

Volatile Corrosion Inhibitor (VCI) Testing – Pitfalls and Surprises in Routine Test Methods.

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ABSTRACT

Volatile Corrosion Inhibitor (VCI) packaging has gained wide acceptance in the logistics world as effective means for the protection of metal fabricated parts during shipping and storage. End users still rely on standard jar tests (Mil-Std VIA, TL8135-0002 and NACE TM0208) to evaluate their supplier paper and film products. Although the laboratory procedures, reagents required and materials used are all specified within these documents, there are several opportunities for test operators to take liberties within the testing and obtain unauthentic results. This paper discusses common pitfalls and some surprising results associated with common variances that would appear, at first glance, to be innocuous for the standard test methods TL8135 and NACE TM0208.

Key words: Organic coatings; Corrosion Inhibitors; Corrosion Tests; Packaging; Test Methods

INTRODUCTION

Corrosion preventative packaging has been used in commercial, industrial, and military applications for over half a century. These products have garnered extensive research in new VCI chemistries, packaging design, and new VCI carrier materials^{1,2}. Initial protective packaging applications of VCIs involved coated paper which was used to wrap or interleave metal parts for transportation and/or storage.³⁻⁶ This type of wrapping evolved into film packaging where the inhibitors were extruded into film. In either form, paper or film, the packaging allows for the protection of metal fabricated parts without complications of rust preventative (RP) oils, which would typically have to be washed off. Using a VCI packaging design decreases processing costs and time prior to the part being placed into service. As VCI chemistries vaporize from the film or paper and diffuse throughout the package, they

are attracted to the polar nature of the metal part^{7,8}, forming a protective molecular layer on metal surfaces.^{2,9} This occurs even when the part is not in direct contact with the paper or film.

The challenge for most users of VCI packaging is that they cannot determine if the VCI packaging sold to them is effective at protecting their products. Specifically, whether the packaging will provide protection in the recesses of their metal parts. If one were to search, volatile or vapor-phase corrosion inhibitor, in the Corrosion Journal or NACE Conference Paper search engine, the results would show more than 1,300 published papers. This number is substantially larger when you count other research journals. For packaging buyers this abundance of information is overwhelming and therefore they are reliant on the performance claims made by the packaging supplier.

Most reputable suppliers of VCI packaging materials are versed at the types of standard test methods that are required to validate their products. When promoting their packaging products, ultimately, they still rely on the same 3 Vapor Inhibiting Ability (VIA) for Corrosion tests: MIL STD 3010 – 4031¹⁰, German Packaging standard TL8135-0002 (paper specific), -0034(film specific)¹¹ and NACE TM0208¹². A fourth, the Japanese Standard VIA, JIS Z 1535 (paper specific), -1542 (film specific)¹³ are like the previous 3 yet is seen most active use in eastern nations. The Japanese Standard will not be discussed in this report.

The VIA methods listed above have 3 main similarities. 1) a polished, cylindrical steel plug is suspended inside a glass jar/flask. 2) humidity is controlled inside to provide a suitable corrosion environment and 3) test strips of VCI paper/film hang inside the flask in proximity to the test plug. Each one of the tests have setup/method subtleties that make them unique to one another. In addition, there are several nuances that require significant attention to detail while performing, otherwise erratic, confusing, or just-plain wrong results will be obtained. These issues make evaluating claims from VCI packaging suppliers even more challenging. How do they know the data they are reporting was collected in a correct manner and valid to the method by which they were obtained? Within this paper we will discuss some of the subtleties and potential pitfalls of the 3 main VIA tests. We hope to shed light on areas of the tests that can have major implications and unforeseen consequences on the results obtained. Ultimately, we hope VCI packaging buyers learn to question the data that is presented to them and only trust claims from suppliers that are running the VIA tests accurately.

Background/Experimental

A review of the test methods and setups is important to establish now. Typically, 1-liter glass containers are used for the experiments. The test methods differ in the type required. The MIL and NACE tests use the same wide-mouth jar with plastic lid. Through the middle of the lid is an aluminum tube in which cold water is added at a specific point during the test. The German TL8135 uses a laboratory type Erlenmeyer flask with rubber stopper. No aluminum or cold water is utilized this test. All tests use low carbon, cylindrical steel specimens yet differ in the grade and design. MIL specifies 1010 cold-roll steel alloy where NACE gives the option of either 1010 or 1018. Both tests utilize the same dimensions with a hole drilled into the backside of the plug of specific diameter. This is an important test-design feature that will be discussed later. The TL8135 test requires the use of solid steel plugs that meet DIN EN10025, hot-rolled structural steel. These do not contain a drilled hole in the back side. In all cases, the plugs are suspended from a rubber stopper inside the flask with the polished side facing down. Next to, but not touching, are two test strips of VCI film or paper. For both NACE and MIL tests the test VCI strips are fed through precut slots in the lid and secured in place with tape. For the TL8135 test the test strips are secured in place with precut slits in the rubber stopper flanking the metal specimen.

	NACE TM 0208-2008	MIL-SPEC Method 4031	TL8135-0002
Apparatus			
Plug			
Metal Type	Type 1010: Federal Specification QQ-S-698 or 1018 Steel AISI Type 1018	SAE 1010 Steel (Cold rolled)	S235JRG2 DIN EN 10025 (material number 1.0038)

TABLE 1. VIA TEST APPARATUS AND SPECIMENS

Preparation of the steel plug all involve abrading the surface with polishing cloth (i.e. sandpaper) and washing with laboratory solvents to remove any further residues. For the NACE and MIL tests, the steel plugs are hand polished first with 240 grit paper followed by 400 grit paper. The plugs are rotated 90 degrees between paper grades to level the plugs and remove any rough striations. The NACE procedure describes a machine polishing method that allows to operator to use a drill press with sample holder on the end. As the plug rotates, abrading clothes are held to sides and surface to provide clean, smooth surfaces. There is no description of using contra-rotational wheel polishing in this method. The TL8135 test is similar with its hand sanding procedure yet requires the use of 320 grit paper.

The metal specimens also need to go through a rigorous cleaning process. Prior to sanding, the MIL specimens are cleaned outside and inside with a scour pad to remove bulk corrosion from previous testing. The well of the plug will contain corrosion and needs to be cleaned with dilute hydrochloric acid to remove any remaining corrosion from within. The plugs are then washed with soap and water, dried and then moved to the sanding phase of cleaning. NOTE: the cleaning procedure for NACE test plugs does not call for specifically cleaning the inside of the well. For all tests, once polished with abrasive cloths, the samples undergo specific, solvent cleaning regimes. The MIL standard calls for the plugs to wiped with a lint-free cloth and soaked in 3 successive baths of boiling methanol for 1 minute then air dried. For NACE, the first soak bath is mineral spirits followed by one soak in boiling methanol and then hot-air dried. The TL8135 test just calls for the plugs wiped/rinsed with ethanol and hot-air dried. No matter the cleaning method, this cleaning step is critical to remove any remaining sanding dust or organic residues that may interfere with the test.

At some point during the test, a glycerin/water solution is placed at the bottom of the test jar/flask to produce a 90-95% relative humidity (RH) environment. For the NACE and MIL tests, this solution is added to the jar once the metal specimen and VCI test strips are installed. A 20-hour conditioning period is performed. For TL8135, the water/glycerin solution is added after a 20-hour, dry, conditioning period. Following conditioning, the humidity environment is aggravated. This is where the 3 tests

differ. For the MIL test, ice water is placed into the aluminum tube which cools the backside of the metal specimen, forcing condensation on the polished face. For NACE, cold water is placed into aluminum tube, but only after the apparatus is placed into a shallow warm water bath for 5-20 seconds, warming the water/glycerin solution. This added heating event increases the relative humidity inside the jar forcing a greater probability of condensation onto the plug. The TL8135 test requires that after the solution be added the full apparatus allowed to condition again for 2 hours at room temperature followed by heating in a forced-air oven at 40 °C for 2 hours. This test does not utilize cold water to encourage condensation.

Upon completion of the test, all methods require a visual inspection of corrosion appearing on the polished surface, compared to that for a non-VCI control. Evaluation and grading of the plugs are followed in two steps. First, the control plugs must contain significant level of corrosion. If no corrosion is observed on the control plug, the entire test must be rerun. For rating of the plug, the system is slightly different for each VIA test. For MIL STD a rating system of 0-4 is applied where 0 represents no observable corrosion spots and 4 represents >4 corrosion spots. For NACE and TL8135 the rating system is reversed where 4 represents zero corrosion (under magnification) and 0 indicates significant corrosion. The NACE and TL provide a rating chart (Chart 1.) with a visual of what constitutes corrosion at each level of corrosion. This is a helpful guide for the users to compare one plug from another.

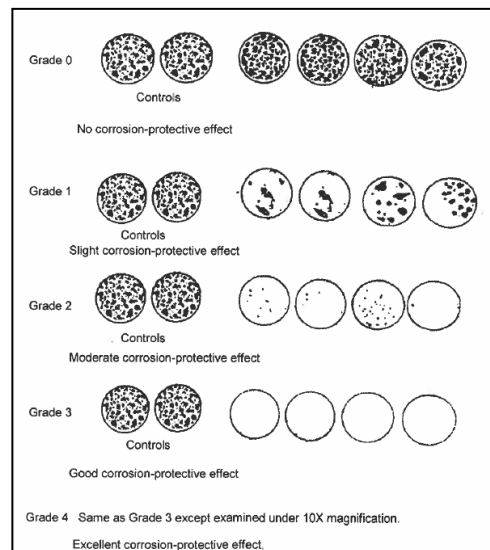


Chart 1. Rating Diagram for NACE and TL8135 VIA Tests.

RESULTS AND DISCUSSION

There are 3 main areas of the tests above that were evaluated in this paper: cleaning solvent, sandpaper quality and conditioning temperature. To assess whether the variable being tested was significant all tests were repeated with 3 different suppliers of VCI paper. The supplier papers will be referred to as VCI A, B and C. These papers are from highly reputable suppliers that have proven effective in several applications protecting steel in shipping and storage. This research paper is not trying to prove the effectiveness of one paper over another. This paper is to clearly demonstrate how slight changes in the procedure can affect the results obtained, no matter the VCI product used. These variables will be evaluated on all 3 VIA tests. NOTE: All tests results, unless otherwise declared, were run by a single operator to remove any variability that could occur between operators and laboratories.

Variable 1: Cleaning

The NACE TM0208 test identifies that recommended solvents for cleaning metal specimens be first hot mineral spirits then 1 boiling methanol wash/rinse. Some users may find these solvents concerning due to their flammability and toxicity hazards. The method does state that *alternate reagents: ethanol, isopropanol, acetone (may be used as alternates to methanol for rinsing specimens)*. If changes are made, they must first be verified to ensure no adverse effects occur. This section discusses variations in test results for NACE, MIL and TL8135 VIA tests when solvent changes are made.

Anticipating a novice operator may try to save time we repeated the testing using a single solvent system. We ran a test without washing the plugs with mineral spirits and just a methanol wash. We ran this test 3 times to ensure the data was repeatable and valid. As you can see from the Table 2, comparing to the mineral spirits/methanol protocol using a single methanol solvent system did not affect the outcome.

	Control	Sample 1	Sample 2	Sample 3
Mineral Spirits, Methanol Boil				
VCI A	0	3	2	3
VCI B	0	3	2	2
VCI C	0	3	3	2
Methanol Boil. Repeatability - 1				
VCI A	0	3	3	3
VCI B	0	2	3	2
VCI C	0	3	3	3
Methanol Boil. Repeatability - 2				
VCI A	0	3	3	3
VCI B	0	3	3	3
VCI C	0	3	3	3
Methanol Boil, Repeatability - 3				
VCI A	0	3	3	3
VCI B	0	3	2	3
VCI C	0	3	3	3

Table 2: NACE TEST RESULTS (0 = no protection, 3 = complete protection)

This was repeated for ethanol, isopropyl alcohol, and acetone, Table 3. For the alcohol series there is slight difference in data. All papers showed excellent, averaged data for the ethanol and isopropyl alcohol series. In Table 2, we saw VCI B repeatedly showed a level 2 amount of corrosion. For the acetone series, VCI paper B showed a significant difference in the performance results. In all 3 specimens tested there was noticeable corrosion observed. This is interesting for two reasons. This data demonstrates that acetone may not be a good enough solvent remove all trace materials on the plug. In addition, if we ran this study with only one type of VCI paper we would have missed this variation in data and assumed there was no difference when alternative solvents are used.

	Control	Sample 1	Sample 2	Sample 3
Ethanol Boil				
VCI A	0	3	3	3
VCI B	0	3	3	3
VCI C	0	3	3	3
IPA Boil				
VCI A	0	3	3	3
VCI B	0	3	3	3
VCI C	0	3	3	3
Acetone Boil				
VCI A	0	3	3	3
VCI B	0	1	1	1
VCI C	0	3	3	3

Table 3: NACE TEST RESULTS (0 = no protection, 3 = complete protection)

To push the limits of the cleaning process, we wondered what results would be obtained if opted to not boil the samples but just wipe the polished surface with a single solvent system. Following sanding with 240 and 400 grit sandpaper, the steel specimens were wiped with a lint-free towel that was soaked in either, methanol, ethanol, isopropyl alcohol, or acetone. A fresh, clean towel was used for every plug so not to cross-contaminate test specimens. This data in Table 4 shows an opposite effect to the previous. By using a clean towel and physically wiping the face of the specimen there is no differentiation in the type of VCI paper used all provides perfect results. We would consider this a false positive scenario and need to further investigate the phenomenon.