Operating principle of volatile corrosion inhibitors in the jar test

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Abstract. An appropriate corrosion protection is required for transport and storage of high-quality goods and semi-finished parts made from metals. The application of volatile corrosion inhibitors (VCI) as a means of temporary corrosion protection is based on the release of corrosion inhibitors from films, papers, diffusers or oils to the gaseous phase. By adsorption on the metal surface, the inhibitors prevent the degradation of the primary oxide layer and hence impede corrosion. In principle, the anticorrosive effect is independent of the part geometry, because the protected surfaces do not need direct contact with the VCI material. Also, the VCI method does not require costly cleaning of parts prior to further use after transport and storage. The EXCOR jar test is a common method to examine the efficiency of VCI. A metallic sample and a VCI material are exposed in a jar. After conditioning in dry and humid atmosphere, corrosive stress is applied to the sample. To clarify the VCI’s mechanism of action, the test steps, their duration and the type of inhibitors were varied. Thus, the operating principle of VCI during the test was identified. The acquired knowledge enables to understand and tailor the corrosion protection by VCI in service.

1. Introduction
Corrosion is an extensive problem for the worldwide industry. The cost caused by corrosion amounts to hundreds of billions of dollars every year. Especially, the manufacturers and suppliers of the metal-processing industry are striving to improve the corrosion resistance of their metallic products during transportation and storage. Bare metals are prone to condensed humidity on their surface, which already leads to corrosive attack, even if no further corrosion-promoting substances are existent in the considered environment. To temporarily prevent corrosion of metallic products, in particular volatile corrosion inhibitors (VCI) present a convenient method. The VCI sublimate from films, papers, diffusers and/or oils – which serve as VCI donors – to the gaseous phase within a packaging. Finally, the inhibitors adsorb on the metal surface to stabilize the primary oxide layer and thus reduce corrosion attack. The corrosion protection with VCI possesses considerable advantages. They offer protection for several years and on any part geometry. Furthermore, except for the above-mentioned common carriers, VCI can be incorporated in manifold packaging products, such as polymer-, paper- or cardboard-based trays, carriers etc. Moreover, no expensive cleaning after transport and storage is necessary. And at last, the VCI ingredients exhibit an eco-friendly behavior. [1–7]

To investigate the corrosion protection effect of the VCI materials, there are different established test methods. The tests are generally based on the exposure of metallic samples in VCI packaging materials, especially films or papers, to alternating climates with varying temperature and humidity so that a corrosive impact occurs on the sample surface. The samples are mostly bare metal sheets made from iron-, copper- or aluminum-based alloys or galvanized steel. In one common test layout
(Figure 1), a metallic sample is mounted in an auxiliary frame, which completely avoids contact between the samples’ surfaces and the VCI packaging (so-called distance test). In another test layout (Figure 2), the metallic sample’s surface is in direct contact with the VCI packaging to simulate contact of metal surface and packaging material, which leads to crevice-like corrosion conditions when humidity accumulates between sample surface and packaging (so-called contact test). In each case, the efficiency of VCI is assessed after a defined number of climate cycles with regard to a reference packaging material, which does not contain any corrosion inhibitors. In the most cases, the duration of these tests amounts to 20 to 30 d to receive significant results. The criterion for the assessment of the VCI products is the number of cycles until significant corrosion occurs on the metallic sample, which is related to the number of cycles until corrosion occurrence on a metallic sample in a non-VCI packaging. In contrast, the so-called jar test is a rapid testing method due to the reduction of the test duration to 24 h instead of 30 d. The jar test procedure conduces to the determination of the efficiency of VCI for steel samples. The metallic sample is exposed in a jar containing VCI films or papers and a corrosive stress is applied by a simple climate regime. Because of its reduced test duration, the jar test is suitable for receiving rapid and efficient test results. The test procedure will be explained in detail in section 2.

![Figure 1. Experimental setup of the distance test. The metallic specimen (metal sheet) is mounted in an auxiliary frame, packed in a film and exposed to a climatic stress test (no contact between metallic specimen and film).](image1)

![Figure 2. Experimental setup of the contact test. The metallic specimen’s surface is in direct contact with the VCI packaging during the climatic stress test.](image2)

To derive comprehensive indications for industrial applications, the inhibition effect of VCI during corrosion attack on different metals requires a more detailed study. With the focus on steel, the test stages of the jar test and their duration are varied in the present examination to determine the functionality and mode of action of two different types of VCI-films.

2. Experimental and materials
The jar test procedure constitutes a rapid test method to examine the VCI effect on steel, which is used for quality control of mainly VCI films and papers. For the present investigation, cylindrical steel samples with a diameter of 16 mm were used. The chemical composition is given in Table 1.

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

Table 1. Nominal composition of the sample material S235JRG.
The steel samples were ground with grade 320 abrasive paper on a grinder Saphir 520 (ATM, Germany) for 90 s each in co- and counterrotation mode followed by rinsing under deionized water and acetone p. a. To place the metallic sample in an Erlenmayer flask with a volumetric capacity of 1 l, a rubber plug with a diameter of 54 mm and an axial bore was used. The axial bore was rimmed by two slots, where the VCI material were fixed during the test. These stripes of VCI-film had the dimension 25 mm x 150 mm. The metallic sample and the VCI stripes are fixed in the rubber plug and put into the flask. After 20 h storage of the flask at room temperature, 10 ml of a water glycerol mixture (density 1.076 g/cm³ at 23±2 °C, mass fraction glycerol to water approx. 1:3) prepared from deionized water and glycerol (p.a. grade) are added to the flask, which is then stored at room temperature for another 2 h. Afterwards, the flask is put into an incubator (ULP500, Memmert, Germany) at 40 °C (pre-heated) for 2 h. Figure 3 shows the complete experimental arrangement of the jar test. The actual prevalent temperatures and humidity in the jar are depicted in Figure 4. The measurement originates from a data logger (temperature, humidity logger RHT10, Extech, U.S.), which was inside the jar during the whole test. Water condenses on the steel sample during the first 30 min due to thermal inertia of the steel sample (temperature below the dew point of the already heated atmosphere). Then, the condensed water remains on the steel surface because of the high humidity of the atmosphere within the jar.

In a variation of the described test, the corrosive load is imposed on the sample differently. Instead of putting the flask into an incubator, pipettes with frozen water are positioned in the rubber plug on the top of the metallic sample. Thereby, the sample is cooled below the dew point, which leads to condensation of humidity on the sample surface and thus to the corrosive attack. The pipettes with frozen water are replaced every 15 min for an overall time of the corrosive load of 2 h. During that time, the flask is positioned in a thermostatically controlled water bath (40 °C). The flask is immersed in the water bath approx. 1 cm, so that the water glycerol mixture on the bottom of the flask partially evaporates and thus increases the humidity in the flask, but the temperature of the atmosphere in the flask is not significantly affected (during the 2 h, the temperature of the atmosphere in the flask does not significantly exceed room temperature).

The total test duration thus includes the dry conditioning for 20 h, the humid conditioning for 2 h and the corrosive stress at elevated temperature (40 °C in incubator) and/or at room temperature (ice-water-filled pipettes) for 2 h, each. Afterwards, the metallic sample is removed from the flask, is dried
in an incubator at 40 °C and is then evaluated by visual inspection. The corrosive impact is described using a generalized evaluation scale. The rating definition is divided into four grades as can be seen in Figure 5. If a steel sample shows an overall corrosive attack, it will receive the evaluation 0 (no corrosion protection). The grade 3 is assigned to samples without any corrosion spot (good corrosion protection). In between the corroded area decreases notably from value 1 (low corrosion protection) to 2 (moderate corrosion protection). [2]

![Figure 4. Temperature and relative humidity of the atmosphere in the flask during the jar test procedure.](image)

![Figure 5. Representative visual occurrence of the steel sample surface for the 4 grades of the evaluation scale with regard to VCI efficiency; 0 – no corrosion protection, 1 – low corrosion protection, 2 – moderate corrosion protection, 3 – good corrosion protection (from left to right).](image)

To identify the mechanism of action of VCI during the jar test, the test stages, their duration and the type of inhibitor were varied. The investigated VCI types in this work are denoted as Type I and Type II. The films consisted of polyethylene (PE). Their thickness amounted to 80 µm. VCI Type I and Type II had fundamentally different composition with regard to the contained corrosion inhibitors. Generally, this includes both organic and inorganic substances, for instance volatile organic acids, cyclic compounds or salts, which act as inhibitors after dissociation as well as non-volatile stabilizers which moderate the inhibitor release and prevent the VCI product from premature decay of its technical properties (both in terms of corrosion protection as well as ageing, discoloration etc.). However, the detailed composition cannot be disclosed here for reasons of confidentiality, since both
Type I and Type II are research VCI compositions similar to commercially available products. The variation of the duration of the three jar test phases are shown in Figure 6. The duration of the dry conditioning was modified between 20 h, 1 h and 0 h. The duration of the humid conditioning was varied between 2 h and 0 h. The duration the corrosive attack was not modified. While normally, the VCI material remains in the flask during the whole test, it was removed from the flask after different stages of the test to investigate into the adsorption/desorption behavior of the VCI during dry and humid conditioning as well as during corrosive stress. Each variation of the test stages and their duration included control test runs without any VCI material. Thus, the appropriateness of the corrosive stress applied in the test should be proven.

For the evaluation of the data, at least four samples per test variation were produced and visually assessed utilizing the scale described above. Moreover, the average value and the minimum and maximum of the obtained data were established for the discussion.

Figure 6. Experimental matrix of the investigated jar test – the corrosive stress applied in the incubator at 40 °C is referenced as “corrosive stress (40 °C)” and the corrosive stress applied by placing ice-water-filled pipettes on the sample is referenced as “corrosive stress (RT)”, since the temperature of the atmosphere in the flask does not significantly exceed room temperature in this case. The variation of the test includes the removal of the VCI material after different stages and the variation of the duration of single stages of the test (a – corrosive stress only at elevated temperature, b – corrosive stress at room temperature and elevated temperature).
3. Results and discussion
The obtained results of the tests including only corrosive stress at elevated temperature (40 °C) (tests A.x) or at room temperature and at elevated temperature (tests B.x) are given in Figures 7 and 8, respectively.

![Figure 7](image_url)

**Figure 7.** Obtained average results and min/max values (8 samples, each) according to the evaluation scale for the corrosion inhibition effect (0 = no inhibition, i.e. heavily corroded sample; 3 = good inhibition, i.e. non-corroded sample) of VCI Type I and Type II (right) in dependence of the variation of the jar test for corrosive stress at elevated temperature (40 °C, left). The effect of the 20 h (test no. A.1–A.4) or 1 h dry conditioning (test no. A.5–A.8) on the inhibition is low compared to the 2 h humid conditioning (test no. A.9–A.11) for both types. When the VCI material is present during the corrosive stress, the inhibition effect is good for both Type I and Type II (test no. A.1, A.5, A.9, A.12). When the VCI is present only during humid conditioning, but is removed from the flask before the corrosive load (test no. A.2, A.6, A.10), the inhibition effect of Type I is more significant than for Type II. When the VCI is removed from the flask after dry conditioning (test no. A.3, A.7), the inhibition is rather low for both VCI.
Figure 8. Obtained average results and min/max values (4 samples, each) according to the evaluation scale for the corrosion inhibition effect (0 = no inhibition, heavily corroded steel sample surface; 3 = good inhibition, non-corroded steel sample surface) of VCI Type I and Type II (right) in dependence of the variation of the jar test for sequential corrosive stress at room temperature (RT) and elevated temperature (40 °C) (left). VCI Type I shows good inhibition when present during the corrosive stress at both room temperature and 40 °C (test no. B.1, B.8). In the test, VCI Type II fails for corrosive stress at room temperature (evaluation 0–1, test no. B.5). The humid conditioning before the corrosive load has a rather low effect on the inhibition effect for both Type I and Type II (compare test no. B.1 and B.8; B.2 and B.9; B.3 and B.10). Test no. B.8 contains a single outlier with moderate inhibition effect for VCI Type II. Dotted lines (Type II, test no. B.9, B.11) refer to tests, which have not been carried out because it was obvious from test no. B.5 that Type II fails under corrosive load at room temperature.

Overall, the jar test displays average grades of 0.8 and 3.0 for VCI Type I, whereas the average grades of Type II are between 0.0 and 2.4. The presence of VCI during the corrosive stress is essential for a good corrosion protection effect in the test for both types. The appropriate grades to confirm this statement vary between 2.5 and 3.0 for Type I and from 2.1 to 2.4 for Type II in Fig. 7 (test no. A.1,
A.5, A.9, A.12). The same statement applies to VCI Type I by considering the results shown in Fig. 8 (test no. B.1, B.5, B.8, B.11). For corrosive stress at room temperature, however, Type II fails in the test even when the VCI is present during said corrosive stress (Fig. 8, test no. B.5). Test no. B.5 was independently repeated with another four samples and yielded identical results, so that the statement was consolidated. Therefore, tests no. B.9 and B.11 were not carried out with VCI Type II (dotted lines in Fig. 8). For both VCI Type I and Type II, when the VCI is present during the corrosive load, the conditioning generally only has a minor effect on the corrosion inhibition ability of the respective products in the considered time scale (Fig. 7, test no. A.1, A.5, A.9, A.12 and Fig. 8, test no. B.1, B.5, B.8, B.11). When the VCI is removed from the flask before corrosive stress, however, VCI Type I and Type II show significantly different behavior with regard to the conditioning. When VCI Type I is present during humid conditioning (2 h) but is removed before the corrosive stress at 40 °C, there is still a significant inhibition effect (Fig. 7, test A.2, A.6, A.10). For VCI Type II under the same conditions, the inhibition effect is significantly less pronounced. The conditioning at low relative humidity – independently of the presence of VCI products in time of corrosive stress at 40 °C – contributes to the corrosion inhibition only to a small amount. Removal of the VCI after 1 h or 20 h of dry conditioning leads to only weak inhibition effect for Type I and no noticeable inhibition effect anymore for Type II (Fig. 7, test A.3, A.7). Also, in case of corrosive stress at room temperature, neither Type I nor Type II show relevant inhibition ability when only present before during humid conditioning (Fig. 8, test B.6). Interestingly, for Type I, corrosive stress at 40 °C after the corrosive stress at room temperature does not lead to enhanced corrosion of the steel sample, whether or not VCI is present during the corrosive stress at 40 °C (Fig. 8, test B.2, B.9).

The performed examination provides some indications of the dominating mechanisms of action of the VCI materials. A graphical representation of the findings is given in Figure 9. Generally, the release of inhibitors and their effect on the sample surface is obviously enhanced in the presence of humidity. Whether this is mainly due to better release and transportation of the VCI in humid atmosphere and/or due to stronger bonding of the inhibitors to the metal surface in the presence of humidity will have to be addressed in future investigation. However, the required amount of VCI for corrosion protection in the atmosphere and especially on the metallic surface is achieved more comprehensively for Type I than for Type II. Further, compared to VCI of Type II, the VCI of Type I are affected to a lesser extent by the removal of the VCI product and by the variation of the temperature of the atmosphere during corrosive load. There is a conception of a “retentive memory” of the metallic sample, implying the remain of the inhibitor on the surface after the removal of the donating product. This memory could be ruled by the different adsorption strength and desorption rates of the inhibitors or it could be caused by a different mode of action regarding the corrosion inhibition, especially with regard to the reaction mechanism. Since VCI Type II obviously shows higher activity in case of higher temperature, the corrosion protection effect for this type could be dominated by a chemical or electrochemical reaction with either a relatively high temperature dependence of the reaction rate and/or a temperature-dependent activation energy. Additional tests equivalent to experiment B.6, but with prolonged conditioning of 20 h and 200 h showed low and moderate corrosion protection for VCI Type II, respectively. According to the reaction model, this indicates a temperature-dependent reaction rate as the dominating factor instead of the activation energy. For the latter, there would have been no effect of the prolonged conditioning time at lower temperature, while a lower reaction rate at lower temperature can be compensated by longer conditioning time. Therefore, in the test, this reaction would take place only during the corrosive load at elevated temperature in presence of the VCI or during a longer conditioning phase and could therefore explain the test results for Type II. In contrast, the behavior of VCI Type I could thus be dominated by an adsorption mechanism and therefore its protection effect would show less temperature-dependence considering that both adsorption and desorption activity increase at elevated temperature. Additionally, the adsorption of inhibitors from Type I is obviously rather strong so that after removal of the VCI from the flask and therefore the shifting of the adsorption/desorption equilibrium in favor of desorption, the corrosion protection effect is still significant.
Figure 9. Mechanism of inhibitor-substrate interaction during the stages of the test. Obtained results indicate an increased release of inhibitors and/or stronger bonding of the inhibitors on the steel surface during humid conditioning (b) compared to dry conditioning (a). Additionally, the activity of the inhibitors during corrosive load under condensation of humidity on the sample surface is temperature-dependent and dominated by a chemical/electrochemical reaction or adsorption/desorption behavior depending on the type of VCI (c).
Further experiments are necessary for clarification and validation of the proclaimed mechanism. These will include the variation of the conditioning time before corrosive stress at room temperature as well as a variation of the amount of VCI in the flask via the surface of the stripes of VCI-film mounted in the rubber plug. Also, the effect of humidity on the release of VCI will have to be addressed by setting a defined humidity during conditioning via the variation of the water/glycerol mixture used for the test. To support the results, methods to quantify sublimation and adsorption of VCI based on chemical analysis of VCI-donating and VCI-adsorbing materials are under development.

4. Conclusions
In the present study, the corrosion protection effect of VCI was examined. Therefore, a jar test procedure was used, which is a rapid testing method to obtain results on corrosion inhibition within a short time period. To identify the operating principle and the VCI mechanism of action leading to the anti-corrosion effect, the test stages of the jar test and their duration were varied and two different types of VCI-films with fundamentally different composition were considered. The results can be summarized as follows:

1. The presence of the VCI-containing films during the corrosive stress decreases corrosion damage at the sample surface significantly. Only in few of the varied test regimes, a corrosion protection effect is still noticeable when the VCI film is removed after conditioning and before the corrosive stress. VCI Type I shows an overall superior protection effect compared to Type II.

2. In the test, humid conditioning contributes to the inhibition effect more than dry conditioning. This can be explained with the enhanced release/transport of VCI and/or a stronger bonding of the adsorbents on the sample surface in presence of high humidity.

3. In the test, the temperature during the phase of corrosive stress plays an important role regarding the protection effect, especially for VCI Type II, which failed in the test when the temperature during corrosive stress was not increased significantly above room temperature. Additional experiments have shown that VCI Type II is generally able to provide corrosion protection also at non-elevated temperatures when the humid conditioning times are increased. This is attributed to fundamentally different mechanisms of action of the investigated types. The results indicate that the dominating effect of the protection by Type I is its adsorption behavior on the metal surface, while the dominating effect for Type II is a chemical or electrochemical reaction with temperature-dependent reaction rate.

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