borne epoxy coating system, 4 layers,  $280 (\pm 25) \mu\text{m}$  thick (supplied by Sigma Coatings Poland),

water-borne acrylic system, 2 layers,  $60 \mu\text{m}$  thick (supplied by Akzo Nobiles Poland).

All systems were applied on mild steel panels according to producer guidelines. The coated panels were stored at room temperature for about 2 months before experiments. Then PVC cylinders were attached on the coating surface using a two-component epoxy adhesive. During the experiment the cylinder was filled with a 3% NaCl aqueous solution in the case of solvent-borne paints and  $0.3\text{g NaCl} + 0.7\text{g Na}_2\text{SO}_4 / \text{dm}^3$  in the case of water-borne paint.

The exposed area was  $81 \text{ cm}^2$  in the case of solvent-borne paints and  $38 \text{ cm}^2$  in the case of water-borne paint. The electrochemical measurements were made in two-electrode system. A platinum mesh with low impedance was used as the counter electrode. The impedance

measurements were performed using a Schlumberger 1255 Frequency Response Analyser and 'home made' high impedance buffer. Measurement and acquisition of data were controlled by a computer. Impedance spectra were determined in the full frequency range from 1 MHz to some mHz. Ten points per decade were measured above 0.1 Hz and 5 points per decade below 0.1 Hz. In order to reduce measurement time narrower frequency range, 100kHz - 1kHz, was used also. A perturbation signal was applied of an amplitude in the 10 - 60 mV range, depending on the impedance of the investigated system. The obtained spectra were analysed using the equivalent circuit presented in Fig. 3. Usually, the high-frequency part of the spectrum was analysed, describing the barrier properties of the coating.

Temperature programme was controlled by computerised 'home made' set-up.

The freezing-thawing cycle was realised between +20 °C (4 hours) and -20 °C (20 hours).

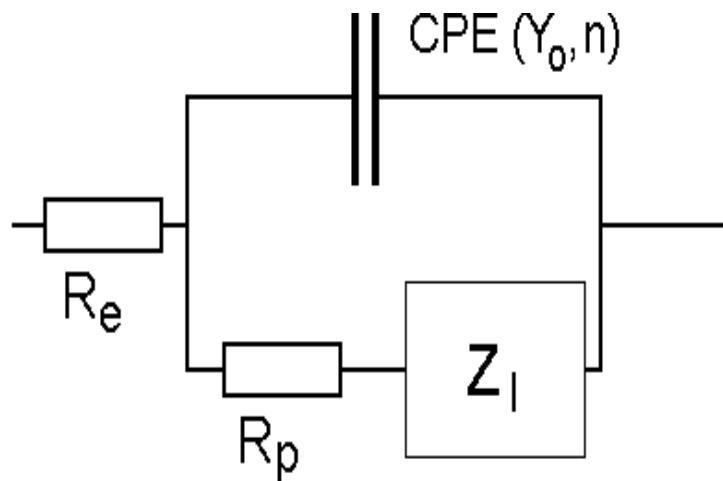


Fig. 3. Electrical equivalent circuit used for analysis of impedance data.  $R_e$  electrolyte resistance,  $R_p$  electrolyte resistance in coating pores, CPE ( $Y_0, n$ ) Constant Phase Element modelling capacitive properties of the coating,  $Z_1$  impedance of the electrolyte/metal interface at the bottom of pores.

### 3. Results and discussion

Two cases were considered for coated sample exposure:

- a) temperature changes above 0 °C,
- b) temperature changes when minimum temperature is below 0 °C and maximum temperature is above 0 °C.

In the second case additional phenomenon may take place that is freezing-thawing of water within coating. In the case of freezing, ice crystals start forming and growing cause damages because of greater volume of ice than water [26]. There are some parts of the world where the temperature cycles around 0 °C occur frequent. Therefore the influence of freezing/thawing cycles should be considered a very detrimental factor and consider separately.

#### 3.1. Results of samples exposed above 0 °C

The first experiments were done in order to isolate the contribution of temperature changes on coating degradation in the presence of water solution. The thick epoxy coating system on steel were exposed in immersion in 3% NaCl and temperature according to course showed on Fig. 4. The sample was kept at 20 °C in 3%NaCl during two weeks before thermal treatment to obtain stable state of investigated system. Impedance measurements were carried out in the frequency range 100kHz - 1kHz every 2 minutes during dynamically temperature

changes. Using software programme [27] coating electrical parameters were determined on the basis of obtained impedance spectra. In Fig.5 relations have been presented in the Arrhenius system, i.e., in the function of  $1/T$ , where  $T$  is the temperature in the Kelvin scale. It results from Fig. 5 that parameter changes of coating are in reality irreversible. Every cycle cause very small shift of coating parameters characteristic for coating degradation. A spiral mode of parameter changes is observed.

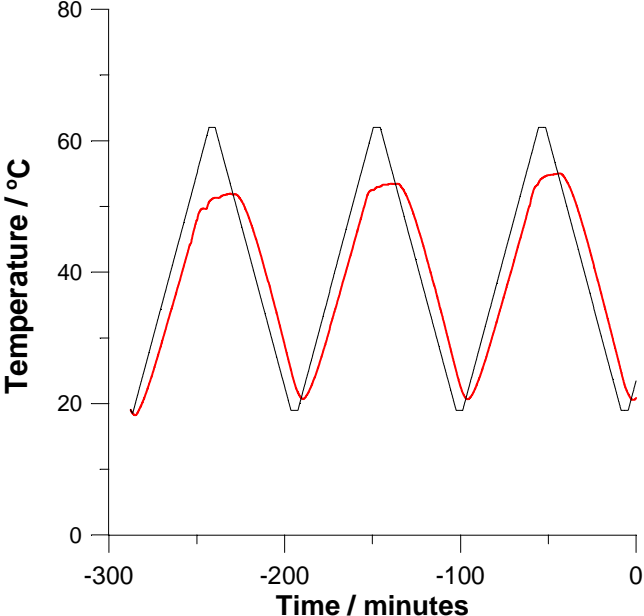
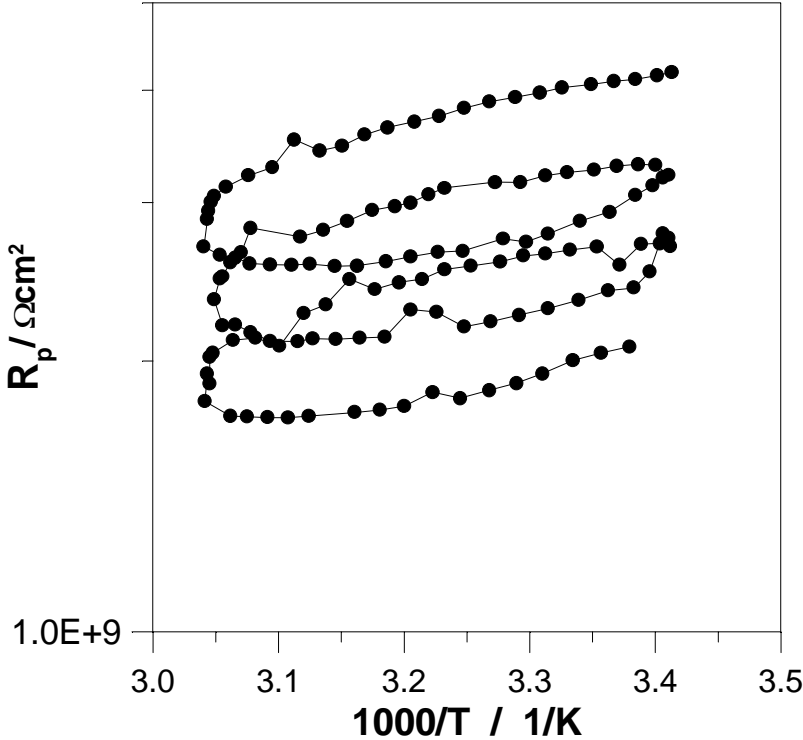


Fig. 4. Course of temperature changes of samples with an epoxy coating programmed (thin line) and measured on sample (thick line).



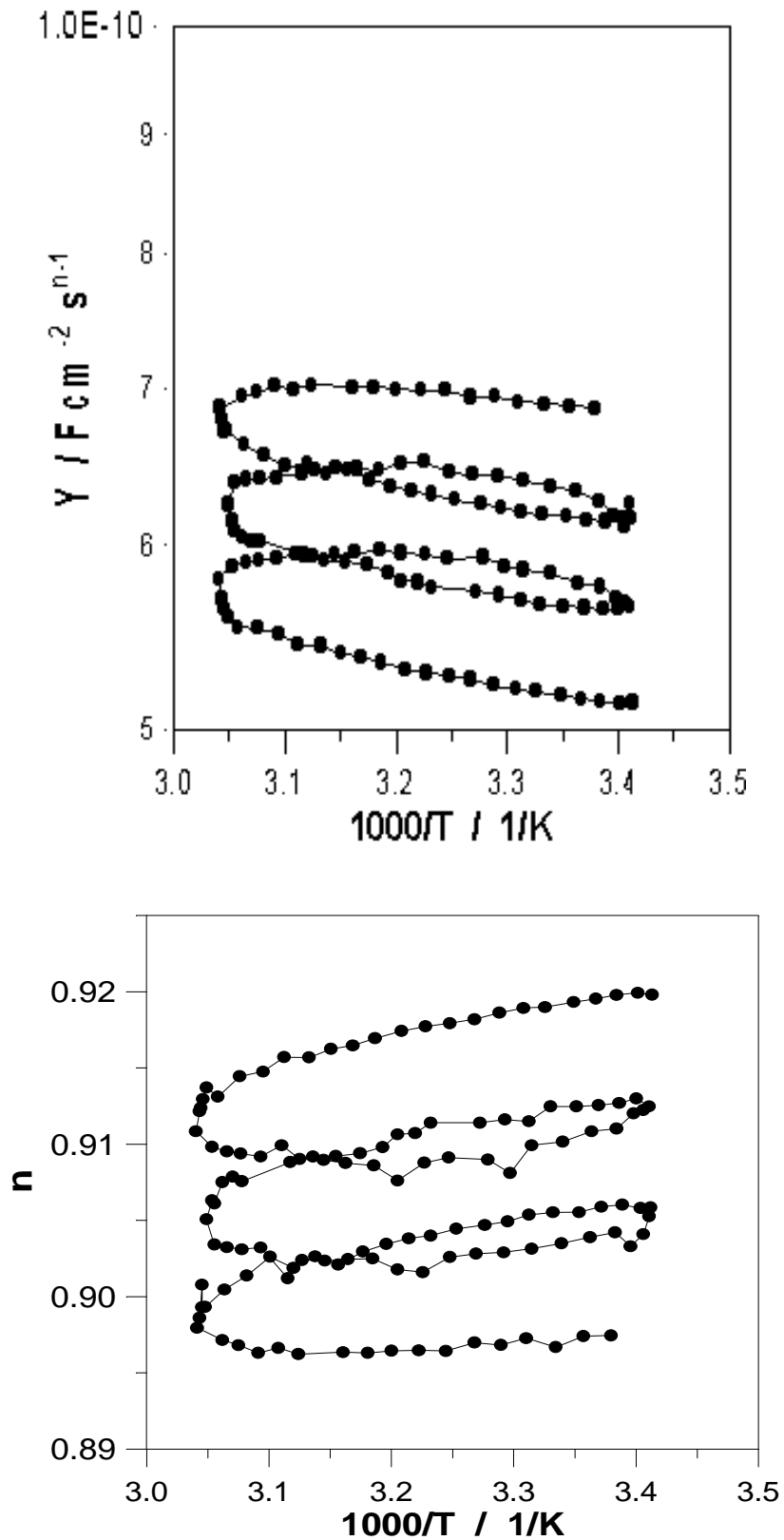


Fig. 5. Changes of coating resistance  $R_p$  (a) and CPE parameters  $Y_o$ , (b) and  $n$  (c) for epoxy coating on steel in the function of  $1/T$ , where  $T$  is the temperature in the Kelvin scale. An arrow indicates a starting point.

It is known that amorphous solids change their physical properties with time as a result of structural relaxation (physical ageing). At a molecular level this phenomenon is connected with spontaneous changes of atomic structure to a lower-energy state. Temperature cycling accelerates self-diffusion and additionally accumulates changes of physical property [28] because the response of diffusion or relaxation rate on temperature is non-linear. This effect results in memory of past cycling [17,29].

The aim of the next part was to isolate the contribution of temperature changes on coating degradation in the presence and the absence of water solution and compare results with exposure in natural conditions. Samples of a water-borne acrylic coating selected on the basis of initial electric parameters were subjected to exposure in condition of an urban-maritime (Gdansk, Poland) climate for a period of 6 months, from the beginning of April to the end of September, 2000. On the basis of regional meteorological data the mean lowest and mean highest temperatures were determined for each month, Tab. 1. Samples taken for laboratory tests were subjected to thermal treatment in accordance with Fig. 6, performing during one day a programme of temperature changes characteristic for one month, hence 30 or 31 shocks of parameters in accordance with Tab. 1. During remaining time samples were stored at 20 °C. Simultaneously, a coating was submitted to thermal interaction, immersed in solution simulating atmospheric conditions: 0.3g NaCl + 0.7g Na<sub>2</sub>SO<sub>4</sub> /dm<sup>3</sup>, and a coating without presence of solution, as presented schematically in Fig. 7 as two extreme cases of exposure in natural conditions: constant presence of water and exposure with no precipitation. Impedance spectrum measurements were performed before and after natural and laboratory exposure. Coatings before natural exposure and a coating subjected to thermal treatment without presence of electrolyte were immersed in solution for 48 hours before performing impedance measurements. In Fig. 8 spectra are presented before exposure (a) and after exposure (b). As can be seen in Fig. 8 the spectrum of a coating exposed in natural conditions takes a similar form and magnitude to that of an impedance spectrum of samples subjected to thermal treatment in the laboratory. Also impedance measurements were performed of immersed samples at constant temperature during the period of performing thermal treatment. In this case relatively small changes were stated, Fig. 9. On the basis of obtained data one may conclude that the degradation mechanism in natural condition and the laboratory with the use of variable temperatures has a similar mechanism.

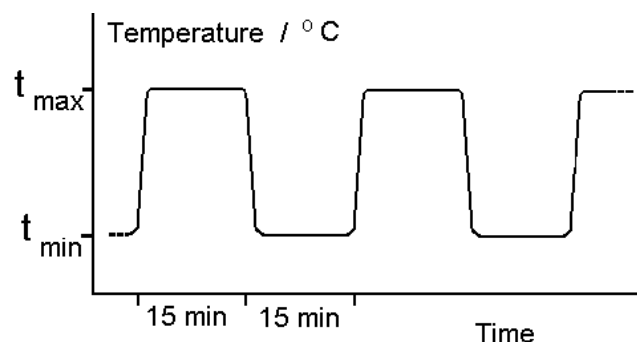


Fig. 6. Course of temperature changes of samples with an acrylic coating.

Tab. 1. Mean maximum and mean minimum temperatures for each month of exposition

Month	April	May	June	July	August	September
$t_{\min}$ [°C]	8	10	13	13	14	9
$t_{\max}$ [°C]	18	21	23	21	23	16

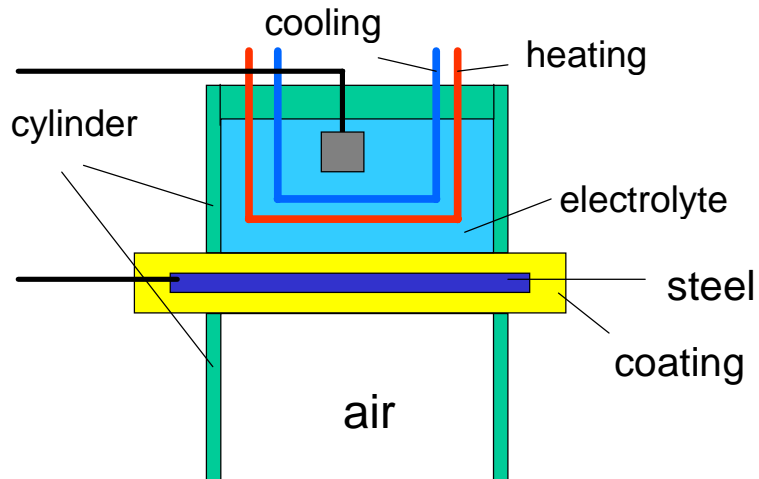


Fig. 7. Experimental cell for simultaneous realisation of thermal treatment of coated sample in immersion in  $0.7 \text{ g Na}_2\text{SO}_4 + 0.3 \text{ g NaCl} / \text{dm}^3$  and with no immersion.

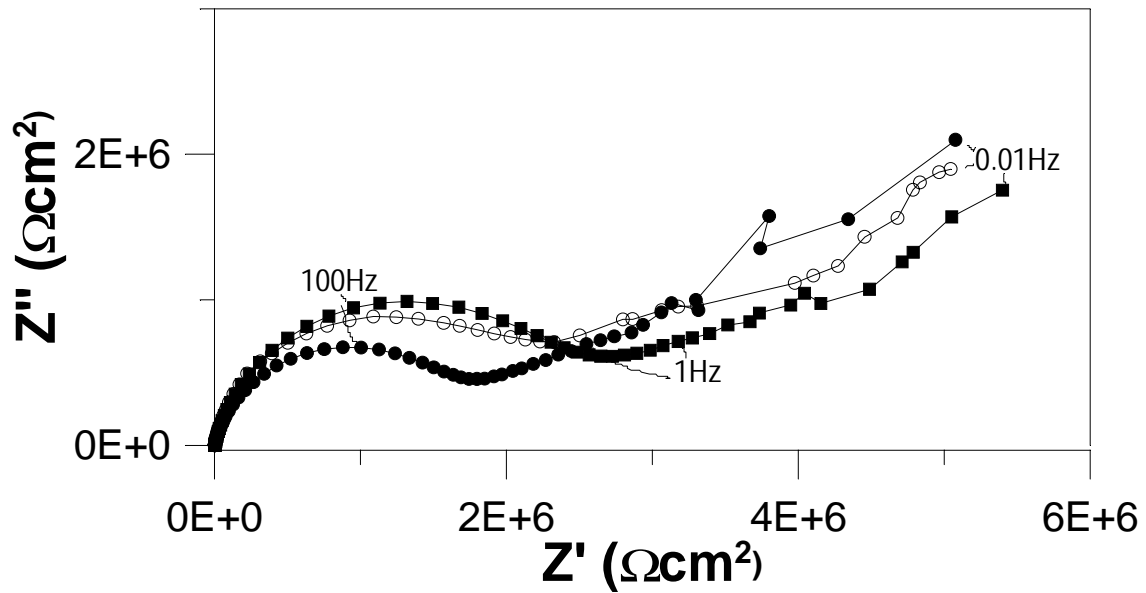


Fig. 8. Impedance spectra of acrylic coatings before exposure (a) and after 6 months atmospheric exposure (o), after thermal treatment in immersion in  $0.7 \text{ g Na}_2\text{SO}_4 + 0.3 \text{ g NaCl} / \text{dm}^3$  (■) and with no immersion (●) (b).

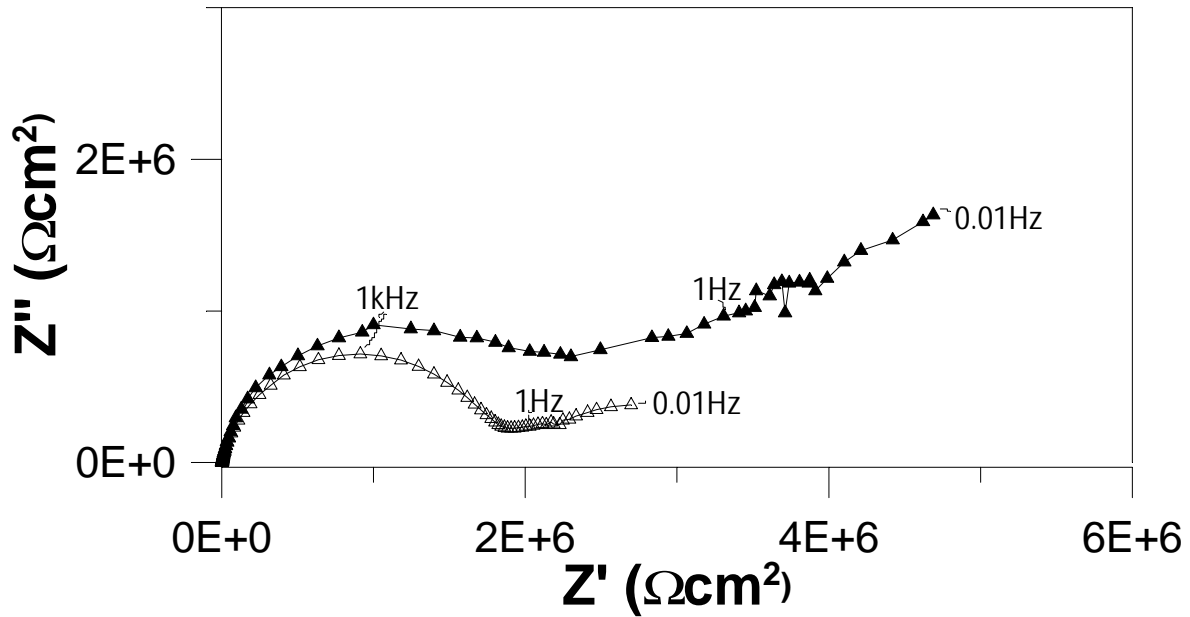


Fig. 9. Impedance spectra of acrylic coatings exposed at constant temperature, 20 °C, before exposure (▲) and after exposure (△).

### 3.2. Results of samples exposed below 0 °C

It is known that three kinds of water, that is bulk-like water, freezable pore (bound) water and non-freezable pore water, are characterised in organic coatings [30]. In every polymer, the freezable water content is lower than the total water content. Non-freezable water interacts strongly with the polymer lowering glass transition temperature ( $T_g$ ). Coating degradation connected with the freezing/thawing cycles are attributed to the freezable water. Ice crystals occupy a greater volume than water. This causes coating damages. In order to study the freezing-thawing resistance of the coatings their impedance spectra were measured before exposure and after each freezing-thawing cycle. The study was made using a polyvinyl system on steel. One half of samples were immersed in 3% NaCl at constant temperature of 20 °C during the whole testing. The second half of samples, which was intended for freezing-thawing cycles were immersed for 6 days before testing to obtain stable saturated water uptake state. All impedance data were analysed using the equivalent electrical circuit, Fig. 3. Fig. 10 shows the typical dependence of the coating resistance on the number of cycles or the time of exposure. Two periods can be distinguished clearly. The resistance of the both coatings does not change significantly with time for the first period. But after about 20 cycles a continuous decrease of coating resistance is clearly observed. This trend indicates that the coating loses barrier properties. In the case of sample exposed in 3%NaCl without freezing/thawing cycles the coating resistance does not change significantly with exposure time.

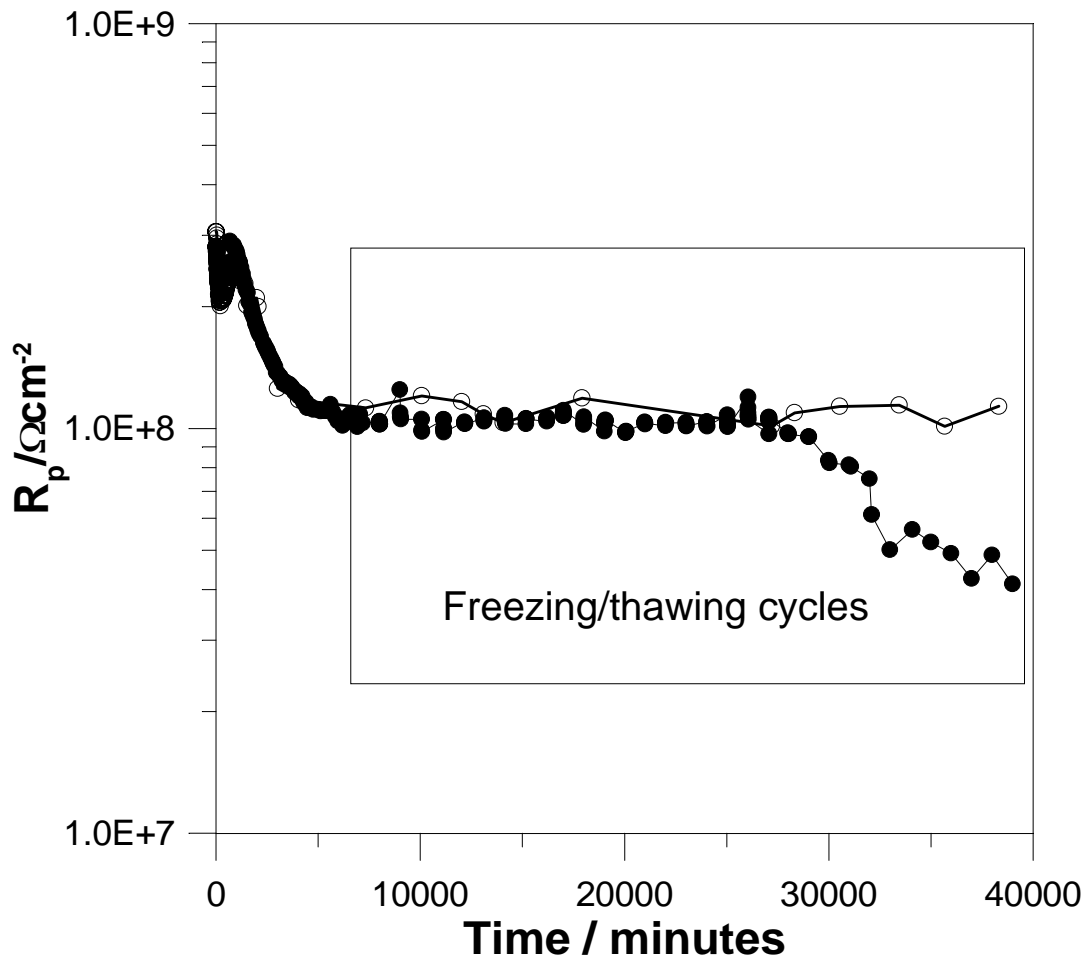


Fig. 10. Typical changes of coating resistance  $R_p$  for polyvinyl coating system on steel for samples immersed in 3% NaCl at constant temperature of 20 °C (o) and exposed to freezing/thawing cycles (•).

#### 4. Conclusions

Natural exposure conditions are characterised by cyclic variability of temperature. Accelerated degradation of coated metal system occurs at cyclic temperature variation in relation to exposure at constant temperature. Accelerated methods for coating testing should include effect of temperature variation characteristic for the future region of coating application. Reduction of difference between thermal expansion coefficients of coating and the substrate metal should improve durability of the coating system in atmospheric conditions.

## 5. References

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