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New Developments in Corrosion Testing: Theory, Methods and Standards

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ABSTRACT

In times when nanotechnology and complex hybrid systems are the leading edge in protective coatings, the neutral salt spray test, ISO 9227, is still the method of choice for evaluating the performance of these systems. The discussions about reliability and informative value are as old as the test itself. Statistical and quality assurance methods were developed to improve the established test (round robin, Weibull analysis). At the same time, new tests were developed to better simulate the real corrosive environment of the ready product (climate tests, accelerated outdoor tests, Russian mud etc.). This paper will give a broad overview of the newest developments in corrosion tests and their implementation in automotive standards.

Keywords: Corrosion testing, salt spray alternatives

Introduction

Corrosion, as partial or total disintegration of a material due to chemical reaction with its surroundings, is the process that, next to wear, determines the lifetime of a part. Whether this lifetime is defined by how long reliable functionality is given or just by how long a desired cosmetic aspect can be maintained, the information on the corrosion behavior is crucial for the use in technical applications. The fundamental chemical reactions leading to corrosion in general and to the oxidation of metal specifically are given in Fig. 1.

The most important extension to the simple model containing only metal, water and oxygen are different kinds of protective, especially passivation, layers and additional reactants in the surrounding atmosphere. Different scenarios taking that into account are the foundation for the development and evaluation of a corrosion test.

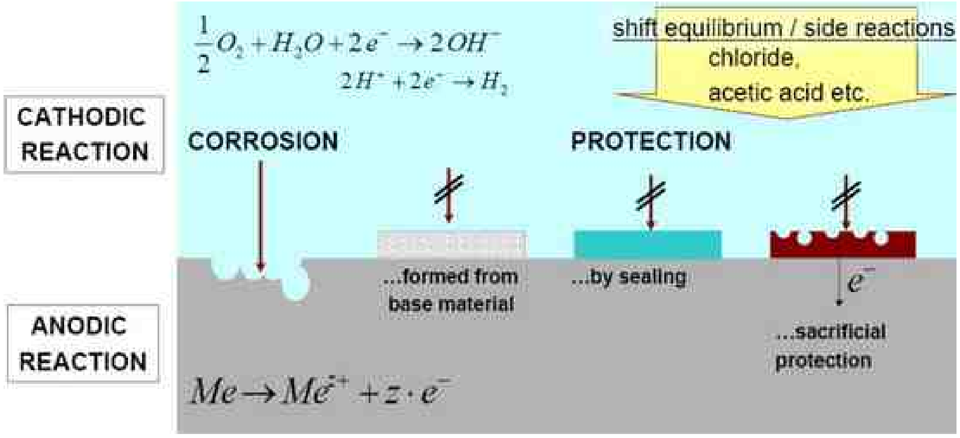

Figure 1 - Overview of different corrosion mechanisms.

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The most significant test of corrosion behavior exposes a material as a component of the actual device (*e.g.*, a screw in a vehicle) to either the most representative or to a realistic, but worst case environment that this material would experience in use ("field test"). This kind of test is real-time and so it takes at least as long as the lifetime of the part in service. Furthermore, these tests are expensive, hard to standardize and provide information only about the very specific system that was tested (Fig. 2).

Standardized tests are generally used to test components under a defined exposure and evaluation protocol. The final use of the component can be defined before and the testing procedure adapted accordingly (*e.g.*, automotive interior/exterior).

The standardized tests are often accelerated tests, making it possible to get the information on corrosion behavior in a fraction of the real lifetime. The acceleration can be caused by aggravated parameters (temperature, humidity, concentration of corrosive species) or just by permanent (or more frequent) exposure to corrosive conditions that occur more rarely in the real application. By acceleration, the mechanism of corrosion can be changed completely, which has to be considered when using the results of such a test. There can be different levels of acceleration, leading to a more or less accelerated test with more or less comparability to the reality. Finally, a compromise has to found between the advantages of the single tests.

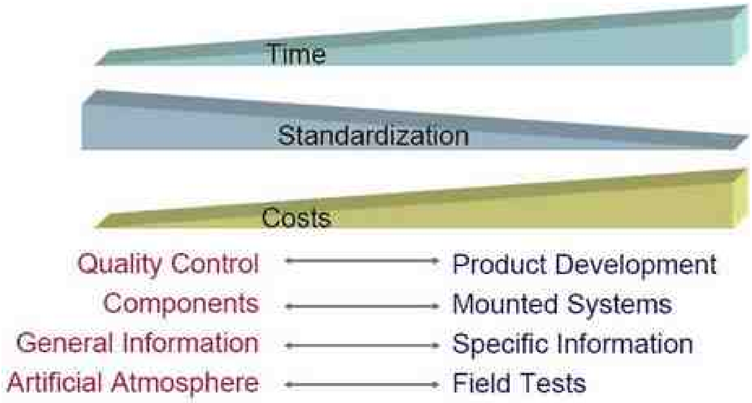

Figure 2 - Corrosion testing for different purposes.

One reason to use alternatives for simple accelerated corrosion tests (*e.g.*, salt spray tests) is that a material can meet different corrosive conditions in succession that cannot be combined to make one realistic permanent condition. That is why cyclic climate tests (*e.g.*, GM 9540P, VDA 621-415) have recently gained importance as complements for the classic salt spray test.

Figure 3 shows the profile of humidity and temperature in a typical cyclic climate test. The reason for increasing and lowering temperature and humidity is the formation of a thin water film caused by condensation. This thin water film is very permeable for oxygen, leading to ideal conditions for the cathodic reaction of corrosion as shown in Fig. 1.

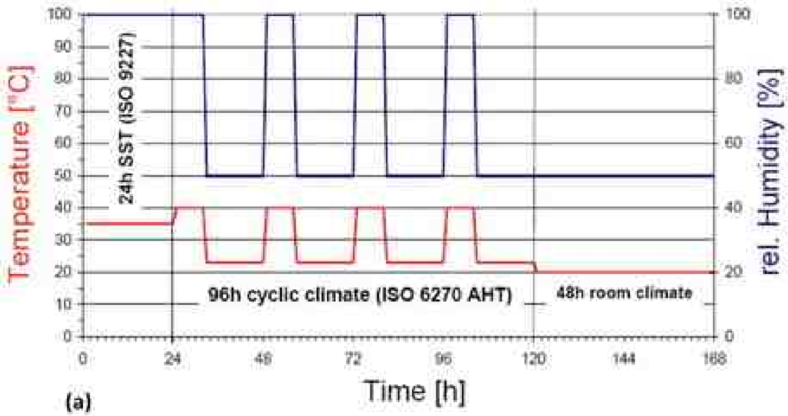

Figure 3(a) - Characteristic profile of humidity and temperature in a climate test according to VDA 621-415

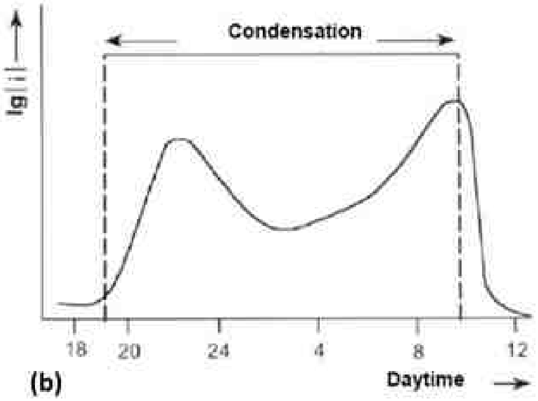

Figure 3(b) - A typical profile of the corrosion current during one day.[1]

Passivation of zinc-manganese during corrosion tests

The zinc-manganese alloy is known to provide extraordinary corrosion resistance after formation of a manganese oxide layer on the surface.[2] We used an ammonium-free, chloride-based, weak acidic electrolyte[3] to deposit a zinc-manganese alloy containing about 20% of manganese

When a part plated with this alloy is exposed to outdoor climate conditions (seawater or urban), a brown layer of manganese oxide is formed. This aspect remains constant after that and no further corrosion can be observed, resulting in superior protection compared to pure zinc. Figure 4 shows a part electroplated with zinc-manganese after 30 months of outdoor exposure. Next to the outdoor exposed part, another part is shown that was plated with the same zinc-manganese alloy and then exposed to a salt spray test. In this case, a voluminous white corrosion product was formed that is comparable to white rust on pure zinc plated parts. Like pure zinc, the corrosion resistance of zinc-manganese can be drastically improved by the right choice of post-treatment (trivalent passivates, sealers). However, the salt spray test performance is generally not superior to the respective pure zinc system.

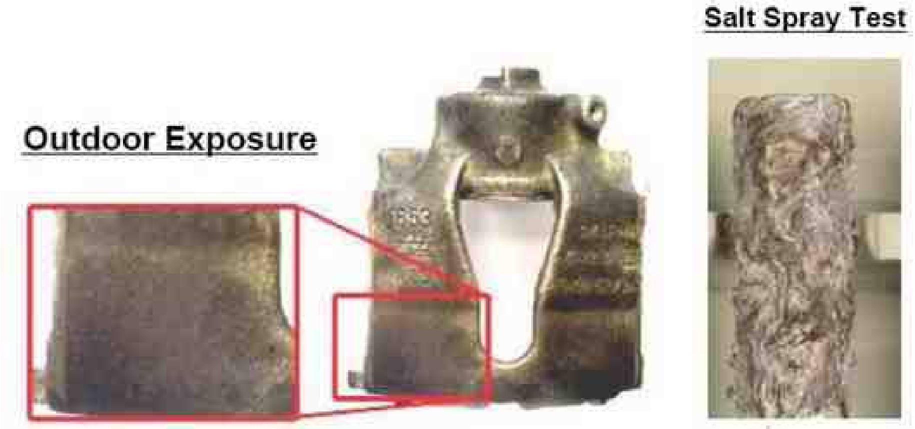

Figure 4 - Corrosion product of the zinc-manganese alloy under different testing conditions.

In order to elucidate the mechanism of corrosion product formation under different conditions, we plated small steel strips with zinc-manganese, exposed them to the standard salt spray test and to a cyclic climate test (compare Fig. 3). Samples were then studied, post cryo-fracturing, by SEM.

The images show a voluminous coarse-grained corrosion product after the salt spray test, whereas the sample from the cyclic climate test presents a smooth surface. An EDX surface analysis of the different deposits was made to determine the metal ratios in the corrosion products. Surprisingly the metal ratio in the sample from the salt spray test is $Zn_{91}Mn_9$, whereas the ratio in the sample from the climate test is $Zn_{67}Mn_{33}$. The original deposit has the composition $Zn_{82}Mn_{18}$. Thus manganese is enriched by cyclic corrosion and depleted in the salt spray test (Fig. 5). An obvious explanation is that in a permanently humid environment, the corrosion leads to Mn(II) salts that are easily soluble and consequently washed away under the conditions of the test. If the sample is allowed to dry in one phase of the cyclic climate test, the Mn(II) species can form insoluble manganese oxide which forms a dense protective film on the surface. What is shown here are improvements of test conditions, yielding a more realistic picture of the corrosion of a part in use.

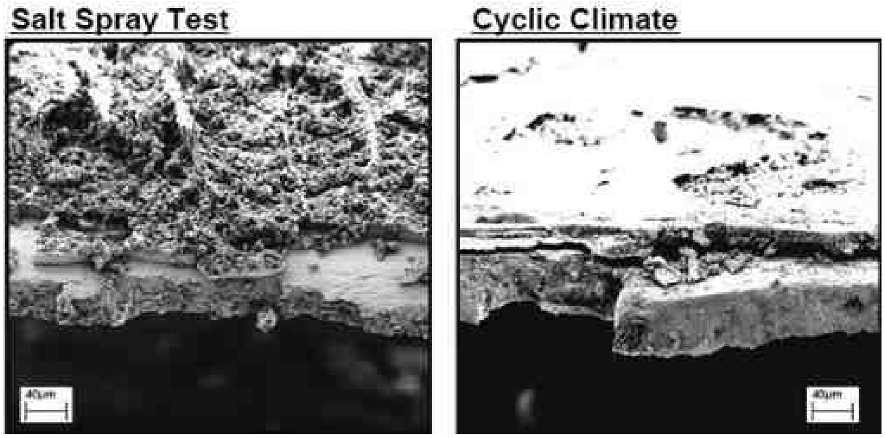

Figure 5 - SEM images of corrosion products from different corrosion tests.

Other approaches were made to improve the reliability of the information from the most common corrosion test, which will be discussed below.

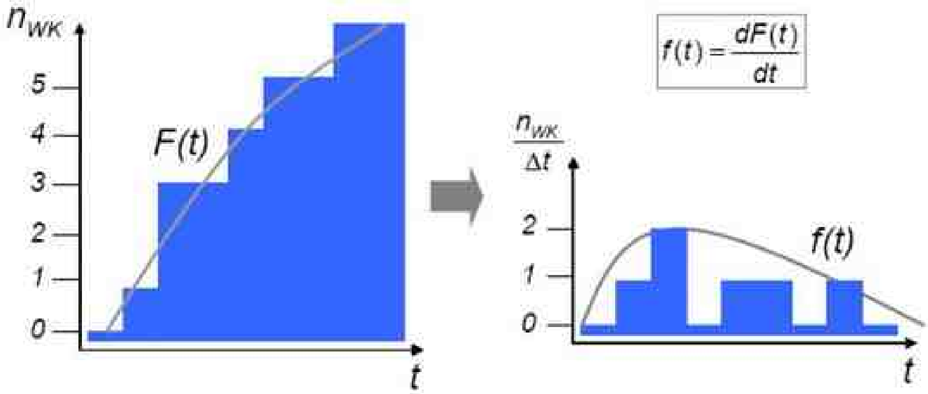

Figure 6 - Plots of failure probability and density function in an end-of-life study.

Evaluation of salt spray test results using the Weibull statistic

End-of-life studies are widely used in the automotive industry to determine the durability of components.[4] The principle is to apply defined stress to the component (*e.g.*, on-off cycles to a switch) until the component fails. After fitting the lifetimes of a sufficient number of probes using an exponential function, a good estimation for the period of reliable operation can be made. It was recently proposed to use an end-of-life study on parts tested in the salt spray test to obtain a more reliable value for white rust or red rust resistance.[5]

Generally two kinds of plots can be used when lifetimes are evaluated (Fig. 6). First, the total number of parts failed after a certain time can be plotted (failure probability). Second, the number of parts that failed in a given period can be plotted (density function).

A function that describes most end-of-life scenarios of real systems is the three-parameter Weibull function. The following equations are the respective failure probability and its deviation.

Weibull failure probability

$$F(t) = 1 - e^{-\left(\frac{t-t_0}{T-t_0}\right)^b} \tag{1}$$

Density function

$$f(t) = \frac{b}{T-t_0} \cdot \left(\frac{t-t_0}{T-t_0}\right)^{b-1} \cdot e^{-\left(\frac{t-t_0}{T-t_0}\right)^b} \tag{2}$$

The three parameters in the Weibull function can be used to describe the characteristics of the parts failure.

T is the scale parameter which is a measure for the mean lifetime and the width of the distribution. t_o is the failure-free time, the offset of the density function before which the probability of failure is zero. b is the form parameter. A small b value corresponds to a left-symmetric curve and a simultaneous start of failure. A large b value corresponds to a right-symmetric curve where single parts show early failure and the failure rate rises slowly.

A number derived from the Weibull statistics is the B_{10} value. It is the time span before 10% of the parts have failed (90% reliability). B_{10} can be found by integration of the fitted density function and is most commonly used as reliability indicator.

In this study, we zinc plated 15 standardized test panels from either an acidic or an alkaline electrolyte. The layer thickness was measured on 19 defined points and the thickness distribution calculated. After that, the parts were exposed to salt spray test. The time to red rust occurrence was examined for every part and analyzed using the Weibull function. The results are shown in Table 1.

Table 1 - Results of statistical analysis of end-of-life corrosion study of zinc plated panels.

	Alkaline Zinc	Acid Zinc
Thickness		
Mean Thickness	9.6 µm	13.3 µm
Std. Deviation	1.0 µm	2.9 µm
Salt Spray Test (Red Rust)		
T	370 hr	443 hr
t_o	260 hr	222 hr
B_{10}	270 hr	261 hr
B	0.9	1.3

The upper portion of the table shows some correlations between the zinc layer thickness and the corrosion test result. An alkaline zinc electrolyte generally provides a slightly lower efficiency but a better metal distribution. This is represented by the lower zinc layer thickness and lower standard deviation. Whereas the higher mean layer thickness out of the acidic electrolyte correlates to a higher mean corrosion performance (scale parameter T), the true reliability of the system given by the B_{10} value is even higher. The reason for that is a more homogeneous deposit and a comparable minimum thickness.

Conclusion

It is obvious that in times of modern, high performance protective coatings, it is crucial, not only to raise the requirements for performance using common corrosion test methods, but to review and improve the information provided by those tests.

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About the author

Dr. Klaus Wojczykowski is Technology Manager for the American sites of the Coventya Group since February 2010. Since 2006, he had worked for the Research and Development department of Coventya GmbH, Germany. There he was responsible for product development processes and research projects of the Coventya group, a leading company for specialty chemicals in the worldwide plating business. His main focus was on protective coatings, namely alloy deposition and passivation processes. A major research focus was on the microstructural investigation of protective layers and on the quality assurance of corrosion protection systems. Several contributions to the public discussion in this field were made. Dr. Wojczykowski studied chemistry (diploma) at the University of Bielefeld, Germany from 1997 to 2002. After that he worked on magnetic nanoparticles in a cooperative project between Prof. Dr. Jutzi (Organometallic Chemistry) and Prof. Dr. Hütten (Physics of Magnetic Nanostructures). He published his Ph.D. thesis on the synthesis and stabilization of metallic nanoparticles in 2006.