Evaluation of volatile corrosion inhibitors in the presence of condensation water by electrochemical methods

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Abstract. Volatile corrosion inhibitors (VCI) are a means of temporary corrosion protection based on the release of inhibitors from films, papers, diffusers or oil to the gaseous phase. By adsorption on a metal surface, the inhibitors prevent degradation of the primary oxide layer and impede corrosion. Thus, VCI provide corrosion protection for high-quality goods and semi-finished parts made from metals during transportation and storage. The application of oil on the metal surface for corrosion protection and its removal can be avoided. Due to rapid volatilization of the VCI after unpacking, no costly cleaning of parts prior to further use is required. In a new approach for evaluation of the protective effect of VCI, a metallic sample is exposed in a small chamber filled with air alongside a VCI-containing product. The air is humidified and the sample is cooled down under dewpoint, which leads to condensation of humidity and represents corrosive stress. The state of the metallic surface under the condensed water film is characterized by electrochemical methods. The present work demonstrates the evaluation of the anticorrosive effect of various VCI-films on mild steel. In summary, the application-oriented test allows for quick and quantified evaluation of VCI-containing products with a tabletop device.

1. Introduction
The globalized, specialized and liberalized economy of modern times comprises a global flow of commodities. Semi-finished products and high-quality goods are not only transported from manufacturers and customers, but the transport chains also include subcontractors, intermediaries and distributors. The immense flow of goods is reflected by a value of exported goods of 1.4 trillion $ for the German economy in 2017 [1]. According to the commodity index, approx. 57% of these goods, still equaling a worth of 820 billion $, are typically made from or at least include metallic materials. During transportation by land, sea and air, even appropriately packaged commodities may meet harsh conditions in terms of temperature and humidity. Especially for products, which do not face intensive corrosive stress during service and are therefore neither made from corrosion-resistant materials nor adequately protected by permanent coatings, the corrosive stress imposed during transportation may cause severe damage. Also, with regard to long-term storage of such parts temporary protection is required to avoid corrosion damage of the bare metallic surfaces. Temporary corrosion protection is classified in the following categories: (1) application of a temporary coating based on organic solvent, water, oil or wax; (2) use of a desiccant within a packaging, which absorbs water vapor and therefore prevents corrosive stress imposed by humidity; (3) use of volatile corrosion inhibitors (VCI), which are set free from the packaging material itself (films, paper) or from a diffuser placed within a packaging.
The major drawback of temporary coatings is the expense for application of these coatings before shipment/storage and the subsequent removal prior to use. The VCI method does not require any operations on the metallic surfaces, but is able to deliver corrosion protection especially under climatic stress. The mode of action includes:

1. the release of the volatile corrosion inhibitors from the packaging material or from a VCI-containing material placed within the packaging,
2. the diffusion of the inhibitors in the atmosphere within the packaging,
3. the adsorption of the inhibitors on the metallic surface and the interaction of the inhibitors with the primary oxide layer of the metal by:
   3.1 formation of a passivating electrolyte film on the surface,
   3.2 formation of an electrolyte film in which the primary oxide layer is hardly soluble,
   3.3 formation of solid compounds or complexes by a reaction of the inhibitor and the base metal and/or
   3.4 formation of a conversion layer.

When corrosive stress occurs, the degradation of the primary oxide layer is thus impeded and the corrosive attack is slowed down significantly or inhibited completely. The corrosion protection is provided independently of the parts’ geometry, since contact between the part and the VCI material is not mandatory. The costly application and removal of temporary coatings and the disposal of any additionally required cleaner is avoided. After unpacking of the parts, the inhibitors volatilize rapidly. Therefore, no cleaning is required prior to further use. Further information on the VCI method and current developments is given in [2-8].

Appropriate evaluation of VCI-containing products is required both for quality control and for research and development. The testing of VCI-containing products with regard to inhibitor content and the corrosion protection effect is classified in three major categories:

1. chemical analysis
   o of a VCI-containing product
   o of an atmosphere, in which a VCI-containing product was exposed
   o of a metallic surface, which was exposed to an atmosphere alongside a VCI-containing product
2. climatic stress test of a metallic sample in a packaging consisting of or enclosing a VCI-containing material
3. electrochemical measurement of a metal surface in an aqueous solution including VCI or in a solution obtained from elution of a VCI-containing product

The chemical analyses give information on the quality and quantity of inhibitors, which are contained in the product or which are set free to the atmosphere, depending on the test setup. However, the actual corrosion protection ability of the product is not considered and the analyses are rather costly in terms of time, required equipment and expertise. Climatic stress tests focus on the actual corrosion protection effect of VCI under the respective conditions. However, they are prone to errors and deviation when carried out in different institutions or by different workers, since subjective visual assessment of the metallic surface after the test almost always provides the basis for the evaluation of the VCI containing product. Further, alternating climate tests are only fully comparable for metallic samples of equal mass, since the thermodynamic inertia of the sample is the ruling factor for condensation of water on the sample and thus for the corrosive load. While electrochemical measurements may provide quantitative results on inhibition effects, the information obtained with this approach is very often misleading. As a matter of fact, the mode of action of the corrosion inhibition under atmospheric conditions, which apply during service, is substantially different to the mode of action in aqueous solution in a conventional electrochemical cell setup.

The present study focusses on a new test method, which uses electrochemical measurements to characterize the surface state of a metallic sample in a test setup, which replicates the VCI mode of action in a more accurate way. A metallic sample is exposed in a small test chamber. A VCI-containing is also placed in the chamber. After a defined amount of time, during which inhibitors
volatilize from the product, reach the metallic sample and there interact with the primary oxide layer, a corrosive stress is applied by humidifying the atmosphere in the chamber and by actively cooling down the sample below the dew point. Electrochemical measurements are carried out under the film of condensed water. The phenomenological test consequently reflects the VCI mode of action, since it covers the release of the inhibitors from the product, the transport to the metallic surface by diffusion, the interaction with the surface and the ability to impede corrosion under a reproducible and defined climatic stress. With regard to the electrochemical measurements, numerous studies have established correlations between values obtained from direct current (d.c.) or alternating current (a.c.) electrochemical methods and the state of a passive or corroding surface. Polarization of a sample with d.c. voltage or application of a voltage sweep will result in high current densities in case of a high surface activity. In an equilibrium state, this almost certainly indicates corrosion under the considered test conditions (only in non-equilibrium state, high activity may shortly occur during passive film formation). In contrast, current densities will be low in case of a passive (non-corroding) surface state. A.c. methods like electrochemical impedance spectroscopy provide further insights, since they include information on the amplitude ratios of potential and current signals as well as on the phase shift between said signals. By varying the excitation frequency, the behavior of the system can be characterized with regard to different time domains. For corrosion of metals in electrolytes with rather low ion concentration, the system behavior is often capacitive due to the dominating double layer of charge carriers at the metal/electrolyte interface. It has been established that a high resistance against charge transfer across this interface and a low capacitance correlate with a passive sample state, while in case of ongoing corrosion, the resistance against charge transfer across the interface is rather low and the capacitance is rather high [9-12]. Only when considerable amounts of corrosion products are formed and block the surface, the resistance against charge transfer will take rather high values although corrosion occurs.

Hereinafter, the use of the developed test method and apparatus to evaluate a VCI-containing product by an electrochemical measurement under a film of condensed water will be demonstrated. A VCI film is assessed with regard to its ability to protect a mild steel surface against corrosion under climatic stress to prove the suitability of the test for quality inspection as well as research and development of new VCI-containing products.

2. Experimental and materials

2.1. Sample material and test arrangement
Metallic samples with a diameter of 16 mm and a height of approx. 10 mm were made from steel 235JRG. The nominal composition of the material is given in Table 1. Sample preparation included grinding the upper surface of the cylindric samples with SiC-paper (600 grit), rinsing with deionized water, rinsing with ethanol and drying under warm air. Afterwards, the samples were stored in a desiccator for at least 3 days. As a VCI-containing material, a commercially available film was used. The film was made from polyethylene and had a thickness of 100 µm. The composition of the film is not disclosed for reasons of confidentiality.

Table 1. Nominal composition of the sample material S235JRG.

| Element | C | Mn | P | S | Fe |
|---------|---|----|---|---|----|
| Concentration in wt-% | <0.2 | <1.4 | <0.045 | <0.045 | balance |

The test arrangement is schematically shown in Figure 1 and Figure 2. The test apparatus is shown in Figure 3. The test setup consisted of a cylindrical test chamber. The chamber was made from poly(methyl methacrylate) (PMMA-tube) and polyoxymethylene (POM-lid). The volume of the chamber was approx. 4.5 l. The VCI film was brought into the chamber so that both the inside of the cylindric tube and of the lid was covered. The bottom of the chamber consisted of 2 aluminum...
plates, which were insulated thermally and electrically by POM. A separate peltier element was mounted to each of the aluminum plates. One of the plates and the POM formed a reservoir, in which water was injected during the course of the test by a peristaltic pump. By heating of the aluminum plate under the water reservoir via the attached peltier element, the atmosphere in the chamber was humidified. Also, an extruded fin-shaped heatsink was mounted on the aluminum plate. Thus, by cooling of the plate via the peltier element, humidity condensed on the fin-shaped heatsink and the atmosphere in the chamber was dehumidified. On the other aluminum plate, a sample holder was placed, which contained the prepared steel sample. The sample holder consisted of polyamide PA12 and was epoxy-coated. The sample holder had an aperture, under which the grinded surface of the metallic sample was positioned. A ring seal was inserted between said surface and the sample holder and thus the active sample surface was defined. Above the aperture, a platinized titanium mesh was positioned in a distance of approx. 2 mm to the sample surface. The mesh served as counter electrode for the electrochemical measurement. A platinum wire was also positioned above the aperture so that its tip had a distance of approx. 1 mm to the sample surface. The wire served as a pseudo-reference electrode during the measurement. The pseudo-reference electrode was chosen to avoid contamination of the system by the use of conventional reference electrodes containing corrosion-promoting ions like chloride, sulfate or the like. The sample holder was such that the sample was thermally connected to the aluminum plate and thus to the peltier element. By cooling via the peltier element, the sample temperature could be set below the dew point of the atmosphere in the chamber so that humidity condensed on the sample surface. This simulates the condensation of water, which typically occurs during transportation when cold parts are brought into a heated room from the outside or during night/day cycle. Additionally, an auxiliary profile made from extruded, anodized aluminum was placed above the aperture in a distance of approx. 10 mm. The profile was thermally connected to the same aluminum plate as the sample and thus to the peltier element. While humidity condensed on the sample, it would therefore also condense on the auxiliary profile. From there, a small amount of condensed humidity would drop on to the sample. This simulates so-called container sweat, which typically forms during transportation when the whole packaging and its included atmosphere is cooled down from higher to lower temperatures and moisture precipitates. In that case, the contained humidity condenses inside the packaging and drops onto the packaged goods. After the end of the test, the metallic sample was dried outside the chamber under a stream of warm air.

![Figure 1. Principal test arrangement with PMMA cylindrical tube (1), POM lid (2), water reservoir with pump (3), two separate peltier elements mounted below aluminum plates (4), sample holder with sample (5), two fin-shaped aluminum heatsinks (6) and VCI-film (7).](image-url)
2.2. Test regime and electrochemical measurements

The requirements with regard to the test regime were as follows: (1) simulate critical climatic stress imposed on metallic goods during transportation, (2) ensure wetting of sample surface and auxiliary electrodes to allow for electrochemical measurement during some state of the test, (3) impose sufficient stress to significantly corrode the sample in absence of any appropriate VCI material, (4) allow for differentiation of VCI-containing products with regard to their corrosion protection effect, (5) allow for short-term examination of the corrosion protection effect of VCI-containing products (preferably within 1 working day). The test regime as well as the principal layout of the apparatus to realize the test regime, which is disclosed in section 2.1, have been the subject of extensive preliminary investigation.

The principal course of the test with regard to the conditions in the test chamber is shown in Figure 4. At the beginning of the test, the chamber as well as the aluminum plates are at room temperature. In the first stage of the test (2 h), both the peltier elements are kept in passive state, i.e. their temperature is not regulated, water is pumped into the chamber and humidifies the atmosphere. Meanwhile, inhibitors are set free from the VCI-containing product and may diffuse in the chamber and reach the metallic sample surface. In Stage 2, a short corrosive load is applied. The sample in the sample holder
is cooled down 3 K below the dew point for 15 min. A small amount of humidity condenses on the surface. The short duration of the cooling phase is neither sufficient to wet all electrodes nor does additional condensed humidity drop on the sample from the auxiliary aluminum profile, which is thermally connected to the sample. The metallic sample is afterwards heated 5 K above the dew point for 15 min. Meanwhile, the water reservoir is emptied and the corresponding aluminum plate with the fin-shaped heat sink is cooled down to 10 °C so that the air in the chamber is dehumidified to ensure that the small amount of condensed humidity on the metallic sample evaporates quickly and completely. Stage 2 thus simulates a mild corrosive stress by short-time condensation of humidity and subsequent drying and is carried out thrice. In Stage 3 of the test, the peltier elements are in passive state again. Again, water is injected into the reservoir in the chamber and humidifies the atmosphere. Afterwards, stage 4 is entered, during which the main corrosive stress is imposed. Therefore, the aluminum plate below the filled water reservoir is heated to 60 °C, which leads to excessive evaporation and thus oversaturation of the atmosphere in the chamber with humidity. In the same time, the metallic sample and the attached auxiliary aluminum profile are cooled down 7 K below the dew point. This leads to severe condensation both on the metallic sample and the auxiliary profile. After approximately 30 min, condensed humidity on the auxiliary profile starts to drop on to the metallic sample. After approximately 45 min in stage 4, the metallic sample surface as well as the auxiliary electrodes are sufficiently wetted to allow for electrochemical measurements. Because of the heating of the water reservoir, the atmosphere in the chamber is also heated and reaches a temperature of approx. 35 °C. The corrosive stress in this stage originates from the condensation of humidity directly on the sample surface, which is below the dew point, and the condensed water dropping on the surface from the auxiliary fin-shaped profile (cf. container sweat).

In the standard procedure, the test is terminated after approx. 60 min in stage 4. This equals a total test duration of approx. 7 h. The corrosion protection ability of the VCI-containing product is assessed on the basis of the measured polarization resistance and/or impedance at this point of time. The described procedure is used for quality assessment of VCI-containing products. In a variation of the test for research and development purposes, stage 4 is prolonged until the electrochemical measurements indicate corrosion initiation (see section 3.2). The point of time in the test when corrosion initiation is indicated serves as another measure to quantify the corrosion protection ability of VCI-containing products.

Electrochemical measurements were carried out with a workstation IM6 (Zahner, Germany). The use of the platinum wire pseudo-reference electrode did not allow for a simple determination of the electrochemical potential of the sample. However, electrochemical impedance spectroscopy (EIS) and the determination of the polarization resistance of the system by a small-range potential-sweep do not require knowledge of the absolute potential, but are based on the evaluation of the change of current density relative to the change of the potential. EIS was carried out with an amplitude of 5 mV in a 10 Hz – 25 mHz frequency range. 4 frequencies were measured per decade. The impedance value at a particular frequency was averaged from 2 full sine-wave periods for each frequency. For reasons of stability and to avoid sample corrosion during the measurement, the absolute d.c. current flow between sample and counter electrode was kept below 150 nA at any time. The impedance spectra were fitted using Microsoft Excel VBA scripts. Polarization resistance measurements were carried out by applying a polarization of 0–9 mV (scan rate: 1 mV/s) relative to the equilibrium potential against the pseudo-reference electrode (open circuit). The small polarization avoids sample corrosion due to the measurement. In the mentioned potential range, the current-density-potential-behavior is approximately linear, so that the polarization resistance is obtained by determination of the mean inverse slope of the recorded curve in the measured range. By sequentially carrying out EIS and/or polarization resistance measurements, time-resolved information on the sample’s surface state was obtained.
Figure 4. Evolution of relative humidity and temperature in the test chamber and of the sample temperature with respect to the dew point over the course of the test. Additionally, the set temperature for the water reservoir in the chamber is plotted (dashed line: peltier element below the water reservoir is in passive state, i.e. no temperature regulation). Corrosive stress is applied on the sample in test phases 2 and 4, when the sample is cooled below the dew point of the atmosphere in the chamber.

3. Results and discussion

3.1. Electrochemical behavior of the metallic sample in the presence of condensation water

Electrochemical measurements under a film of condensation water are peculiar because of the very low electrical conductivity of the water film, which acts as electrolyte. Insight into the system behavior is gained by EIS. The system behavior is capacitive (negative phase angles) and is ruled by two distinguishable processes, dominating in the higher frequency range (greater than approx. 10 Hz) or in the lower frequency range (lower than approx. 10 Hz). By deliberate variation of the electrolyte conductivity and the corrosivity of the electrolyte (addition of small amounts of inhibiting or corrosion-promoting salts to the water film) and of the distances of the auxiliary electrodes to the sample surface, it was established that the high-frequency capacitive behavior is due to the low-conductive electrolyte, which acts as an imperfect dielectric between the sample surface and the auxiliary electrodes. Meanwhile, the low-frequency capacitive behavior is ruled by the charge transfer at the interface between the water film and the metallic sample’s surface. It therefore represents the metallic sample’s surface state with low capacitance and high charge transfer resistance in case of passivity and high capacitance and low charge transfer resistance in case of activity, i.e. corrosion.

Only in prolonged measurements with the occurrence of greater amounts of corrosion products, the charge transfer resistance will potentially increase again after some time due to blocking of the surface by corrosion products. With the formation of the corrosion products and their solution in the electrolyte, the conductivity of the electrolyte is also significantly increased up to the point where the high-frequency capacitive behavior vanishes completely, since the electrolyte no longer acts as an
imperfect dielectric, but provides higher electrical conductivity. In comparison, the absorption of any VCI has a rather small effect on the electrolyte conductivity so that the high-frequency capacitive behavior can still be observed in presence of VCI-containing products in the test chamber. The validity of the d.c. measurement despite of the contribution of the high electrolyte resistance will be addressed in the discussion of the results in section 3.2. The assessment of the corrosion protection ability of VCI-containing products in d.c. (sweep) mode saves effort in terms of instrumentation of the test apparatus and analysis of the measured data. However, EIS measurements will potentially provide additional information depth for research and development of both the test method and VCI-containing products and therefore are carried out, too. Since only the low-frequency behavior reflects the sample’s surface state and allows to distinguish between the passive and the active, i.e. corroding, state, the impedance measurement is limited to this frequency range. Different electrolyte conductivities due to solution of corrosion products and/or small deviations of the distance between the electrodes are accounted for by normalizing the spectrum with regard to the obtained impedance at the highest measured frequency.

The resulting equivalent circuit for fitting of the impedance data consists of a normalized resistance (electrolyte resistance) in line with a parallel connection of another resistance (charge transfer at the interface between electrolyte and metallic sample surface) and an imperfect capacitance (constant phase element reflecting capacitive behavior at the interface between electrolyte and metallic sample surface with a pseudo-capacitance $Q$ and an exponent $n$). The exponent $n$, which is a measure for the imperfectness of the electrolyte/metal interface in terms of heterogeneous distribution of time constants (e.g. influenced by surface roughness, homogeneity of primary oxide layer etc.), is mostly in a range of 0.8–0.95 for the system under investigation. The transition from the passive state to the active, corroding state is denoted by values of the pseudo-capacitance of approx. $10^{-4}$ F·s$^{-1}$·cm$^{-2}$. The value has preliminarily been established by stopping tests immediately after impedance measurements and examining the sample for traces of corrosion. For a pseudo-capacitance exceeding the mentioned value, corrosion spots are visible on the sample. For values just slightly exceeding $10^{-3}$ F·s$^{-1}$·cm$^{-2}$, the corrosion spots are invisible to the bare eye, but can be identified using a light microscope with at least 5x magnification. In the same way, a decrease of the polarization resistance obtained from the DC (sweep) electrochemical measurement to values below approx. 30 kΩ·cm² indicates corrosion initiation, while values below approx. 5 kΩ·cm² indicate severe corrosion (either pitting or corrosion of large fractions of the surface). For support, Table 2 shows representative images of the sample surface and the obtained values from the EIS and polarization resistance measurements from preliminary experiments.

**Table 2.** Preliminary tests – correlation of the visual appearance of the active sample surface (diameter: 0.95 cm, contrast and color intensity increased by image manipulation), the pseudo-capacitance $Q$ and the polarization resistance $R_{pol}$ obtained from electrochemical measurements immediately before the end of the tests.

| Corrosion State       | $Q$ Value       | $R_{pol}$ Value |
|-----------------------|-----------------|-----------------|
| not corroded          | $7 \times 10^5$ F·s$^{-1}$·cm$^{-2}$ | 57 kΩ·cm²      |
| slightly corroded     | $1,2 \times 10^4$ F·s$^{-1}$·cm$^{-2}$ | 23 kΩ·cm²      |
| moderately corroded   | $5,3 \times 10^3$ F·s$^{-1}$·cm$^{-2}$ | 7 kΩ·cm²       |
| heavily corroded      | $1,8 \times 10^3$ F·s$^{-1}$·cm$^{-2}$ | 0.1 kΩ·cm²     |
3.2. Assessment of the corrosion protection effect of a VCI-containing polyethylene film

Figure 5 shows the evolution of the charge transfer resistance and the pseudo-capacitance obtained from EIS measurement during a climatic stress, which was prolonged compared to the original cycle (cf. Figure 4) by cyclically applying an increase and decrease of the sample temperature with respect to the dew point. While this is accompanied by evaporation and condensation of humidity and consequently increased corrosive stress in the respective cycles, the water film, which wets the sample surface and the auxiliary electrodes, stays intact during the rapid temperature variation and thus allows for continuous assessment of the sample’s surface state by electrochemical measurement. In the present case, both the polarization resistance $R_{pol}$ and the pseudo-capacitance $Q$ at the interface between the metallic sample and the film of condensed water indicate corrosion initiation during the first two of the additional temperature cycles. Additionally, the charge transfer resistance $R_{ct}$ obtained by fitting of the obtained impedance spectra with the described equivalent circuit (section 3.1) is shown alongside the polarization resistance in Figure 5. $R_{ct}$ shows larger fluctuation over time compared to $Q$, which is mainly due to the fact that $Q$ is of higher significance for the fit of the spectra. However, the values of $R_{ct}$ and $R_{pol}$ are in the same order of magnitude, which proves the validity of the d.c. measurement to obtain $R_{pol}$. The comparably large electrical resistance of the film of condensed water, which serves as the electrolyte, contributes to the overall polarization resistance $R_{pol}$, but not to the value of $R_{ct}$. The latter one is obtained only from the low-frequency range and thus exclusively represents the charge transfer behavior at the interface between the metallic sample and the film of condensed water. Since both are in the same order of magnitude, the polarization resistance is obviously not greatly affected by the low electrical conductivity of the water film under the considered circumstances.

Two major test modes are derived for the assessment of VCI-containing products, regardless of the carrier material (e.g. films, paper, diffuser, oils etc.):

1. The polarization resistance is measured once after 6 h in the presented climatic regime (Figure 4). The obtained value is used to determine, whether the sample is in a corrosion-active or in a passive (inhibited) state. Thus, the corrosion protection effect of the VCI-containing product is assessed. This method is especially suitable for quality inspection purposes, since the assessment can be carried out automatically with respect to the established limit value of the polarization resistance $S_0$, no electrochemical expert knowledge is required to evaluate a VCI-containing product as ok/not ok.

2. The test is prolonged by a number of cycles, which impose further corrosive stress on the metallic sample by variation of its temperature with respect to the dew point. The polarization resistance is measured repeatedly during the cycles and the moment of corrosion initiation as well as the severity of the corrosive attack can be evaluated. This allows for discrimination between different VCI-containing products, which pass test mode (1) and is especially suitable for research and development purposes.
Figure 5. Evolution of the electrochemical parameters, namely the pseudo-capacitance $Q$, the charge transfer resistance $R_{ct}$ (both obtained from EIS) and the polarization resistance $R_{pol}$ (obtained from d.c. potential sweep) over the course of a climatic stress, which adds a cycled temperature variation to the regime shown in Figure 4. Comparison of both the obtained values for pseudo-capacitance and polarization resistance with the established limits for corrosion initiation (dotted lines) shows that corrosion is initiated during the first two additional temperature cycles. The increased activity at the interface between the metallic sample and the film of condensed water is reflected by decreasing resistance values and an increasing value of the pseudo-capacitance.

4. Conclusions

The VCI-method provides temporary corrosion protection during transport and storage of goods with metallic surfaces. A new test method and test apparatus for the assessment of the corrosion protection effect of VCI-containing products have been presented. The test includes exposition of a bare metallic sample to a defined volume of atmosphere within a test chamber alongside a VCI-containing product. During the course of the test, the metallic sample is cooled down below the dew point of the atmosphere. Consequently, humidity condenses on the sample surface and imposes a corrosive stress. The sample’s surface state under the film of condensation water is evaluated objectively and quantitatively by electrochemical measurements. The values obtained from a.c. as well as d.c. electrochemical measurements correlate with the occurrence of corrosion on the metallic sample surface. For the evaluation of VCI-containing products for quality inspection or R&D purposes, a test regime and limit values of the polarization resistance and the capacitance at the metal/electrolyte interface have been established. The test arrangement is integrated in a tabletop device and allows for the assessment of the corrosion protection effect of VCI-containing products within a working day.

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References

[1] German Federal Statistical Office: Exports and imports in 2017 (foreign trade), last accessed on 2018-08-09

[2] Subramanian A, Natesan M, Muralidharan V S, Baiakrishnan K and Vasudevan T 2000 An Overview: Vapor Phase Corrosion Inhibitors Corrosion 56 144–155
[3] Kuznetsov Y I 2015 Progress in the science of corrosion inhibitors *Int. J. Corros. Scale Inhib.* **4** 15–34

[4] Andreev N N and Kuznetsov Y I 2012 Volatile Inhibitors of Metal Corrosion. I. Vaporization *Int. J. Corros. Scale Inhib.* **1** 16–25

[5] Andreev N N and Kuznetsov Y I 2012 Volatile Inhibitors of Metal Corrosion. II. Interaction of systems being protected with the environment and corrosion prevention conditions *Int. J. Corros. Scale Inhib.* **1** 146–153

[6] Koehler S and Reinhard G 2014 VCI containing package material – mode of functioning *Int. J. Corros. Scale Inhib.* **3** 286–306

[7] Ansari F A, Verma C, Siddiqui Y S, Ebenso E E and Quraishi M A 2018 Volatile corrosion inhibitors for ferrous and non-ferrous metals and alloys: A review *Int. J. Corros. Scale Inhib.* **7** 126–150

[8] Valdez B, Schorr M, Cheng N, Beltran E and Salinas R 2018 Technological applications of volatile corrosion inhibitors *Corros. Rev.* **36** 227–238

[9] Kim K T, Kim H W, Chang H Y, Lim B T, Park H B and Kim YS 2015 Corrosion Inhibiting Mechanism of Nitrite Ion on the Passivation of Carbon Steel and Ductile Cast Iron for Nuclear Power Plants *Adv. Mater. Sci. Eng.* **2015** 408138-1–408138-16

[10] Tan Y J, Bailey S and Kinsella B 1996 An investigation of the formation and destruction of corrosion inhibitor films using electrochemical impedance spectroscopy (EIS) *Corros. Sci.* **38** 1545–1561

[11] Khaled K F and Abdel-Rehim S S 2011 Electrochemical investigation of corrosion and corrosion inhibition of iron in hydrochloric acid solutions *Arabian J. Chem.* **4** 397–402

[12] Popova A, Sokolova E, Raicheva S and Christov M 2003 AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives *Corros. Sci.* **45** 33–58