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thesis entitled

CORROSION INHIBITION: ART OR SCIENCE?

presented by

William J.O. Green

has been accepted towards fulfillment
of the requirements for

Master of Science degree in Packaging

Major professor

Date 7/2/97

CORROSION INHIBITION: ART OR SCIENCE?

By

William J.O. Green

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

School of Packaging

1997

ABSTRACT

CORROSION INHIBITION: ART OR SCIENCE?

By

William J.O. Green

A Volatile Corrosion Inhibitor or VCI is a chemical, which can be incorporated into a packaging medium, that vaporizes to inhibit the corrosion of metals. Three of the several theories about the mechanism by which VCIs inhibit corrosion are the neutralizer, scavenger, and barrier-former theories.

Federal Standard 101C Method 4031B is a published test used by the Federal Government to simulate the aging process of a VCI material, by removing a portion of its VCI coating before testing. MIL-P-3420F is another published test used by the military to measure a VCI material's compatibility with copper, as well its long term protection of steel in an outdoor environment.

The VCI industry does not have any standardized tests which gauge the performance of VCI materials. The question of whether or not a standardized test would be beneficial was posed to six VCI manufacturers and 10 end users of VCI products. Three of the six manufacturers said it would not be beneficial, while nine of the 10 end users said it would.

A recommended standardized test, based on Federal Standard 101C Method 4031B and other studies done on VCI and other related fields, enables the user to evaluate the short term effectiveness, as well as project the long term protection of a VCI paper product.

Dedicated to all African-Americans who opened the doors of educational opportunity for all people. Your legacy lives on.

ACKNOWLEDGMENTS

I would like to extend a special thanks to my major professors, Dr. Selke and Dr. Lockhart, for their direction and guidance throughout the course of this study and in preparation of this manuscript.

I would also like to extend my deepest gratitude to my father George, my mother Shirley, my sister Roni, and my beautiful bride-to-be Karla, whose love, support, and friendship have inspired me to new heights. This is as much your accomplishment as it is mine.

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Background and Overview of the VCI Industry

Background

In 1943, Dr. Aaron Wachter was experimenting with nitrate compounds in hopes of finding an additive that would prevent the corrosion of gasoline pipes. He discovered that the compound he had placed in a desiccator had gone from solid phase to solid phase, without going through a liquid phase. Part of the compound had crystallized on the lid of the jar, and he analyzed the newly formed crystals, which turned out to be amine nitrates. Dr. Wachter realized that the volatility of amine nitrate might be combined with its corrosion inhibiting potential. Thus were born Vapor Phase Inhibitors, later to be named VCI (Volatile or Vapor Corrosion Inhibitors) (1).

Dr. Wachter, along with other researchers at Shell Oil Co., decided to experiment with the compound, in order to incorporate it into a paper substrate. They came up with a diisopropyl amine nitrate which could be used with paper in the form of a coating. The coating did inhibit corrosion of ferrous metals; however, it was extremely volatile and would only offer short-term protection. In order to counterbalance this, they combined diisopropyl amine nitrate with dicyclohexylamine nitrate, a similar compound with a much lower volatility. This new compound was able to inhibit the corrosion of ferrous metals for a much longer period of time (1).

One of VCI paper's first applications on a large scale was in the protection of U.S. M1 rifles in the Korean War. Traditionally, the rifles were coated with a heavy coating of a preservative grease known as cosmoline. Using this method, however, proved to be time-consuming when the rifles were unpacked and made ready for combat. Each rifle had to be taken apart and degreased, a process that took approximately 2 hours and 45 minutes (2). When the same rifles were coated with a light oil substance and wrapped in a VCI treated paper, they could be unpacked and made ready for combat in 3 to 7 minutes. The man-hours saved were approximately 2,600,000 hours for every 1,000,000 rifles shipped. There was also a savings of approximately $2 in packaging costs for every rifle shipped (2). Therefore, the VCI packaging application saved time and money in a period when both were at a premium.

What is VCI?

VCI is a chemical which can be incorporated into paper, plastic, and foamed plastic cushions or used in crystalline, powder, or liquid form, which inhibits the corrosion of metals. The VCI chemical vaporizes and the VCI treated packaging material does not have to be in contact with the metal it is protecting. Also, VCI can inhibit corrosion in the presence of humidity and oxygen. There are no published standards for the performance of VCI products. There are, however, conditions which the VCI treated packaging needs in order for it to provide adequate protection.

1. The VCI formula has to be compatible with the metal it is protecting. In some cases, VCI has been known to cause corrosion instead of inhibiting it, and in other cases, a particular VCI chemical has no effect on inhibiting the corrosion of some types of metals (3).

2. There has to be proper air circulation over the products to be protected in order for the VCI vapor to effectively inhibit the corrosion of all the parts of the product. If the vapor cannot surround the entire product, the parts that are not surrounded by

the vapor will not be protected, and may corrode.

3. There has to be active VCI (VCI which is vaporizing and not VCI which is "dormant" within the packaging substrate) in adequate concentrations present in the system in order for it to inhibit corrosion. When the VCI is used up, or permeates out of the system, the protection against corrosion ceases.

The exact mechanism by which VCI works is unknown; however, there are several theories on this subject. One theory is that it prevents oxygen from reaching the surface of the metal, by combining with the oxygen in the atmosphere. Another theory is that VCI works like a neutralizer, and removes H^+ ions from the environment. What seems to be the most popular theory is that the VCI vapor is adsorbed onto the metal surface and forms a protective layer against corrosion (3). This process is similar to the passivation process. The actual mechanism could incorporate one or all of these theories; however, it is known is that VCI does indeed inhibit corrosion of metals, under the conditions previously stated.

The mechanism may also be difficult to discern because of the variety of VCI formulas. The diisopropyl amine nitrate and dicyclohexylamine nitrate formula is not the only formula on the market today. There are now several different formulas that can be classified as Volatile Corrosion Inhibitors. Some published formulas include: dicyclohexylammonium nitrite; sodium nitrite and urea; sodium nitrite, urea, and monoethanol amine benzoate; amine salts; diisopropyl amine nitrite (4); and dicyclohexylamine nitrite (1). Many other formulas incorporate, but are not limited to, combinations of these compounds. Other compounds, not listed here, are also included in VCI formulas, but are kept secret by VCI manufacturing companies for proprietary reasons. It is because of the many different VCI formulas and the fact that several are kept secret that it is difficult to ascertain the exact mechanism for their corrosion inhibition. The mechanism or mechanisms could be different for every formula.

There have also been several advancements since the early 1950's. For one, VCI protection is no longer limited to ferrous metals. There are now formulas that can inhibit the corrosion of non-ferrous as well as ferrous metals. This is useful, because many products today are not only made of steel, but other metals and alloys as well.

Another advancement is that the VCI chemical can be incorporated into other substrates, such as plastic, as well as into paper. VCI formulas can be impregnated into polyethylene films which can provide a water vapor barrier as well as slow the VCI vapor from permeating out of the system. They can also be incorporated into polystyrene foams, which can be used for cushions as well as insulation. Other products include VCI crystals and tablets that volatilize and protect metals, liquid inhibitors, and petroleum-based inhibitors.

An Overview of VCI in Industry

The VCI industry has changed since the 1950's, when there were just a few industries which used VCI products. VCI is not limited to the military and oil industries any more. Now applications of VCI span many different industries. A few of these applications include: preservation of ball bearings, preserving automotive parts, and placing VCI products between the inside and outside hulls of double-hulled ships.

VCI is not just limited to one or two suppliers, either, like it was in the beginning.

There are several companies that manufacture and distribute VCI products, in a now-competitive VCI industry. Contributing to this competition is the fact that there are many different VCI formulas that are used, most of which are kept secret by the VCI manufacturers. Also, there is not much sharing of information between the VCI manufacturers, especially of new advancements, because of this competition. However, with competition comes the drive to keep moving ahead, and finding new and better ways to improve your product and services, before your competitor does the same.

Informal discussions were held with representatives of six companies, all of whom manufacture VCI products. The question asked was whether having an ASTM or other standardized test regulated within the VCI industry was a good idea. Three company representatives said that there was no reason to have this type of test, for various reasons:

1. The federal and military standards that deal with the testing of VCI products are sufficient for their information. The tests have been used for years, and seem to do an adequate job in predicting the performance of their products.

2. Their main objective is to solve their customers' problems, and they do not need this type of test to do this.

3. They already have their own tests which do a good job in helping them predict the performance of their products.

One company abstained from commenting, for proprietary reasons. Of these three companies, two said that they would get involved with the design of a standardized test if one was being made.

Two of the companies said that a standardized test was a good idea, and gave these reasons for their opinions:

1. They were concerned that other companies were passing off contact inhibitors as VCI products. As stated earlier, a VCI product must be able to inhibit corrosion without contact with the metal it is protecting.

2. It can let them tell their customers just how well it will work for them. In their experience, many customers just want to know how the product will work for them. Many of them cannot interpret the results from some of these tests, and want the test results in a terminology that they will be able to understand.

3. The VCI companies want to know how their product will perform compared to their competitors' products. Again, because of the competitive nature of their industry, the VCI companies are always wondering how they stack up against the companies they are competing against.

Informal discussions were also held with 10 end users of VCI products. Nine of the 10 companies were in favor of a standardized test, while one said that it would not matter to them either way. The nine companies in favor of a standardized test gave these reasons:

1. They wanted to know just how long a product would give them protection, in certain environments. A few companies were concerned that the tests now being used were not telling them the longevity of the products they were using. Also, they were not sure if the product would work in a tropical as well as a temperate environment for an extended period of time.

2. Certain tests do not emulate the conditions that their product would be in. Some were unaware of any cyclic tests that would simulate the conditions on a ship or in a warehouse. Also, tests done are usually of short duration, in high temperature and high humidity environments. However, if a company wants a longer-term storage in a tropical environment, which has high temperature and humidity all the time, they are unsure that the VCI will work in this situation.

3. They want to be able to make comparisons between VCI suppliers. Some end user representatives said that they have seen test results from different VCI suppliers, all showing different results. These representatives think that some of the results may have been slanted for the VCI supplier that did the testing.

4. Some end users are concerned that some VCI companies are making false claims about their products. Again, they cannot interpret the results of the tests done, so they cannot draw their own conclusions from these tests.

5. Some are unaware of any long-term testing done. These companies were not convinced of the performance of the products, when the results were taken from accelerated tests.

This was an informal discussion, not a survey; however, it did bring to light many questions concerning testing that are coming up today in the VCI industry, such as:

1. Should there be a standardized test for VCI products?

2. Are any of the present tests (for example, military and/or federal standards) good enough, or should there be new tests designed for this purpose?

3. Could short-term tests be adequate for predicting long-term performance?

4. Can the competitive VCI industry reach some kind of consensus on this matter?

Chapter 2
Testing Process

Decisions Made Regarding Testing of VCI Paper

A VCI manufacturing company, referred to here as Company A, wanted to test several of their VCI products for ferrous metals, and their Multipurpose Inhibitor (MPI) products, which provide protection for nonferrous metals. MPI products are used to protect ferrous as well as nonferrous metals. They wanted to see how well their products would perform over a longer period of time, in an environment in which the conditions could be controlled. Company A also wanted to test a few of their competitors' products to see how they compared with each other. The objectives were different than in those in the federal standard (6), and military specifications (5). They wanted a long term storage test in a controlled atmospheric environment set at 100°F and close to 100% relative humidity. Federal standards (6) and military specifications (5) use these tests just to see whether the VCI papers will meet their specifications. These publications were used as a benchmark; however, since the testing goals were different, the procedures needed to be modified. This required that a number of decisions be made.

The first decision was what type of container the samples would be stored in. Military Standards call for single specimens stored in glass jars approximately 3 inches in diameter with screw tops (5). This method presented a difficulty because of the number of samples to be tested, which would require too much space in the humidity chambers, which were also in use for other non-related experiments. So, from the standpoint of space, it was better to use larger 5 gallon plastic buckets with many specimens in each one.

Another question faced was how to wrap the metal test panels in the VCI paper. Due to the nature of the VCI chemical, the test panels did not need to be completely wrapped in VCI paper. To work, they only needed to be in close proximity with the paper, and in a semi-contained environment. The decision was made to wrap the test panels in the VCI paper, using a conventional drugstore wrap (see Figure 1), which completely covers the test panels. This decision was made because of the nature of the VCI chemical, as well as the kraft paper that contained it. Paper is an extremely poor water vapor barrier, and an even poorer oxygen barrier. Because water vapor and oxygen are the primary contributors to the corrosion process, it was concluded that even if the VCI paper completely covered the test panel, it would still not stop the water vapor and oxygen from reaching the test panel.

After deciding how to wrap the test panels, the next decision was how to keep the paper on the test panels. The MIL-P-3420F (5) calls for nylon string to keep the paper in contact with the test panels. However, using a string to close over 200 samples would be a very time-consuming task. The decision was made to keep the VCI paper closed with rubber bands, which was much faster and easier.

The next decision to be made was how the samples were to be stored inside the buckets. The decision was to put them in racks and place them on top of a sufficiently ventilated platform (see Figure 2). The racks were thin and hollow, and had less than ⅛ inch contact with the samples. This allowed the air to flow over most of the surface area of the test panel. The racks were made of High Density Polyethylene, which is inert.

Figure 1 - The Conventional Drugstore Wrap

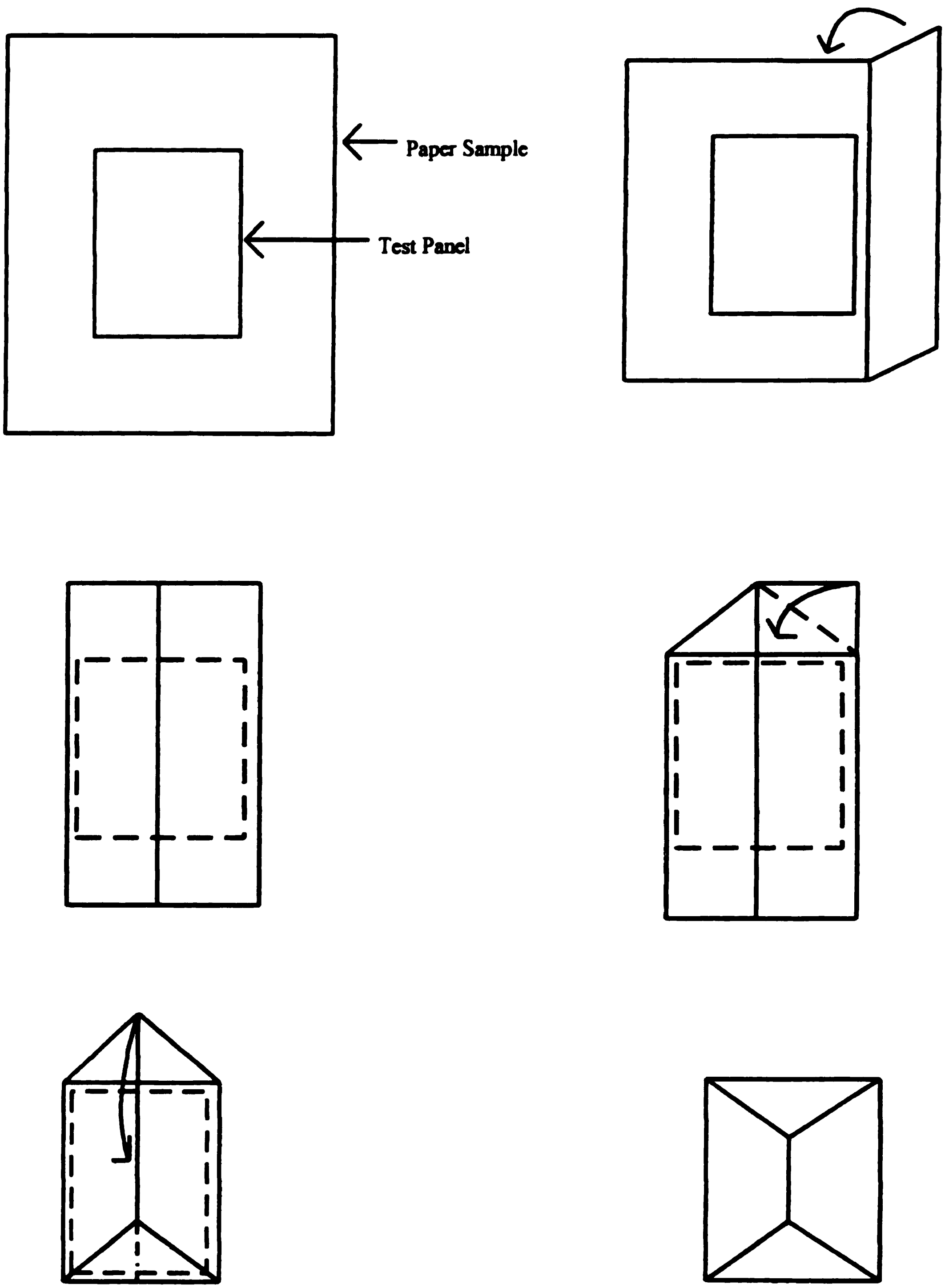
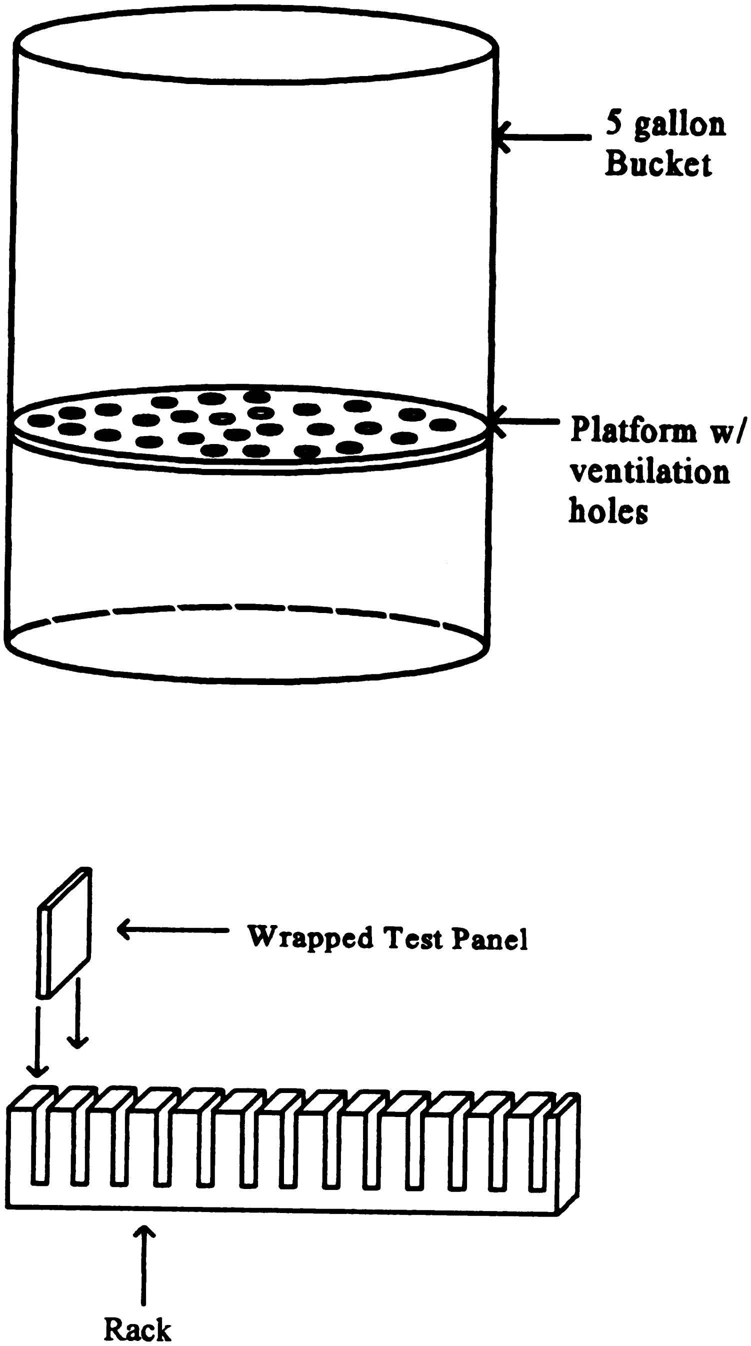


Figure 2 - Apparatus for VCI Test



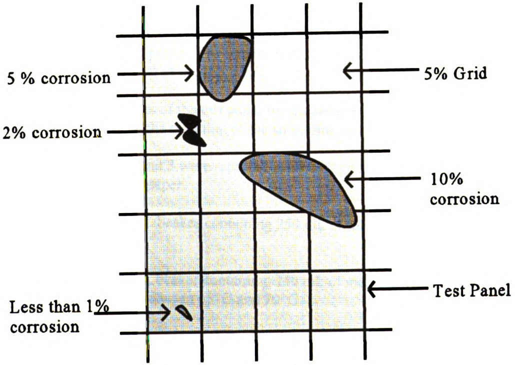
The platforms were strong enough to provide support to the sample racks, but ventilated enough to provide the airflow needed to keep the bucket at a level close to 100% relative humidity.

The method for evaluation was the next decision, and for this a "grid system" was used. The 2-inches by 1-inch test panels were divided conceptually into squares, each representing 5% of the surface area. The corrosion was evaluated visually. When corrosion was present inside one of the squares, the amount of corrosion was quantified by estimating the percentage of corrosion inside the square (5% being the maximum amount possible within a single square). If corrosion covered less than 1/5 of the square, less than 1% was reported (see Figure 3). This method is similar to the method that ASTM D 610-95 (7) uses.

The cleaning of the test panels was another issue that needed to be addressed. Grease, fingerprints and other substances that could affect the results of the test had to be removed before the test could start. The cleaning procedure chosen was similar to that of MIL-P-3420F (5). The 1020 alloy steel test panels were covered with a coat of grease, grime, and paint before they were cleaned, so it took several hours to effectively clean, polish and degrease them. In contrast, the brass and copper test panels were covered with only a thin coating of grease and could be cleaned much more quickly. During and after cleaning, the test panels were handled with plastic gloves and tongs only. After the cleaning process began, the test panels never came in contact with bare skin, or with contaminated surfaces, and they were stored in a desiccator until use.

The controls used in this test were the same test panels that were used with the

Figure 3 - Corrosion Evaluation



(18% corrosion on this face)

VCI paper, but these test panels were wrapped in 50# Kraft paper without VCI coating. They were stored and cleaned identically. The controls were used to demonstrate that corrosion took place if VCI was not used. However, due to a shortage of test panels, controls were not used for the nonferrous metals.

Test Methods for Testing of VCI Papers

Cleaning:

1. While holding the test panel stationary, use a wire brush to remove any visible corrosion from both sides of the test panel.

2. The test panel was then slid against 240 grit Aluminum Oxide abrasive paper. The strokes followed the direction of the short dimension of the test panel.

3. The edges of the test panel were then slid against the abrasive paper in the direction of the short dimension of the test panel.

4. Steps 2 and 3 were repeated using 400 grit Aluminum Oxide abrasive paper.

5. A 500 mL beaker containing 250 mL of toluene was heated to 75°C.

6. A 500 mL beaker containing 250 mL of methanol was heated to boiling, between 65°C and 70°C.

7. The test panel was then placed into the hot toluene bath for 20 seconds, using stainless steel tongs.

8. While in the toluene bath, the test panel was swabbed with gauze. It was then removed and placed on absorbent paper.

9. Steps 7 and 8 were repeated using a methanol bath in place of toluene.

10. The test panel was then stored in a desiccator until use.

Preparation and Storage:

1. The test panels were wrapped using the conventional drugstore wrap style (see Figure 1).

2. The wrapping was held in place with 2 rubber bands around the length and width of the sample.

3. A 5 gallon bucket was filled with approximately 5 inches of distilled water.

4. A ventilated platform was then inserted into the bucket and rested approximately 1 to 3 inches above the water.

5. 12 samples, each of the same type of VCI paper and containing the same type of metal, were placed in the rack so that they did not touch each other.

6. The bucket was sealed and marked for identification.

7. The bucket was placed into a chamber at for 100°F. The bucket maintained a relative humidity close to 100%.

Weekly Evaluation:

1. The bucket was opened, one sample taken out of the rack, and the bucket immediately closed.

2. The sample was opened.

3. Excess moisture was dried off the test panel using a clean paper towel. A dabbing technique was used, since a wiping motion could have caused corrosion to smear, giving a false percentage.

4. The test panel was visually evaluated for corrosion.

5. The amount of corrosion was compared to a paper square, whose size was equivalent to 5% of the surface area of the test panel. The corrosion present inside one of the squares was quantified by estimation (5% being the maximum amount possible within that particular square). If corrosion covered less than 1/5 of the square, "less than 1% was reported." <u>All</u> spots of corrosion were reported.

6. The test panel was then wrapped with an identifying mark including: the type of metal, type of paper, and the date.

7. The evaluated test panel was placed in a desiccator, in case further evaluations or comparisons were required.

Results of VCI Testing

Several different VCI products were tested. However, the purpose of this discussion is simply to illustrate the types of results which were obtained, so results from only five products are reported. These five products were manufactured by three different companies, which will remain anonymous. The results are listed in Table 1.

Table 1 - Results of Testing of VCI Paper

Ferrous Metals

Steel:

Control

Week 1	Heavy corrosion present over 40% of test panel. There are also two heavy concentrations of corrosion on the edges of the test panel.
Week 2	Heavy corrosion present on approximately 50% of test panel.
Week 3	Heavy corrosion present on 80% of test panel.
Week 4	Corrosion present on 80% of test panel. A extremely high concentration of corrosion is present on one side.

Sample X

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	No corrosion.
Week 5	No corrosion.
Week 6	No corrosion.
Week 7	No corrosion.
Week 8	No corrosion.
Week 9	No corrosion.
Week 10	No corrosion.
Week 11	No corrosion.
Week 12	No corrosion.

Table 1 (Cont'd)

Sample Y

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	No corrosion.
Week 5	No corrosion.
Week 6	No corrosion.
Week 7	No corrosion.
Week 8	No corrosion.
Week 9	No corrosion.
Week 10	No corrosion.
Week 11	No corrosion.
Week 12	No corrosion.

Sample Z

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	No corrosion.
Week 5	No corrosion.
Week 6	No corrosion.
Week 7	No corrosion.
Week 8	No corrosion.
Week 9	No corrosion.
Week 10	No corrosion.
Week 11	No corrosion.
Week 12	Faint corrosion present on 30% of face.

Table 1 (Cont'd)

Nonferrous Metals

Brass:

Sample A

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	No corrosion.
Week 5	No corrosion.
Week 6	Black marks beginning to form following the pattern of the rubber bands.
Week 7	Black marks increasing in size. Still following the pattern of the rubber bands.
Week 8	Black marks increasing in size. Still following the pattern of the rubber bands.
Week 9	Black marks widening and now are still following the pattern of the rubber bands.
Week 10	Black marks widening. Still same pattern.
Week 11	Same as last week.
Week 12	Same as last week.

Copper:

Sample B

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	Small black dots, on one facing, in the middle of the test panel, where rubber band is. Covers less than 5% of test panel.
Week 5	Black dots covering approximately 20 - 30% of the test panel. Dots are still located in the center where the rubber bands are.

Table 1 (Cont'd)

Week 6	Black dots covering approximately 25% of faces. Dots are increasingly darker, and more prevalent. Dots are in the same place as past weeks.
Week 7	Black dots covering approximately 25% of faces. Dots are increasingly darker, and more prevalent.
Week 8	Black dots covering approximately 25% of faces.
Week 9	Black dots covering approximately 20% of faces.
Week 10	Black dots covering approximately 20% of faces. However, no other corrosion present.
Week 11	Black dots covering approximately 20% of faces, black dots are following the same pattern, and look the same as last week.
Week 12	Black dots covering approximately 20% of faces, black dots are following the same pattern, and look the same as last two weeks.

Discussion of Results

Following a minor complication during the first weeks of testing, which necessitated retesting and will be discussed later in this section, the steel control samples showed signs of corrosion after the first week of testing. The amount of corrosion increased significantly from the first week to the second week. The third and fourth week samples were almost completely covered with a thick coat of rust, and the evaluation of the controls was discontinued after the fourth week.

Sample X and sample Y both showed no signs of corrosion throughout the entire duration of the 12 week test. Significant condensation occurred on all of the samples, due to the high humidity level, but the two samples offered protection for the duration of the test. If the time it takes to exhaust the VCI coating is to be determined, a longer duration test would be needed. Sample Y showed faint corrosion after the twelfth week of testing. From this it can be assumed that at this particular temperature and humidity, protection will cease after 12 weeks of exposure. The corrosion did not follow the pattern of the rubber bands, as it did with the nonferrous metals. Therefore it was determined that the rubber bands did not have an effect on the rate of corrosion in the ferrous samples.

Sample B, which contained a test panel made of copper wrapped in MPI paper, showed unusual corrosion after the fourth week of testing. The tarnish followed the pattern of the rubber bands holding the VCI paper closed, and it was determined that the rubber bands were causing the corrosion. Sample A, the brass test panel, showed signs of corrosion which followed the same pattern as Sample B. It was determined that it too was corroding prematurely because of the rubber bands.

As discussed below, even though every contingency thought of was covered, problems still arose during and after the testing process. Some of these problems were frustrating, but these mistakes proved to be invaluable for learning about the testing processes of VCI materials.

During the first few weeks of testing, the controls did not rust. Because of previous testing, it was known that the controls usually rust within a few days of testing, and almost always after 1 week of testing. However, this did not occur in this case. The samples and the bucket were evaluated, and it was found that the platform in the bucket was not sufficiently ventilated. The platform used in the control bucket was different than that used in all the other buckets, because of a shortage of suitable platforms. Another platform was made for the control bucket, but it did not contain as many ventilation holes and they were not as wide as the ones in the other platforms. In response to this problem, a new platform, with the same size and amount of ventilation holes as the other platforms, was built. Also, new test panels and 50# Kraft paper were used to rerun this part of the test. The result was that the samples showed signs of corrosion after the first week. All the VCI papers lasted longer than 1 week, so this proved that using the VCI papers instead of nothing did make a difference in inhibiting corrosion.

In MIL-P-3420F (5), nylon string is used to keep the paper closed on the metal samples. This method proved to be time-consuming for the large number of samples involved, so the decision was made to use rubber bands to keep the paper closed on the metal samples instead of the nylon string. It was not known until later that the acid in the rubber bands would cause premature tarnishing in the copper and brass samples. A thick mark of black tarnish appeared on the samples, and followed the pattern of the rubber bands contact with the paper outside the samples. This invalidated the results we got for the copper and brass samples. The remaining metals were unaffected by the rubber bands.

Another concern that arose after the testing was over, was that tight rubber bands or even nylon string might "squeeze" the VCI chemical out of the paper, and cause premature corrosion of the samples where the rubber band or string was tied. Also, rubber bands or nylon string might impede the air flow over the area that they are covering. These situations do not usually arise when VCI is used in non-contact situations.

As stated before, all these setbacks contributed to problems with this particular test; however, they were very valuable in improving knowledge about VCI testing. This knowledge was used in later tests performed on VCI materials.

Decisions Made Regarding Multipurpose Inhibitor VCI Paper Long Term Testing

As stated earlier, the Multipurpose Inhibitor (MPI) is a type of VCI product that is used for both ferrous and nonferrous metals. MPI paper was evaluated in the first test; but the results were invalid, because the rubber bands used to close the paper on the test specimens affected the results. Therefore, Company A decided to test these materials again. Because there were difficulties with the last test, some changes in the test procedure were initiated.

First, a shorter time frame, 6 weeks instead of 12 weeks was used. Therefore, only 6 test specimens were required instead of 12. This served to speed up the preparation time, as well as the testing procedure.

Another decision made was to use different test panels. Even though the steel test panels were made from the same alloy as the previous test (1020 steel), the two types of test panels differed in other ways. The test panels used before were very small and did not have a hole in them to facilitate hanging. The new test panels had a hole near the top and because of higher initial quality (they were much cleaner than the previous test panels) were much easier to clean than the panels used in the previous test. The dimensions of the new test panels were 3 ½ inches by 6 inches , which was considerably larger than the test panels used previously.

The next decision was about how to replace the rubber bands used in the first test. As stated before, the rubber bands caused premature tarnishing of the copper and brass samples so they could not be used. Nylon string was considered, but as stated before, there was concern that it might squeeze the VCI chemical out of the paper, and have an effect on the test. Therefore, it was decided to use duct tape to keep the MPI paper closed during the testing procedure. Duct tape was chosen because it is durable, and does not come off when subjected to moisture. The tape would not squeeze the paper on the test panel, but it would still keep it closed.

Because the samples were much larger in size, putting them in racks to be tested, as in the first test, was not practical. Therefore, it was decided to use a hanging method similar to the long term storage test listed in MIL-P-3420F (5). The samples were hung using a folded-over piece of duct tape attached to the top of the sample with a long piece of nylon string threaded through it. The same nylon string was threaded through all the samples in the bucket, and attached to the top of the bucket. However, due to technical difficulties, explained later in this chapter, this method was changed. The new method threaded a small piece of nylon string through the hole near the top of the test panel. This string was then tied to a nylon string which ran across the top of the bucket (see Figure 4). Nylon string was used in this case because it is relatively inert and would not affect the results of the test.

Test Methods Used for Long-Term Testing of MPI Papers

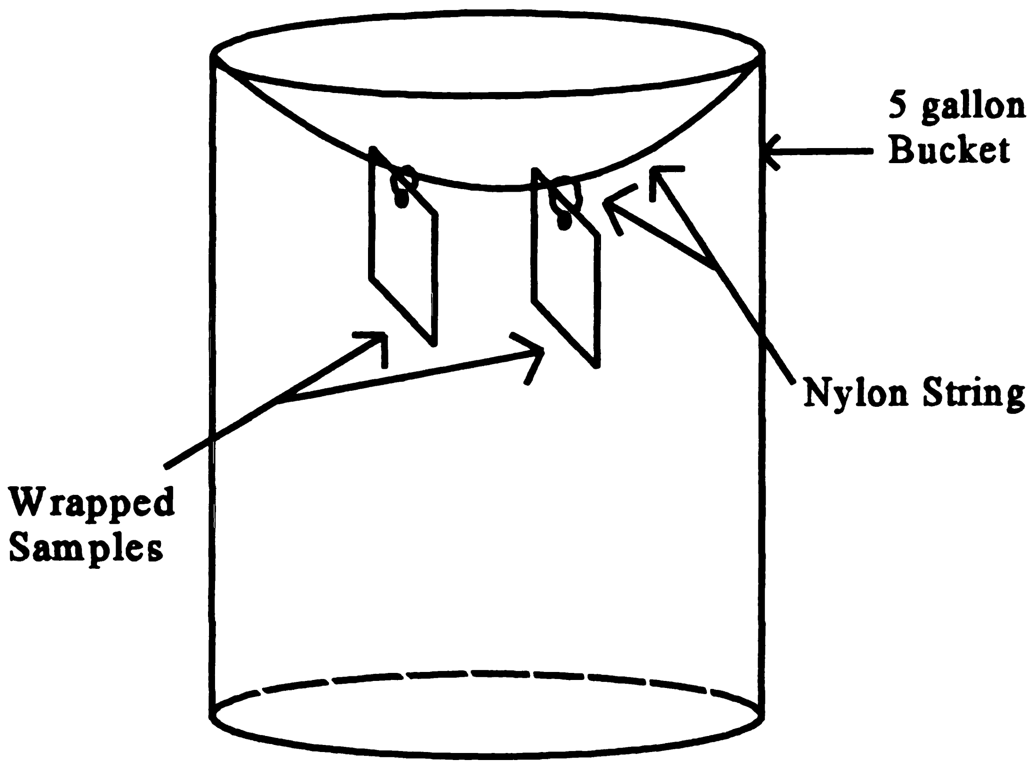
Cleaning:

See Cleaning Procedure for Long-Term Testing of VCI Paper.

Preparation and Storage:

1. The test panels were wrapped using the conventional drugstore wrap style.
2. A piece of duct tape was placed over each triangular fold on the closed sample.
3. A piece of nylon string was threaded through the hole in the test panel.
4. A 5 gallon bucket was filled with approximately 5 inches of water.
5. A long piece of nylon string was strung across the top of the bucket. The string was attached so as not to compromise the seal of the bucket.

Figure 4 - Apparatus for MPI Test



6. The piece of string threaded through the hole of the test panel was then tied to the string that was strung across the top of the bucket (see Figure 4).

7. Duct tape was rolled over the nylon string to act as partitions to keep the samples from sliding together.

Weekly Evaluation:

See Weekly Evaluation for Long-Term Testing of VCI Papers.

Results of Testing

The two products displayed here give a good illustration of the results obtained from this test. Each product is manufactured by a different company. Results are listed in Table 2.

Table 2 - Results of Test on MPI Paper

Steel:

Control

Week 1	Heavy corrosion on both sides and all edges.
Week 2	Heavy corrosion.
Week 3	Heavy corrosion.
Week 4	Heavy corrosion.
Week 5	Heavy corrosion.
Week 6	Heavy corrosion.

Sample F

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	No corrosion.
Week 5	4 very small spots of corrosion.
Week 6	Some very light spots of corrosion. Corrosion has increased since the last week.

Sample G

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion in test area, however corrosion outside of test area.
Week 4	No corrosion in test area, however corrosion outside of test area.
Week 5	Slight corrosion in test area (failure).
Week 6	Three small spots where corrosion is present.

Table 2 (cont'd)

Aluminum:

Control

Week 1	No corrosion.
Week 2	9 very small spots of corrosion on 1 side, and 6 spots on the other side. Spots are light but unmistakable.
Week 3	Very small flakes of corrosion with a very faint line of corrosion. Flakes are brown in color, but not from paper.
Week 4	Several small, light spots of corrosion.
Week 5	Same as week 4.
Week 6	Increased corrosion from week 5.

Sample F

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	No corrosion.
Week 5	A very light reddish discoloration that moves against the sanding grain. Uncertain if this is corrosion or not, this is not like the control.
Week 6	The reddish discoloration has increased from week 6.

Sample G

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	No corrosion.
Week 5	No corrosion.
Week 6	No corrosion.

Table 2 (cont'd)

Galvanized:

Control

Week 1	Corrosion on both sides. Also, test panel is hazy.
Week 2	Heavier corrosion with large spots of corrosion where wet paper contacted the test panel.
Week 3	Hazy corrosion on one side while hazy and more black spots on the other side.
Week 4	Dark grey spots all over test panel. Entire test panel covered with a haze.
Week 5	Entire test panel is hazy. Several gray spots are prevalent, and white spots are beginning to form inside the gray spots.
Week 6	Same as week 5.

Sample F

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	Several spots (10) of corrosion on one side of test panel. Corrosion is gray with a white center.
Week 5	More than 50 small spots of corrosion, on both sides of test panel.
Week 6	Corrosion has become extremely heavy, and the paper has rusted to the metal test panel.

Sample G

Week 1	Corrosion on both sides. However, corrosion is very dense and pronounced, with large black dots with white dots in the center. These results are in the test area.
Week 2	Heavy spots of corrosion continue to multiply, now have approximately 9 in test area.
Week 3	Same amount of heavy spots this week. Test panel is starting to become hazy.

Table 2 (cont'd)

Week 4	Gray spots with white center, continue to grow and multiply.
Week 5	Increased corrosion.
Week 6	Same as week 5.

Brass:

Control

Week 1	No corrosion.
Week 2	Slight tarnishing on several areas of the test panel.
Week 3	Light tarnishing on test panels.
Week 4	Tarnishing has increased, edges have black dots.
Week 5	Due to a shortage of test panels, 4 weeks was done instead of 6.
Week 6	n/a

Sample F

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	No corrosion.
Week 5	No corrosion.
Week 6	Very light tarnishing of test panel.

Sample G

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	Water spots on test panel, but this is not corrosion.
Week 4	A lot of tarnishing on test panel, however, there were fingerprints. Test panel was deemed invalid.
Week 5	Due to a shortage of test panels, 4 weeks was done instead of 6.
Week 6	n/a

Table 2 (cont'd)

Copper:

Control

Week 1	No corrosion.
Week 2	Tarnishing present on most of the test panel.
Week 3	Increased tarnishing present on test panel, tarnishing is heavier than last week. Black dots are present this week.
Week 4	Increased tarnishing present. Black dots have increased in number and size.
Week 5	Test panel is almost totally covered with tarnish, and black dots are still increasing in number.
Week 6	Test panel covered with tarnish, and black dots are covering most of test panel.

Sample F

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	Light tarnishing is present in one small spot.
Week 5	Increased tarnishing from last week, but still not more than a few spots.
Week 6	Same amount of tarnishing as last week.

Sample G

Week 1	No corrosion.
Week 2	No corrosion.
Week 3	No corrosion.
Week 4	Several small spots of tarnishing on both sides. Tarnish is very light but unmistakable.
Week 5	Increased tarnishing from last week on both sides.
Week 6	Several spots of tarnishing on only one side of test panel. The other side is unchanged. Tarnished spots are darker than last week.

Discussion of Results

The steel and galvanized control panels both showed signs of corrosion after the first week, while the aluminum, copper, and brass control panels all resisted corrosion until after the second week of testing. This is due to the corrosion resistant properties of brass, copper and aluminum (3).

The steel test panels wrapped in both Sample F and Sample G showed signs of corrosion after the fifth week of testing. This demonstrated that the formula for the VCI paper that is used for ferrous metals gives much longer protection than the multipurpose inhibitor which is supposed to protect nonferrous as well as ferrous metals.

It seems that in the case of Sample F paper on the Galvanized test panel, the metal was attacked by the formula in the paper. Sample G actually did worse than the control. This could be due to an incompatibility between the formula in the VCI paper, and the zinc coating of the galvanized metal. In contrast, with of Sample F paper on the Aluminum test panel, there was no corrosion during the entire duration of the test. This was better than the control, which corroded in the second week.

The two different VCI paper samples performed differently on the various metals. Sample G outperformed Sample F on galvanized, and brass; however, Sample F performed better than Sample G on aluminum. It seems that different formulas give longer protection to certain metals than others. It may be advisable to develop more than one multipurpose inhibitor product, so that each product can be specialized more for specific metals. These two products demonstrated that there may not be a "cure-all" inhibitor for all ferrous and nonferrous metals.

As in the previous test, there were problems that arose during and after the testing procedure. The first problem was that after the first week, the tape holding the samples on the nylon string at the top of the bucket gave way, and the samples fell into the water at the bottom of the bucket. Thus, a new method of hanging the samples had to be devised.

As stated above, the test panels had pre-drilled holes in them near the top, and it was easy to make a hole in the paper. Therefore a string was threaded through the holes, and tied to the string that ran across the top of the bucket (see Figure 4). The holes were then covered with a small piece of duct tape in an attempt to prevent water vapor entering through the hole in the paper. However, the duct tape did not prevent moisture from reaching the hole in the test panels.

Another problem was that corrosion was concentrated around the hole. Sometimes there would be a small amount of corrosion around the hole, but nowhere else on the test panel. This may be because of the duct tape around the hole. It might have stopped the airflow around the hole, and hindered the inhibiting vapor from protecting that part of the test panel. Another reason could be that the moisture was concentrated at that part because of the string. Condensation could have traveled down the string, and into the hole, where it caused the corrosion. Because of this, a "test area" was established. The test area incorporated the area 1/8 inch and greater below the hole. All results located above the test area were disregarded.

Chapter 3
Theoretical Background and Literature Review

Theories About the Mechanism of VCI Corrosion Inhibition

As stated earlier, there are several theories about how VCI formulas inhibit corrosion. This is because there have been no published studies about the mechanism that VCI formulas use to inhibit corrosion, and that many of the theories about corrosion inhibition, as a general subject, have not been proven. Three of the most widely accepted theories about the VCI formulas' mechanism(s) are that VCIs act as neutralizers, scavengers, or barrier-formers. These theories were identified by Sheldon, Derby, and Van Dem Bussche in 1981 (3).

The neutralizer and scavenger theories are widely known but are accepted to a lesser extent than the barrier former theory. The neutralizer theory states that the corrosivity of an environment is reduced by the VCI formula reducing the amount of H^+ ions in the environment around the metal to be protected (3). The scavenger theory uses a similar mechanism to nullify the oxygen in the atmosphere, inhibiting the corrosion process by preventing it from combining with the water vapor molecules (8).

The most widely accepted theory today is the barrier former theory. This theory states that a thin layer of inhibitor, usually a small number of molecules in thickness, is adsorbed onto the metal surface (3). Once this is done, this layer retards the anodic / cathodic reactions and slows the corrosion process to an acceptable rate. This layer behaves similarly to a passivation layer, in that it satisfies the chemical affinity of the metal and significantly reduces the corrosion process (11). There are also theories on how the VCI formula achieves this. One theory suggests that when a nitrite is adsorbed onto the surface of the metal, a reaction occurs which produces oxide and ammonia. The same mechanism was proposed for other oxidizing inhibitors (3).

In all the published VCI formulas, there is one factor that remains constant. That factor is the presence of nitrogen, in one form or another (most of the formulas listed contain nitrite compounds). However, corrosion inhibiting properties are not limited to compounds containing the element nitrogen. Other elements from Groups V and VI of the Periodic Table (phosphorous, arsenic, oxygen, sulfur, and selenium) contain corrosion inhibiting characteristics, when used in aqueous solutions (3).

One or all of these theories could provide the actual mechanism or mechanisms for VCI's corrosion-inhibiting characteristic. Knowing the mechanism of corrosion inhibition is not important in determining if a product should be classified as VCI. VCI's defining characteristic is that it gives off a vapor that inhibits the corrosion of a particular metal to which it is in relatively close proximity. Nonetheless, knowing the mechanism and understanding how and why VCI works could aid in the advancement of VCI technology.

Factors Which Influence VCI Performance

The purpose of tests is to simulate how a product or package will perform when it is used in the distribution environment. The problem with simulations is that they cannot account for all of the variables which occur in reality. Nonetheless, they can be very good tools in estimating how well a product or package will perform, if they can account for enough of the variables which are most likely to occur in the distribution environment.

There are several factors that can influence how harsh a distribution or storage environment is for a metal product. The process of corrosion is electrochemical, electrons flowing from a higher energy area (anode) to a lower energy area (cathode), either between two metals, or within the same piece of metal (9). The electrochemical process is self-sustaining; however, it can be accelerated considerably by the presence of an electrolyte (commonly water) on the surface of the metal. There are many different factors that influence the performance of VCI products. The most important factors to consider in the construction of a standardized test are (1, 4, 8):

1. **Climate.** Location and time can influence what the climate will be like at any instant. The climate of Philadelphia, in a louvered shed, in the winter, at 8:00 a.m. will be different from that of Thailand, outside by the ocean, in the spring, at 11:00 p.m.. The global location, the relative location, whether it is inside or outside, the temperature, the time of the year, and the time of day all have a bearing on what the temperature and humidity levels will be. Many VCI end users ship products to many different places around the world. The climates can vary from temperate to tropical in a single trip.

2. **Temperature Changes.** In many cases, the temperature can vary from one time of day to another. This is especially the case if a product is stored in a location which is not climate-controlled. Temperatures generally increase in the daytime and drop at night. If a product is transported by cargo ship and stored near the top of a cargo hold, the sun can make the temperature go very high during the daytime, but at night when the sun goes down, the temperature can drop to a very low level. When this happens, there can be significant condensation within the package, which can reach the metal product and accelerate the corrosion process.

3. **Time.** How long will the product have to be protected? The VCI coating may be exhausted before the end of storage if a product needs a very long survival time.

4. **Volatility of the Formula.** What is the volatility of the VCI formula? This also relates to time. As stated in Chapter 1, the presence of active VCI formula in adequate concentrations is a key factor in the inhibition process. If a formula volatilizes too quickly, it will offer only short-term protection. On the other hand, if a formula volatilizes too slowly, significant corrosion might already take place before the formula has a chance to inhibit it. This is similar to the dilemma faced by Dr. Wachter when he was first working with VCI (1). Also, some VCI formulas have one or more components, which volatilize at different rates. These multi-component VCI formulas usually have one component which volatilizes quickly to provide short term protection, and one component which volatilizes more slowly to provide longer term protection.

5. **Compatibility.** Is the VCI formula or material compatible with the product it is supposed to protect? This is an important issue, because if a VCI formula or material is not compatible with the metal it is supposed to be protecting, it could <u>cause</u> corrosion, as was illustrated in Chapter 2.

6. **Contact or Non-Contact.** Will the product be in contact with the VCI material? It is possible that the contact could cause corrosion. It is also possible that the material will only inhibit corrosion if it is in contact with the metal substrate. The non-contact aspect is very important, because in many cases, the VCI material cannot be in contact with the entire surface of the product at all times. If the VCI material is only a contact inhibitor, it not only cannot be classified as a VCI product, but it may not effectively inhibit corrosion on the entire product (specifically the parts with which it is not in contact).

7. **Package Permeability.** Is the product in a package, and if so, what is the package's permeability? As stated in Hohf and Mohaupt (4), the duration for which VCI vapors remain inside a package is directly influenced by the permeability of that package. If a product is packaged with a strip of VCI paper and then placed in a corrugated box, the VCI vapors will permeate out of the package more quickly than if the same product and VCI paper

were packaged in a polyethylene bag (4).

8. **Salt and Other Electrolytes.** The presence of salt and electrolytes can also accelerate the corrosion process. When products are stored near oceans or distributed on ships, they can come in contact with significant amounts of salt water. This can accelerate the corrosion process faster than water alone.

9. **Type.** The type and amount of protection that a particular VCI formula supplies can vary. Different formulas in different circumstances work differently. Once again this was illustrated by Dr. Wachter when he experimented with different formulas in the 1940's (1).

10. **Intangibles.** There are many different situations and factors which arise during distribution and storage. Sometimes these unknowns can be predicted, but many times they cannot. A test cannot predict everything that will happen. Something different can happen to every package whether it is shipped at the same time or not.

Some or all of these factors can greatly influence how a VCI material will perform. These factors have to be taken under consideration when deciding what type of VCI material, packaging, and performance test or tests are to be used.

VCI Studies Done

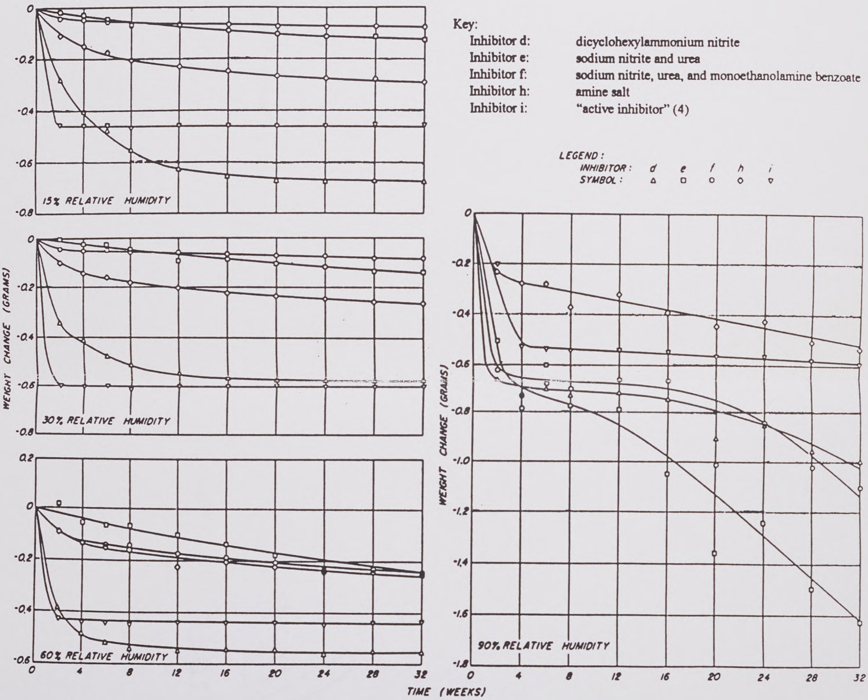
As previously stated, the permeability of the package that the VCI material is in can directly influence the longevity of the protection afforded. When VCI vapors permeate out of the system, they are no longer of use to the particular product which the VCI material is supposed to protect. In 1955, Hohf and Mohaupt (4) studied the effect of barrier materials in containing VCI vapors.

In this study, 19 different barrier materials containing six different VCI formulas, were tested for 32 weeks. Five of the VCI formulas were contained in a paper medium, and the sixth was in crystal form. The barriers were made into pouches and hung in several different humidity chambers with circulating air systems. Each humidity chamber exposed them to the same temperature (100°F) and a different level of humidity (15%, 30%, 60%, and 90% relative humidity). Every sample period, a new pouch was taken out of the humidity chamber and weighed and the difference in weight (for the entire pouch) from the initial weighing was recorded. This method could be used because a VCI coating has weight, and as the VCI coating vaporizes, a loss in weight can be observed. The controls used in this study were the five VCI papers that were used to provide the VCI vapors.

The researchers concluded that the barrier materials that contained aluminum foil were the most effective in containing the VCI vapors. Polyester scored the highest amongst the plastics tested. Polyethylene scored relatively low for five of the six formulas, but was effective in containing the sodium nitrite and urea formula. Kraft paper was determined to be ineffective in containing VCI vapors. All of the results (including the controls) were plotted on a graph of weight change vs. time. Hohf and Mohaupt also concluded that VCI volatility as well as transmission rates through the barriers increase as the relative humidity increases (4).

Because the controls were plotted on the graph, it is possible to get an understanding of how the VCI paper products examined in this study performed without the use of barriers to contain their vapors. Figure 5 displays the graphed results of the controls used in this study (4). From the 15%, 30%, and 60% relative humidity graphs, it

Figure 5 - Average Weight Loss of VCI Controls (4)



Key:

Inhibitor d:	dicyclohexylammonium nitrite
Inhibitor e:	sodium nitrite and urea
Inhibitor f:	sodium nitrite, urea, and monoethanolamine benzoate
Inhibitor h:	amine salt
Inhibitor i:	"active inhibitor" (4)

can be observed that *Controls e, f,* and *h* began displaying constant rates of weight loss by the eighth to twelfth week periods, illustrated by a downward sloping straight line. In comparison, *Control d* showed a much higher weight loss in the initial weeks of the test, then showed a constant rate of weight loss much later. *Control i* showed a large weight loss at the beginning of the test, then displayed a horizontal line (no continuing weight loss) for the rest of the test. The "horizontal behavior" displayed here is due to the complete exhaustion of the VCI coating.

At 90% relative humidity, only *Controls e,* and *h* exhibited behaviors consistent with 15%, 30%, and 60% relative humidity, the other *Controls d* and *i* displayed behaviors atypical of those observed at lower humidity levels. Also, the measurements for *Controls d* and *i* were not as precise as the other control samples. This atypical behavior and lack of precision is likely due to high amounts of moisture absorbed by the VCI paper. One of the observations made during the testing done for Company A (Chapter 2) was that some of the VCI products absorbed much higher amounts of moisture than others. This would account for the difference in behavior observed at the 90% relative humidity level. It may be possible to eliminate this variable, if a drying procedure was done to eliminate excess moisture before and after exposure. If this variable can be eliminated, it could be possible to extrapolate the downward sloping line and predict the length of time it would take for a VCI paper to be exhausted when it is exposed to a certain temperature and relative humidity.

Lee in 1987 (3) analyzed the effectiveness of sodium nitrite for corrosion inhibition. Because sodium nitrite is commonly used as a component in VCI formulas, parallels can be drawn from this study. Lee found that sodium nitrite's corrosion inhibition properties were directly influenced by temperature of the environment in which it is used. In the absence of any inhibitor, the corrosion rate increases for iron as the temperature is raised to 140°F, but at temperatures higher than 140°F, the corrosion rate decreases because of lower oxygen solubility. Conversely, when an inhibitor (sodium nitrite) is added in insufficient quantities to inhibit corrosion, the corrosion rate steadily increases as the temperature is increased above 140°F (3).

A study done by the U.S. Army in 1993 (10) evaluated the use of a differential scanning calorimeter (DSC)in determining properties of VCI formulas and materials. Because the VCI formula would, in many cases, volatilize at sub-ambient temperatures, it was difficult to determine its properties. However, in eight out of the 15 different samples tested, a peak was recorded at around 36°C, and properties such as temperatures of transition, energies of transition, and weight loss could be determined. The study concluded it was possible for a DSC to be used in determining some of the aspects of VCI exhaustion. However, the tests would probably need to be run at sub-ambient temperature for this type of procedure to work.

Federal Standard 101C Method 4031B

Federal Test Standard 101C entitled, "Test Procedures for Packaging Materials," contains test procedures which are used by the military, civilian federal agencies, and others for testing a wide range of packaging materials, including VCI products. Method 4031 "Corrosion Inhibiting Ability of VCI Vapors" (also called Vapor Inhibitor Ability or VIA) is used to determine the effectiveness of VCI products. This test method is divided into two parts, Methods A and B. Method 4031A is used for the testing of crystalline or liquid VCI products, while Method 4031B is used for the testing of "VCI treated materials" (6), which applies to VCI paper.

There are two main parts of this test procedure: a VCI exhaustion procedure and Corrosion Inhibiting Ability (CIA) test. The exhaustion procedure involves the removal of a portion of the VCI formula impregnated in the paper. The purpose of this procedure is to simulate a longer term storage situation, where some of the VCI impregnated in the paper has been used up. The CIA test follows the exhaustion procedure, and is used to determine if the VCI material will protect the metal product at the material's current state.

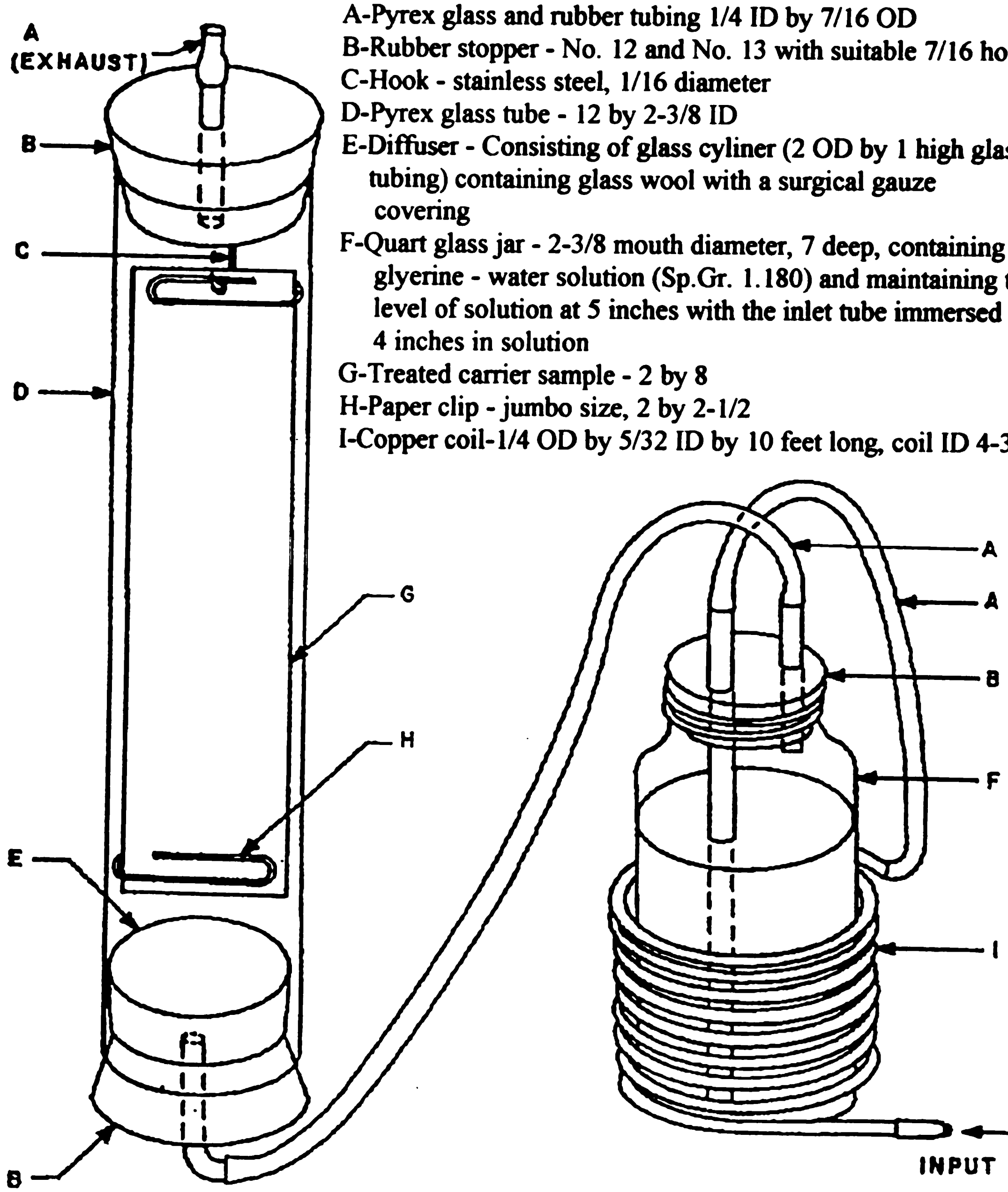
Methods and Materials for Exhaustion Procedure

The exhaustion procedure is done to simulate aging in the VCI material. There are two different sizes of the VCI treated materials that are used in this procedure, depending on whether the VCI material is used in bag or wrap form. If the material is to be used in bag form, then a 2 ½ by 8-inch sealed pouch (with the VCI-treated side forming the interior of the pouch) is used. The material is tested in pouch form, simulating how it will be used in the field, to allow a small amount of VCI vapor to be temporarily trapped on the inside of the package, thus giving the material a limited resistance to the loss of the VCI vapors. If the materials are used in wrap form, a 2 by 8-inch strip is used. An enamel or wax coated paper clip is placed on each end of the sample, and then a hole is punched 1/8-inch from one end of the sample.

The apparatus used in this procedure consists of a glass cylinder with rubber stoppers on each end (see Figure 6). Each rubber stopper has a hole through its center which is connected to a rubber tube. One tube is used as an inlet, and the other is used as an exhaust. The inlet tube is connected to the lid of a glass jar containing a glycerine-water solution, with a specific gravity of 1.180, which provides a relative humidity of 50 ±2% at 140°F. The glass jar's lid also has a second hole which is connected to another tube which is an input for fresh air which is blown in at 100 cubic centimeters per minute.

The sample is hung on the rubber stopper, which contains the exhaust tube, with a stainless steel hook. Once this is done, the sample and stopper are placed into the glass cylinder, so that the stopper plugs up one of the ends of the cylinder and the sample is inside the tube. At the bottom of the cylinder, a piece of glass wool wrapped in surgical gauze is sealed in with the inlet stopper. The entire assembly is then placed in a forced draft oven at 140 ± 2°F for 12 days. The air that is blown into the jar carries the air (which is at 50% relative humidity) into the glass cylinder. The air then passes over the sample and out of the exhaust tube. This means that the atmosphere inside the cylinder is 50% relative humidity. Fresh air is constantly circulated through the cylinder so that the air inside the cylinder is not saturated with the VCI vapor. All the VCI chemical that vaporizes is forced out of the system through the exhaust tube. Once the 12 day period has expired, the VCI specimen is taken out of the apparatus and cut into two 1 by 6-inch strips, in preparation for the CIA test.

Figure 6 - Apparatus for Exhausting VCI Treated Material (6)



A-Pyrex glass and rubber tubing 1/4 ID by 7/16 OD
B-Rubber stopper - No. 12 and No. 13 with suitable 7/16 holes
C-Hook - stainless steel, 1/16 diameter
D-Pyrex glass tube - 12 by 2-3/8 ID
E-Diffuser - Consisting of glass cyliner (2 OD by 1 high glass tubing) containing glass wool with a surgical gauze covering
F-Quart glass jar - 2-3/8 mouth diameter, 7 deep, containing glyerine - water solution (Sp.Gr. 1.180) and maintaining the level of solution at 5 inches with the inlet tube immersed 4 inches in solution
G-Treated carrier sample - 2 by 8
H-Paper clip - jumbo size, 2 by 2-1/2
I-Copper coil-1/4 OD by 5/32 ID by 10 feet long, coil ID 4-3/8

Materials and Methods for Corrosion Inhibitor Ability (CIA) Test

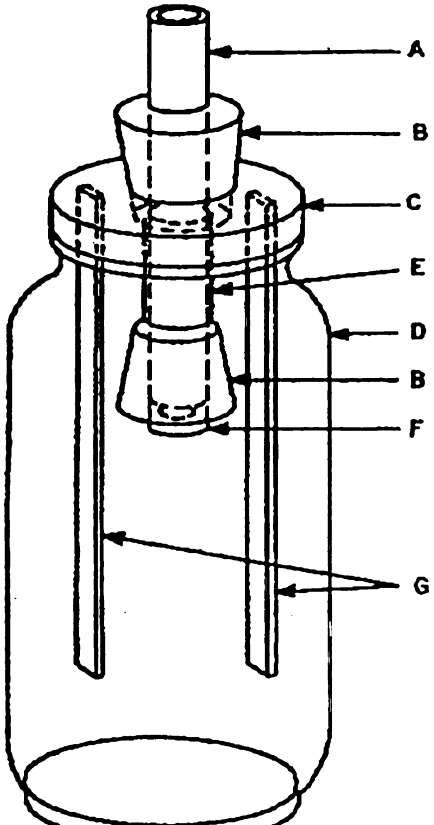
The CIA test is performed to determine if the VCI material can offer short term protection. This test uses a small steel cylinder, or plug, which is 5/8-inch in diameter and ½-inch in length. In one end, a hole measuring 3/8-inch in diameter and 3/8-inch in depth is drilled into the center of one of the round faces of the metal plug (see Figure 7).

The undrilled round face is abraded using 200 and 400 grit aluminum oxide abrasive. Iron oxide abrasives are not used, because they leave a residue which cannot be removed. The metal plug is then scrubbed with a clean brush or surgical gauze in a bath of hot mineral spirits (toluene). After this the plug is immersed in boiling methanol. The plug is then removed and allowed to air dry. The metal plugs must be stored in a desiccator until ready for use in the CIA test.

The apparatus for this test requires assembly before the test can be performed (see Figure 7). A hole, 1 3/16-inches in diameter, is drilled into the center of the lid of a quart size glass jar, and two slits, 1/4-inch wide by 1 ½-inches long, are made on either side of the hole. An aluminum tube is placed through the hole, and a stopper (with a hole bored through the center) is placed over the tube, holding the tube in place (the stopper should be on the outside of the lid). The metal plug is then placed on the aluminum tube, so that the hole faces the inside of the tube. Another stopper, similar to the one on the outside of the lid, is placed over the metal plug and part of the aluminum tube, so that it holds the plug onto the tube.

The precut VCI specimens are threaded through the slits in the lid, so that 1/4-inch is bent and taped onto the outer surface of the lid. The bottom of the jar is filled

Figure 7 - Apparatus for CIA Test (6)



A - Water retainer - Aluminum tube 4-1/2 in length, 5/8 OD and 1/2 ID. The tube shall have a capacity of 16 ml of distilled water at 75° ± 3°F.

B - Rubber stoppers - 2 #6-1/2 rubber stoppers with 1/2 hole bored through centers.

C - Jar lids - Plastic screw type lid, holes 1-3/16 drilled through center with parallel slits, 1/4 wide and 1-1/2 long formed 1/4 from the edge of the center hole.

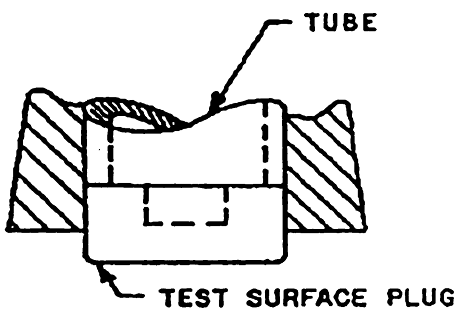
D - Jars - Quart size, mouth size 2-3/8 dia., 7 in height, ID of 3-1/4

E - Insulating sleeve - 1/2 ID rubber tubing, length 1-1/2.

F - Test surface plug - 5/8 dia., 1/2 long with flat bottom drilled in center with hole 3/8 deep and 3/8 dia.

G - Treated carrier samples 1 by 6.

DIMENSIONS IN INCHES.



ENLARGED VIEW OF "F"

with 10 millimeters of synthetic glycerine-water having a specific gravity of 1.076 which provides an atmosphere of 90% relative humidity at 75°F. The jar lid is closed tightly and sealed with a low water vapor transmission tape.

The assembly is then exposed for 20 hours at 75° ± 2°F. Once this is done, cold water, which is "40°F below ambient temperature" (6), is added to the aluminum tube, to cool the metal plug inside the jar. After three hours the water is removed from the tube, and the abraded part of the metal plug is examined for any corrosion. A control sample using kraft paper without a VCI coating is also run in accordance with the test procedure. If the control plug does not corrode, both the control and the VCI material are to be put through the procedure again. If the plug with the control paper corrodes, and the plug with the VCI material does not, then the VCI material passes, as it has been proved that the presence of the VCI material inhibited the corrosion of the metal plug. If both plugs show signs of corrosion, the VCI material fails, since it has been proved that the presence of the VCI material did not sufficiently inhibit the corrosion of the metal plug.

When used together, the exhaustion procedure and the CIA test provide the user with an idea of how well the VCI material works after it has been in the distribution/storage environment for a period of time. The exhaustion procedure is used to simulate aging by removing a portion of the VCI coating, and the CIA test is employed to determine if the VCI material can still offer adequate protection after it has been used for a period of time.

About Military Specification MIL-P-3420F

The military specification MIL-P-3420F, "Packaging Materials, Volatile Corrosion Inhibitor Treated, Opaque," is used by all the departments and agencies of the Department of Defense. Its function is to determine whether or not a type of VCI treated paper (or other type of VCI product that falls within the class of "opaque VCI treated packaging material") is acceptable for use. This specification contains not only tests to determine whether the VCI material is capable of inhibiting corrosion, but also tests for burst strength, tearing resistance, seam strength, blocking resistance, and water resistance. MIL -P-3420F also refers to several different tests outside the specification that must be met in order for the quality standards to be met. In addition it contains several nonperformance specifications, including but not limited to the size of rolls, methods of identification, and quality assurance provisions.

As stated earlier, a new opaque VCI material must be subjected to certain performance tests in order for the material to meet quality standards. The tests that pertain to the corrosion-inhibiting properties of the VCI material in question include: compatibility with copper, vapor inhibitor ability or VIA (taken from Federal Standard 101C Method 4031B) (6), VIA after exhaustion (taken from Federal Standard 101C Method 4031B), and long term protection. The compatibility with copper and the long term protection test methods are described in detail within MIL-P-3420F, while the VIA, VIA exhaustion, and contact corrosivity test methods are all described in different documents. The criteria of these tests must also be met in order for the VCI material to meet the quality standards for MIL-P-3420F.

There are two test methods that are described in MIL-P-3420. They are the compatibility with copper test, and the long term storage test. The compatibility with copper test is used to make sure that the VCI material will effectively protect copper from corrosion. The long term storage test is used to determine if the VCI material will effectively inhibit corrosion of steel for a 12-month period in a temperate climate.

Materials and Methods for Copper Compatibility Test

The procedure for preparing the copper samples is similar to that in Federal Standard 101C Method 4031. The samples are abraded with aluminum oxide abrasives and "washed" in hot baths of toluene and methanol. However, instead of using a small metal plug, a rectangular shaped test panel measuring 1/16 inch by ½ inch by 3 inches is used. Another difference is that after the test panels are abraded, they are bent into "U" shapes. The inside of the "U" will be the area that will be inspected for corrosion when the test is completed. As in the federal standard, the test panels are stored in a desiccator until they are ready to be used.

The samples are wrapped with a sample of VCI treated material measuring 3/4-inch by 3 ½-inches, with the treated side facing toward the panel. The barrier material is wrapped so that the length of the material is "perpendicular to the longitudinal axis and at the base of the open section of the U" (5). The material is then secured with nylon thread.

The apparatus for this test is simpler to assemble than its federal standard counterpart. A glass jar having a capacity of one pint is filled with 50 ml of synthetic glycerine-water solution, with a specific gravity of 1.103 at 75°F, which will give an atmosphere of 85 ± 3% RH at 150° ± 2°F. A glass vessel which would be suitable for a stage is then placed inside the jar with the flat part of the vessel facing upward. The stage should be higher than the glycerine solution, so that the flat part does not contact the glycerine solution. Three wrapped test panels are then placed on top of the stage so that the "legs" of the "U" rest upon the flat part of the stage. Caution should be taken, to prevent contact of the test panels with the glycerine solution. The lid is closed tightly onto the jar, and the test assembly is placed in a circulating air oven at 150° ± 2°F for seven days. After seven days has elapsed, test panels are unwrapped and the inside of the "U" is inspected for corrosion.

Materials and Methods for Long Term Test

Four rectangular steel test panels, measuring 2-inches by 4-inches by 1/8-inch with rounded edges, and containing two 1/8-inch diameter holes drilled at opposite corners of the 4-inch side, are used in this test. The test panels are abraded with aluminum oxide abrasives and "washed" in hot baths of toluene and methanol, using the same procedure as in Method 4031 in Federal Standard 101C (6).

A one cubic foot capacity RSC[1] or CSSC[2] style corrugated box, with all the dimensions being equal, is assembled for this test. All of the inner faces, except the top, of the box are completely lined with the VCI material to be tested, using staples to keep the material in place. The VCI treated side of the material should be facing the inside of the box. One of the four test panels is wrapped with a 6-inch by 6-inch piece of VCI

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[1]Regular Slotted Container.

[2]Center Special Slotted Container.

material, with a double fold in the middle of the panel face, and a single fold at each end. This is done to determine whether having the metal in contact with the VCI paper makes a difference.

The wrapped panel is then placed in the bottom of the box, with the folds facing down. The remaining three panels are suspended with stainless steel wires, with each end of the wires connected to the top edges on opposite sides of the box. The three panels suspended in the box are there to determine whether the vapor phase of the VCI material lining the box works. The box is then sealed with tape, and placed in a "louvered shed located in a temperate zone with climatic conditions similar to the Philadelphia area," for 12 months (5). After the 12 month time period has elapsed, the panels are removed and inspected for corrosion.

Performance Tests Some VCI Suppliers Use

As stated earlier, there are no industry-regulated standardized tests that pertain to the performance of VCI paper or other materials. Federal Standard 101C Method 4031B and MIL-P-3420F are both widely accepted test procedures. However, because the VCI industry is not government regulated, VCI suppliers are not required to use these tests. Some VCI suppliers use these published tests; however, they either change the tests or they use only part of them to see how well their product performs. Other VCI suppliers use their own tests to ascertain how well their products work. As stated in Chapter 1, this nonconformity has served to confuse the end users of VCI about what kind of protection they should expect from the VCI products they are buying. The following is a brief summary of performance tests used by some VCI suppliers, obtained during informal discussions.

Company A used the test described in detail in Chapter 2. To summarize, it is done at 100°F at 100% relative humidity, with a constant temperature and humidity. The duration is 84 days, and it is a contact test.

Company B uses a three-day four-cycle test. The test samples are placed in a jar over 40 ml of water and cycled through four different temperatures for different durations. The conditions are: eight hours at 70°F, 16 hours at 158°F, eight hours at 77°F, and 16 hours at 150°F. They use both a contact and a non-contact test.

Companies C and D both use Federal Standard 101C Method 4031B. However, they do not perform the exhaustion procedure, only the CIA test.

Company E uses Federal Standard 101C Method 4031B, but also does not perform the exhaustion procedure, only the CIA test. They also do a contact corrosion test where the test panels are wrapped in VCI material and placed in a quart jar over 30 ml of water for 72 hours at 120°F. In addition they perform an accelerated short term test. In this test, the test panels are placed on a small Lucite table and the VCI material is placed around the outside of the table (so that it is not in contact with the test panels). The test panels are then placed in a quart jar above 30 ml of water (see Figure 8). The test assembly is placed in an oven at 140°F for 60 minutes, and then allowed to cool for 40 minutes at room temperature. The test lasts for two cycles, with a period in between each cycle for a brief inspection of the panels for corrosion.

Discussion of Tests

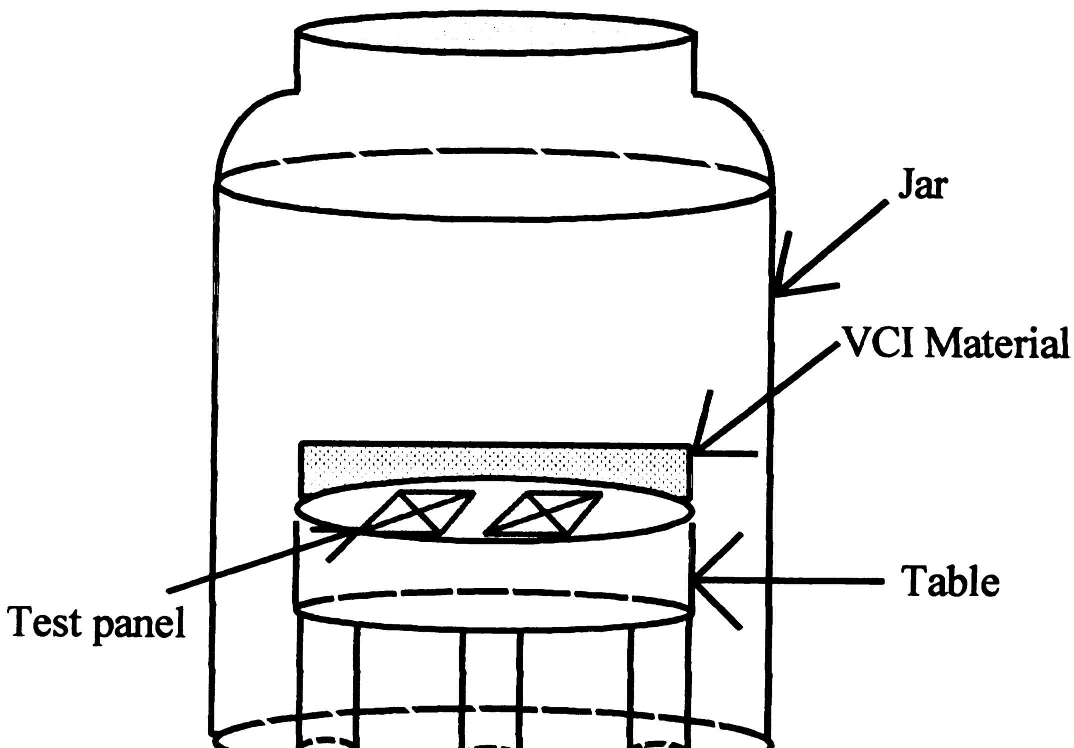
It can be difficult to determine what factors come into effect in a given distribution or storage environment, but it can be even more difficult to formulate a test that will effectively incorporate some or all of these factors. As stated earlier, the purpose of a test is to simulate what will happen in reality, and the more factors that are accounted for, the more accurate the test will be.

Discussion of CIA Test, Federal Standard 101C Method 4031B

Strengths of CIA Test

The Federal Standard 101C Method 4031B, CIA test takes many factors into consideration. There is also a provision in Method 4031B that says: "For other materials, the test surface material, the environment, and the duration must all be considered in specifying the conditions necessary to determine whether or not a specimen will inhibit corrosion of the test surface" (6). This part of the test does account for climate, temperature

Figure 8 - Test Apparatus for Company E



changes, short time periods, short term volatility, vapor compatibility, and the non-contact vapor characteristic of VCI.

1. Climate: The CIA test is done at 75°F and 90% relative humidity, and "40°F below ambient temperature" (6). However, the provision previously stated allows for the alteration of the test environment to better simulate the actual environment that the product will see.

2. Temperature Changes: The CIA test cycles from 70°F and 90% relative humidity, to 40°F below ambient temperature. This simulates a non-regulated atmosphere environment.

3. Time: The test duration is for only a 23 hour period, so it does account for a short time period, but not a longer time period. However, the duration can be altered to match the desired distribution and/or storage time.

4. Volatility: It does test whether the short-term protection is good. However, as stated earlier, the formula may volatilize too quickly. If this happens, it will not offer longer term protection, and this test would not detect this fact.

5. Compatibility: This part of the test determines whether or not the vapors are compatible with the metal, but not whether direct contact between the metal and the VCI material would cause corrosion.

6. Contact: The CIA test is a non-contact test, which will determine if the vapor phase of the material in question is in fact a VCI material.

7. Type: The type of metal and material can be altered to see how different products will work on different types of metals.

Weaknesses of CIA Test

The CIA test does account for some, but not all factors of the distribution and storage environment. It does not account for the permeability of the package, whether or not contact may cause corrosion, and the exact volatility of the formula.

1. Package: The CIA test does not account for the presence or permeability of a package. Because it is done in a closed jar, it cannot simulate the vapor permeating out of the system.

2. Contact: This test is a non-contact test; it cannot determine the effects of contact of the VCI material with the product.

3. Volatility: The exact volatility of the formula cannot be determined by the CIA test. Only assumptions about the volatility of the formula can be made. There is no exact way to measure how much vapor was given off, and at what times.

Discussion of Exhaustion Procedure and CIA Test, Federal Standard 101C Method 4031B

The exhaustion procedure is used in conjunction with the CIA test. Its purpose is to "age" the VCI material, in order to simulate how it functions after long term exposure to the distribution and/or storage environment. As stated earlier, the VCI material to be tested is put into a tube where air circulates over the surface of the material. When the VCI formula volatilizes, it is blown out of the Pyrex tube through an outlet tube, and clean air is circulated in its place. The tube is placed in a 140°F oven, and air containing 50% relative humidity is circulated through the tube. The duration for the exhaustion procedure is 12 days. The same provision that allows the user to alter the environment and duration applies to this procedure as well.

When used in conjunction with the CIA test, the exhaustion procedure can account for the volatility of the formula, as well as what happens if the VCI vapor permeates out of the package. However, siphoning clean air through the exhaustion assembly may increase the volatility of the formula. A VCI formula would be expected to volatilize more slowly in air that already contains VCI vapor than in clean air. Because the VCI vapor is removed from the Pyrex tube so quickly, this part of the test should be looked at as a worst-case scenario (the VCI vapor would not permeate out of a closed package as quickly).

Discussion of MIL-P-3420F

MIL-P-3420F contains two tests that gauge the performance of a VCI material. It also refers to Federal Standard 101C for other tests in order for the VCI material to meet the quality criteria in this standard. This means that the tests contained in this standard were not meant to be performed on their own, but in conjunction with other tests.

Strengths of Copper Compatibility Test

The copper compatibility test measures how a VCI material will interact with copper, which means that it is not intended for use with any other metals except copper. Nonetheless this test does account for the climate, time, compatibility, volatility and non-contact variables.

1. Climate: This test is done at 150°F and 85% relative humidity. As opposed to Fed. Std. 101C, there is no provision for changing the climatic conditions in this test. Therefore, this test cannot be an accurate assessment for conditions other than those stated in the test method.

2. Time: The test duration is for a seven day period, and cannot be altered to increase the duration. Consequently, this test cannot be an accurate assessment for a time period of more than one week.

3. Compatibility: This test does account for the compatibility of the VCI material with copper, however, not with any other metals.

4. Volatility: This test does account for the volatility of the VCI formula for one week, however, not for any longer than that.

5. Non-contact: This test does account for the vapor phase of the VCI formula. It achieves this by having the "U" shaped test panels, and instructing the user to inspect the inside surface of the "U" for corrosion. This test does not specifically account for a contact variable; however, part of the test panel is in contact with the VCI material. It should be possible to inspect the contact parts, and determine if contact had any detrimental effects.

Weaknesses of Copper Compatibility Test

Even though MIL-P-3420F does refer to Fed. Std. 101C for supplementary tests, the copper compatibility test by itself does not account for several variables. It does not account for temperature changes. It is done only in a high temperature, high humidity environment. It does not account for the volatility of the formula after one week. This could mean that the VCI material could offer short term protection, however, it would be unclear whether it could provide protection for a longer period of time. As stated earlier, this test does account for the compatibility of the VCI formula in vapor form, but it does not state that it can be used for contact compatibility tests. Another variable that this test does not account for is the permeability of the package. The test apparatus is a closed environment. Therefore, air is not circulating in or out of the environment. In certain situations, air is permeating in and out of the package or system (if no package is used). In addition, VCI vapor is permeating out of the package or system. As stated earlier, the permeability of the package or system directly influences the performance of the VCI material. This test also does not account for the presence of salt or other electrolytes, which can speed up the corrosion process. This test can only be used for copper, which eliminates the possibility of using this test for any other metals.

Strengths of Long Term Storage Test

The long term test in MIL-P-3420F is a 12 month test for the performance of VCI materials, under temperate climate conditions such as found in the Philadelphia area. This test does account for climate, temperature changes, time, volatility, compatibility, contact, and permeability of the package.

1. Climate: This test does account for the climatic conditions of a temperate zone similar to that of Philadelphia. Since this product is stored in a shed without a controlled atmosphere, the environment that the package and product are exposed to will be almost the same as they would be in the distribution / storage environment (if it was in a climate similar to that of the Philadelphia area).

2. Temperature changes: The conditions inside the test area are very similar to that of the climatic conditions of the area. This means that the temperature and humidity the package and product see will change in accordance with that of the climate.

3. Time: This test will determine if the VCI material will adequately protect the metal for a period of one year in a climate similar to that of the Philadelphia area. Even though this is a long term test, the results can be transferred to the short term, because if the product failed in the short term, the corrosion will still be present after the one year has elapsed.

4. Volatility: This test will determine whether or not the formula will work for a one year period. As stated earlier, this test will account for the short term as well as the long term.

5. Compatibility: This test will determine whether or not the VCI formula is compatible with the metal for contact as well as vapor form.

6. Contact: This is both a contact and a non-contact test.

7. Permeability of the package: Since the test panels are packaged in a corrugated box, this test can account for the permeability of a corrugated box.

This is the simplest of all the tests in terms of apparatus and number of steps used, as compared to the federal standards (6), and the Copper Compatibility Test (5). This simplicity reduces the chance for errors in replicating the test, as well as decreases the possibility of "corners being cut" to simplify the test.

Weaknesses of Long Term Storage Test

One of this test's main drawbacks is its lack of flexibility. As stated earlier, there is no clause that permits the user to change the environment, the type of metal used, or the type of package. If the product is to be packaged in another type of container, for example a plastic bag with a piece of VCI paper placed inside, this test would not accurately predict its performance. Similarly if the product was to be stored in Vietnam rather than Philadelphia, this test could not accurately simulate the conditions experienced in the different locale. There is also no provision for substituting different metals for the steel. If this test were made more flexible, these factors could be accounted for and this test could be applied to all metals and packaging materials. Another drawback is that there may be variations of the climate in a certain area from year to year. Philadelphia may have a particularly harsh winter one year, and the next year a very mild one. These variations can change the results even if the test has been performed in exactly the same way it was the year before. This is why a controlled environment can be favorable in some cases.

Discussion of Performance Tests Used by VCI Suppliers

The test that was done for Company A simulated a high temperature, high humidity environment for 84 days. The test duration is longer than the CIA test, the copper compatibility test, and many of the other tests used by the other VCI manufacturers, but the test is shorter than that of the long term test in MIL-P-3420F.

This test does account for performance at 100°F and 100% relative humidity, and could be altered to accommodate any temperature and humidity desired. The temperature and humidity remain the same throughout the test, so it does not account for temperature changes. However, there is still substantial condensation occurring at this high humidity. Condensation is one of the primary characteristics of a rapid temperature change, and it can be achieved if the relative humidity is high enough, regardless of temperature. The presence of condensation tells the user whether the VCI material can inhibit corrosion in the presence of moisture concentrated on the metal, which accelerates the corrosion process. The test also considers protection for a longer period of time (84 days), which accounts for short term as well as a longer term in a high temperature, high humidity environment. This test does account for the compatibility of the formula with the metal, but only in contact situations. It does not account for the protection afforded by the VCI formula in its vapor state. This test can also be used for a variety of metals and VCI materials.

This test does account for some factors; however, as with all tests, it does have its shortcomings. It does not account for the permeability of the package. The test panels are sealed inside a closed environment, and the VCI vapor cannot permeate out of the system. This gives the VCI material being tested an advantage over a VCI material used in the distribution / storage environment. If the VCI vapors stay within the system, they can afford protection until they are used up, instead of leaving the system and in essence being lost (not affording protection to the product). This test does not account for salt or other electrolytes that can be introduced in the environment and accelerate the corrosion process.

Company B uses a test similar to the CIA test, with a few significant differences. One main difference is the fact that they use water instead of glycerine solution to provide the relative humidity. The duration of this test is also longer than the CIA test (four days as opposed to 23 hours). Another difference is that this test accounts for contact as well as non-contact situations. As with the CIA test, this test also accounts for climate and short term volatility, and it does not account for package permeability, and long-term volatility of the VCI product.

Company E also uses a non-contact short term corrosion test which tests the vapor phase of the formula by moving from a high temperature and high humidity environment, to low temperature and lower humidity environment for a short period of time (two cycles of one hour at 140°F and 40 minutes at room temperature, with a test panel placed over water to provide humidity). This test is much like the CIA test; however, the test environment is at a much higher temperature and humidity, and the duration is considerably shorter. This test uses temperature changes and a harsh environment to accelerate the corrosion process of the metal, in order to prove that protection can be afforded by the vapor phase of the VCI formula. This is not a test of the longevity of the VCI product, it is only a test to see if the VCI product can afford non-contact protection to a certain type of metal. The duration is too short to try to extrapolate any other information about the performance of the VCI product, except short term vapor protection. Another test that this company uses is a contact corrosion test which determines if contact with the VCI material will cause corrosion on a metal part.

Companies C through E use the CIA test in Fed. Std. 101C, without using the exhaustion procedure. The positive and negative attributes are the same as those discussed earlier in this section.

Chapter 4
Recommendations and Conclusion

Summary

Ever since Dr. Wachter discovered them in 1943, Volatile Corrosion Inhibitors (VCIs) have been a valuable tool in fighting corrosion. The benefits of VCI were first demonstrated on a large-scale in the Korean War. Rifles that were packaged with VCI paper were ready for use in a fraction of the amount of time that it took rifles that were coated with grease. Today, VCI is used for the protection of a variety of products, spanning several different industries.

VCI is a chemical which can be incorporated into several different media, and gives off a vapor that inhibits the corrosion of metals. Also, because the chemical vaporizes, it does not need to be in contact with the metal it is protecting. However, certain criteria that must be satisfied in order for the VCI material to work: the VCI material must be compatible with the metal it is protecting; there has to be proper air circulation over the entire area of the product which needs protection; and there has to be active VCI in adequate concentrations within the system containing the product.

The mechanism of inhibition is unknown; however, there are theories on how it inhibits corrosion in metals. The neutralizer theory states that the VCI chemical reduces the amount of H^+ ions, thus reducing the corrosivity of the environment. Another theory is that it works as a scavenger by "handcuffing" the oxygen in the atmosphere and preventing it from combining with humidity. The most popular theory is that VCI vapor condenses and forms a barrier, usually a small number of molecules in thickness, around the metal it is protecting. This barrier works as a passivation layer, and retards the anodic / cathodic electrochemical reactions of the corrosion process.

The VCI industry today is competitive, with several different companies supplying VCI products, and several different industries buying those products. VCI formulas are kept as proprietary secrets, and there is little sharing of information. As a result of this, many different VCI companies use different performance tests for VCI products. Some use published federal government tests; others design tests that are similar to the published tests. The question of whether or not it would be a good idea to have standardized tests used by all VCI companies was posed to representatives of six VCI companies, and to 10 end users of VCI. The VCI companies were split on this subject, two saying that they were for it, three saying that they were against it, and one who abstained from commenting. Conversely, nine out of the ten end users were very much in favor of having a standardized performance test for VCI products.

There are several factors which influence the performance of VCI products. These factors would have to be taken into consideration when devising a performance test for VCI products: climate, temperature cycling, time, volatility of the VCI formula, compatibility with the metal, contact or non-contact, package permeability, the presence of salt and other electrolytes, type of VCI product as well as the type of metals, and other intangible factors. There are several different tests that companies use for evaluating the performance of their VCI products, and each test simulates the distribution / storage environment in different ways. With these differences comes the fact that each test has its own strong points as well as shortcomings.

Recommendations for a VCI Paper Performance Test

A new performance test for VCI paper, which could accurately supplement or replace existing tests, would require several considerations or goals in order to be successful. The most obvious goal would be to simulate, as closely as possible, the distribution / storage environment that the product and package would be exposed to, without having to put it through a field test. Field test means putting the actual packaged product into the same environment that it will be subjected to when it is distributed and/or stored, and for an extended period of time. The test would have to account for as many as possible of the variables that occur in the distribution / storage environment. This type of test would best be used as a tool to estimate the amount of time for a given environment in which the VCI material will offer protection.

Another goal might be for the test to give results that a user, without VCI experience, could understand. As stated earlier, many of the end users that I talked to were confused about how to interpret the results of the tests done on the VCI products they were using. Having easy-to-understand results of tests would help end users to plan for the type and quantity of VCI materials needed for a certain project.

The test procedure, as well as the apparatus used in the test, should be kept as simple as possible. This would reduce the chance for errors in the reproduction of the test. When test procedures are difficult to follow, or when the apparatus is expensive or difficult to prepare, there is the risk of "corners being cut" (meaning some procedure steps or apparatus may be omitted or improvised upon, changing the test results).

This proposed test is based on experiences with testing of VCI materials, evaluation and comparison of VCI tests used in industry, analysis of research projects, study of VCI theory, and knowledge gained from interviewing VCI suppliers and end users. The purpose of this test is to provide the user with an estimate of how a particular VCI paper product will perform throughout its life, under certain environmental conditions.

There are three parts to this test: the coating weight determination, exhaustion procedure, and corrosion inhibitor ability. See Figure 9 and Table 3 for a flow chart and description of the test. The results of the coating weight determination are used with the exhaustion data to extrapolate the test results into the long term, and reduce the amount of time needed to complete the test. The exhaustion procedure is used because it removes a portion of the VCI chemical, simulating the aging process that a VCI material goes through during its life. The corrosion inhibitor ability procedure is the same as in the federal standard (6). Its purpose is to make sure the VCI paper is still capable of inhibiting corrosion upon completion of the exhaustion procedure.

It has not been determined how much a test is accelerated when the temperature and humidity are increased. Also, an increase in humidity may not increase the reaction the same as an increase in temperature. Therefore, for the most accurate prediction, it is desirable to conduct the test at the maximum temperature and relative humidity expected in the distribution / storage environment. Until further studies are conducted, it would not be advisable to accelerate the process by increasing the temperature and/or humidity.

Figure 9 - Flow Chart for VCI Paper Performance Test

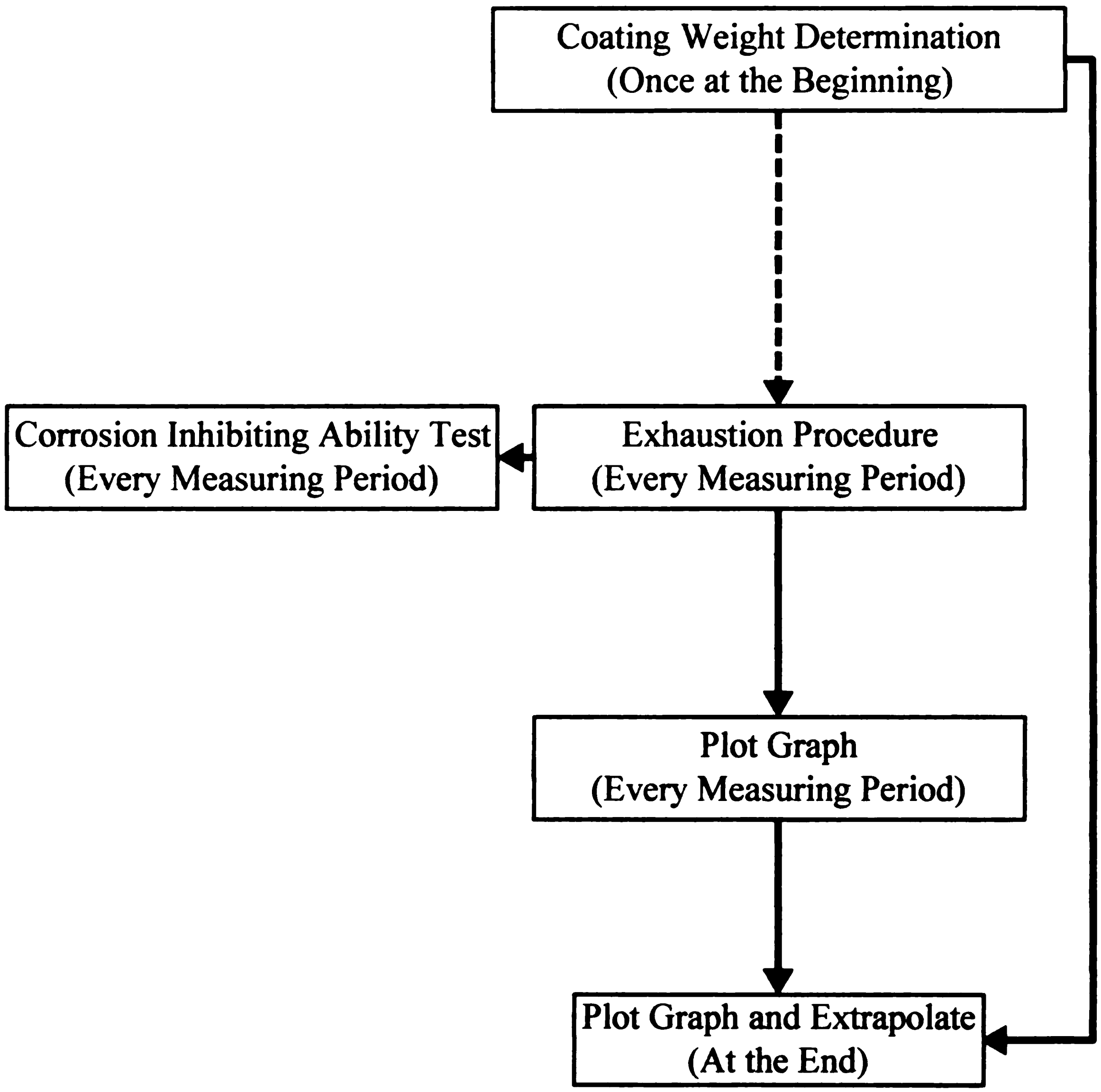


Table 3 - Summary of VCI Paper Performance Test

Coating Weight Determination

"Washes" the VCI chemical out of the paper.

Coating Weight = Initial Weight - Weight After Washing.

Used to determine the point of exhaustion.

Exhaustion Procedure

Similar to the Exhaustion Procedure in Federal Standard 101C Method 4031B (6).

Done in a controlled humidity environment.

Removes a portion of the VCI chemical to simulate aging.

Measures the weight loss of the paper when the VCI coating evaporates.

After every measuring period the weight loss is recorded and plotted on a graph.

Weight loss vs. Time.

Exhaustion Procedure ends when the weight loss follows "straight-line" behavior for 3 consecutive measuring periods.

After 6 weeks have passed to ensure the high initial volatility of the formula is over.

Graph

Figures taken from the Exhaustion Procedure and the Coating Weight Determination.

After Exhaustion Procedure is over, extrapolate the best-fit line until it reaches the exhaustion point calculated by the Coating Weight Determination.

Coating Weight Determination

In order to extrapolate how long the coating will last, the weight of the coating must be determined. Because the VCI chemical is water soluble, a simple washing procedure, using distilled water, can be done to remove the coating. The coating weights should be determined for five VCI strips and then averaged. This procedure also indicates whether the coating weight meets specified parameters. A control paper is not used, because previous tests showed the weight loss of control papers after washing was negligible. This part of the procedure should be done before the exhaustion procedure has begun.

Methods and Materials for the Coating Weight Determination:

1. Cut 5 samples of the VCI paper to be tested, into 2-inch by 6-inch strips.

2. Place the VCI paper strips into a 160°F oven for 10 minutes.

This procedure removes any excess moisture that has been absorbed by the paper, which might increase its weight, and alter the results.

3. Remove the VCI paper strips from the oven, and weigh them on an analytical scale. Round the weight to the nearest 0.001g.

4. Place the five VCI strips in a dish pan filled with distilled water.

5. Allow the VCI strips to stand for one hour, stirring for 30 seconds every 15 minutes.

6. Carefully remove the VCI strips at the end of one hour and replace the water in the dish pan with clean distilled water. Reimmerse the specimens for another one hour period.

7. Repeat steps 5 and 6 for a total of 4 cycles.

8. Remove the VCI strips from the dish pan and place them in an oven set at 160°F for 45 minutes, or until thoroughly dry.

9. Remove the VCI paper strips from the oven and weigh them on an analytical scale. Round the weight to the nearest 0.001g.

10. To find coating weight, subtract the weight after washing (determined in step 9) from the weight found in step 3.

Exhaustion Procedure

The exhaustion procedure of this test is based on a combination of the procedures in the study done by Hohf and Mohaupt (4), and the exhaustion procedure in the federal standard (6), with a few modifications. One modification is a very short period of oven drying, before and after exposure, to remove any water absorbed by the paper medium that may affect its weight. Another modification is that the weight loss observed during each measuring period is tabulated and graphed immediately. This graph will determine the duration of the exhaustion procedure, which has been shortened from the 32 week time period in the study done by Hohf and Mohaupt (4). As stated in Chapter 3, the rate of weight loss for some of the VCI papers became constant at around the eighth week of testing. This consistency in weight loss manifested itself as the linear part of the graphs shown in Figure 5. Also, for some of the formulas, the rate of weight loss during the first four weeks of testing was much higher than the rest of the test duration (see Figure 5). This is due to the high initial volatility of some VCI formulas, as explained in Chapter 3. Therefore, for the purposes of this test, the exhaustion procedure can be ended when the weight loss measured continues in a linear fashion for three consecutive measurements, after the initial six weeks of testing. In other words, after six weeks of testing, when the graphed results of the weight loss become linear for three measurements in a row, the exhaustion procedure can be ended if desired. Because data rarely yields a perfect straight line, a correlation coefficient and other calculations will have to be done to assure that the best-fit line is straight enough. From the straight line part of the graph, the results can be extrapolated to determine what the coating weight will be at a much later period of time. The method for extrapolation is explained later in this section.

The weight loss measurements are taken every week for the first four weeks, and then every other week thereafter (measurements taken after: week 1, 2, 3, 4, and then week 6, 8, 10, 12, 14, 16, etc.). This particular schedule is used, because many multi component VCI formulas vaporize quickly at the beginning, then slow down after the initial weeks of storage are over (as described in chapter 3). Three strips should be weighed at each measuring period, and the weight loss after the exhaustion procedure (the initial weight taken before the exhaustion procedure minus the weight measured after the exposure period) for those three strips should be averaged. This averaged result gives you one data point, which is then plotted on a graph of weight loss vs. time, after each measuring period. An amount of no fewer than 30 strips, coinciding with a 16 week test duration, is suggested for the exhaustion procedure, to ensure there are enough VCI strips to complete this procedure.

Methods and Materials for Exhaustion Procedure:

1. Cut the VCI paper to be tested into at least 30 2-inch by 6-inch strips, and place an identification number in the lower left-hand corner of each.

The VCI paper used must be from the same roll stock that the VCI paper in the coating weight determination came from. The strips that were used in the coating weight determination cannot be used for this procedure.

No less than 30 VCI paper strips, coinciding with 16 weeks of testing, is the recommended for this procedure. Measurements are taken every week for the first four weeks, and then once every other week thereafter.

The identification number should be used to match the VCI strip with the weights recorded before and after exposure.

2. Place the VCI paper strips into an oven set at 160°F for 10 minutes.

This procedure removes any excess moisture that has been absorbed by the paper, which might increase its weight, and alter the results.

3. Remove the VCI paper strips from the oven, and weigh them on an analytical scale. Round the weight to the nearest 0.001g. Record the weight of each strip

This weight will be used in determining the weight loss during exhaustion.

4. Place a plastic or stainless steel hook through one end of each VCI strip, so that the strip hangs with its length perpendicular to the floor. If a stainless steel hook is used, it should be wax or enamel coated, so it does not react with the VCI strip.

Caution should be taken to be sure that the hook does not tear off a piece of the VCI strip, or alter its weight in any other way.

5. Hang the VCI strips in a controlled atmosphere environment, so that there are at least two inches of space between adjacent strips.

The environment should be maintained at a constant temperature and humidity, and the air inside the area should be continuously replaced with fresh air. This prevents the saturation of the air with VCI vapor. The two inches of space is to ensure that there will be proper air flow over the entire surface area of each VCI strip tested.

6. After the exhaustion period has elapsed, remove three strips from the controlled environment, and place them in an oven set at 160°F for 15 minutes, or until completely dry.

As with step 2, this procedure will remove from the paper any water that was absorbed during the exhaustion procedure.

7. Remove the hook, and weigh each strip, rounding to the nearest 0.001g.

Caution should be taken to be sure that removing the hook does not tear off a piece of the VCI strip, or alter its weight in any other way.

8. To determine the weight loss during the exhaustion procedure, subtract the weight taken after exposure (step 7) from the weight recorded before exposure (step 3). Use the average for all three strips, for the results of each measuring period.

9. Plot the data point found in step 8 on a graph of weight loss vs. time, using a best-fit line to illustrate the results.

10. After the sixth week of exposure, when the results become linear for three consecutive measuring periods, the exhaustion procedure can be ended, if desired.

Corrosion Inhibiting Ability Test

After each weighing, the corrosion inhibiting ability of the VCI strips will be determined using the CIA test procedure (6) found in Federal Standard 101C method 4031B. As stated earlier, this will determine whether or not the VCI material is still able to inhibit corrosion in its vapor state after exhaustion. This test also includes a change in temperature to cause condensation on the test panel. The duration of the test is short, but because the exhaustion process has already been performed, there is no need for a longer term test. A control sample will determine how long this procedure will last. The CIA procedure will be over when the control metal plug shows signs of corrosion. If the VCI material tested shows no signs of corrosion, it will have passed for that time period.

Also, the introduction of salt or other electrolytes into the test environment could be done to better understand the protection provided by the VCI material in the presence of these corrosion accelerators. This part of the test must only be used in conjunction with the exhaustion procedure.

For methods and materials for the corrosion inhibitor ability test, refer to Federal Standard 101C, method 4031B sections 3.4.2, and 6.1.2 (6), or for a brief synopsis, refer to Chapter 3.

Final Graph

Once the data have been compiled, the results can be plotted on a graph of weight loss vs. time. Extrapolate the weight loss taken from the results of the exhaustion procedure, by extending the best-fit line that occurs at the end of the exhaustion procedure. When the weight loss equals the calculated coating weight, the VCI coating has been exhausted, and protection will cease. Using this graph, the user can estimate when exhaustion occurs, and know how much time it takes for the material to exhaust its VCI coating for a given temperature and humidity. This part of the test would have to be done only once for a specified temperature, relative humidity, and VCI material. Any change in these three factors would require a new test.

This entire test could be run at any levels or combinations of temperatures and humidities, and for any duration desired. This is a flexible test which allows the user to adapt the test to better suit his or her needs. Nonetheless, this test does not account for the permeability of the package, and thus in some cases should be taken as a worst case scenario of how the VCI product will perform in the field.

Obviously, a field study would provide a better illustration of how the material performs for a particular product, but this test can be done in a more controlled environment. This test gives its results in figures that are easier for people who are not familiar with VCI products to understand.

As stated earlier, this test has not been proven. It is just a model for future tests to follow. The theories and hypotheses used in the designing of this test should be investigated further if they are to be used for this or any other tests.

Conclusions and Suggested Areas for Research

Investigating the theory that the volatility of VCI formulas can be predicted for a certain temperature, humidity, and duration by using the differences in weight (like that proposed in the VCI Paper Performance Test explained earlier in this chapter), would be beneficial. If this is possible, one would only have to look at a chart to see how a VCI material performs at a given temperature and humidity level. Also, a correlation coefficient and other calculations will have to be developed in order to assure that the best-fit line utilized for extrapolation of the results is indeed a straight enough line. If this method for predicting the volatility of VCI formulas can be used, it could save time in determining what type of VCI material to use for a given distribution/storage cycle.

Another research project could be to determine what concentration VCI vapors need to be in to effectively inhibit corrosion. As stated in Chapter 1, in order for a VCI material to inhibit corrosion there has to be active VCI vapors in adequate concentrations present in the system. However, it is not known what the concentration of VCI vapor has to be to adequately inhibit corrosion. The VCI Performance Test, described earlier in this chapter, states that when the VCI coating is completely exhausted, protection will cease. However, it is possible that protection ends before the coating is exhausted. There is also the question of how much VCI material should be used for different size products and packages. You cannot use a 2 inch by 2 inch piece of VCI paper to protect a large car engine packaged inside a five cubic foot crate.

Because there has not been very much research done on VCI within the last 30 years, there are several possibilities for research that have not been covered. One possibility would be to create a database that contains theses, articles, tests, and other published literature that relate to VCI. During this study, it was difficult to locate literature on the subject of VCI, and it was even more difficult to obtain some of the government documents that contain the tests and standards related to the subject. The database could be maintained by the National Association of Corrosion Engineers (NACE), because many of the VCI suppliers are members of NACE. This type of service would prevent the loss of valuable information similar to what has occurred over the last 30 years.

Another research project would be to send out a formal survey to get the opinions of the VCI suppliers and end users on whether a standardized test would be beneficial. Also, if the VCI suppliers got together and discussed this subject, as well as discussed it with their customers, they would get a better idea of the industry's needs, as well as their customers' needs.

Further research on the mechanism that the VCI chemicals use in order to inhibit corrosion is suggested. There has not been a study done on an actual VCI formula, even though there have been studies done in closely related fields. Proving some of the theories about the mechanism will aid in the understanding of how VCI works, and how it can be improved upon.

VCI products other than paper are potential areas for research. Materials such as VCI plastic, foamed pads, crystals, and liquids could all be investigated for their properties. Also, the tests for these products could be investigated as well.

The issue of whether or not a performance test for VCI materials could be accelerated without compromising its accuracy is another area which can be investigated. If a test could be accelerated without jeopardizing its accuracy, months could be saved when investigating the performance capability of a VCI product.

Volatile Corrosion Inhibitors are relatively young compared to many other forms of corrosion inhibition. The industry is competitive, which tends to motivate some companies, but also serves to fragment much of the knowledge obtained by VCI companies as well as others who work with VCI materials. If this knowledge was consolidated, much could be learned about how, why, and in what situation VCI products work best. This could lead to significant advancements in Volatile Corrosion Inhibition.

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