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CORROSION PROTECTION EVALUATION OF FLEXIBLE PACKAGING MATERIALS

PERFORMED FOR CORTEC CORP.
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TEST REPORT

PURPOSE

The purpose of this test is to investigate the relative corrosion protection afforded by various products available in the market. The test products are either plastic films where the volatile corrosive inhibitors (VCI) compounds are impregnated into the resin during film extrusion or papers which have been coated with the VCI compounds. There are other types of VCI protection methodologies utilized in the market for different applications but the use with flexible packaging materials is particularly useful. When a protection feature is added to the packaging process so that there is no additional step in the handling process efficiency increases. The simple idea of having existing packaging films and papers carry the VCI compounds and then packaging the product normally adds to product protection without additional handling or manipulation. This keeps the same level of packaging efficiencies and increases the VCI product protection offered.
These products have been used for years in the market to protect metal surfaces on products which have exposed surfaces. It is a fact that increased protection of the metal surfaces reduces corrosion. The reduction in corrosion eliminates the cost of reworking product and the costs of ruined products. The gained efficiencies of protecting a metal part before it becomes compromised by corrosion are obvious and numerous. The small increase in cost of packaging materials far outweighs the larger costs of inspecting handling and reworking the products. Many manufacturers are now investigating the new VCI products created because of the advances in this technology. The real benefits to the manufacturer become apparent as their markets become world markets and the distribution environments become more hostile and aggressive. As companies manufacture, ship and source components around the world the need for product protection becomes even more acute and the simplest way to provide this corrosion protection is by using packaging materials treated with VCI compounds.

The corrosion inhibiting features of the films and papers are gained from the compounds which volatilize from the flexible materials. The plastic films are extruded with the VCI compounds imbedded in the resin and the papers are coated with the compounds in a liquid solution. The nature of the two materials suggests that there may be some differences in amount of volatile compounds released with the plastics releasing the VCI compounds at a slower rate because they are imbedded in the material. The papers fibers are coated with the VCI compounds and the paper structure allows an open pass through because of the fibrous structure.

There are several manufacturers of VCI products on the market and one of the ways in which they differ is the compounds used for corrosion inhibiting. Several of the older products use a sodium nitrite compound as it effectively inhibits corrosion. The main concern with these nitrite VCI compounds is the toxicity of the nitrites themselves. There has been quite a bit of research concerning the toxicity of nitrites as they have been used in the food industry as a color enhancer in processed meats. The results of the investigation by the food industry was quite serious. Nitrites are a compound which causes health problems in the human population. The more alarming fact is that nitrites will combine with amines, which occur naturally in foods and our bodies, and produce a even more toxic compound. The research findings show that at high temperatures, such as found in frying bacon or cooking, the amines bind with the nitrites to form nitrosoamines which are found to be carcinogenic. The changed compound is more harmful than the original. These findings are not new and have reduced the use of nitrites in processed foods to much reduced levels. The science of toxicity and risk assessment is a relatively difficult field as it is very hard to correlate a low dose exposure to an exact reaction in a population. The FDA has taken the position of being cautious in the populations exposure to these compounds. This is the basis for the FDA limiting exposure levels on harmful compounds.

SCOPE

This report describes the test procedures and results obtained in the evaluation of 12 different VCI packaging materials. The test group was composed of 8 plastic films and 4 papers. There were two different tests performed, a contact and a non-contact evaluation of the sample materials ability to inhibit corrosion. Tests performed between May 4th and June 7th 2000

TESTS

Razor Blade Test

This test determines the corrosion inhibiting properties of various flexible packaging materials, (paper and plastics) in direct contact with metal samples. The sample metals tested were Copper, Galvanized Steel and Carbon Steel.(appendix A)

German VIA Test

This test utilizes German standard TL 8135-0002 to determine the effect of corrosion inhibiting properties of various packaging films (paper and plastics). The unique component of this test is that the metal samples are prepared and the protection from the packaging materials comes from the ability of the VCI compounds to protect without contact. The VCI compounds impregnated into the packaging materials must move out of the film or paper and then travel through the air to react with the exposed metal surface. Protection occurs as a function of the movement of the compounds as well as their reaction with the exposed metal surface. The sample metals tested were Copper, Galvanized Steel and Carbon Steel. (appendix B)

METHODOLOGY

The test methods used for each of the two tests were provided to RIT by Cortec Corporation and were strictly adhered to (appendix A and B). Test samples and apparatus were also provided by Cortec Corporation.

Razor Blade Test

Cortec provided samples of Carbon Steel, Copper and Galvanized Steel. These sample metal plates approx. 2" x 3" were pre-sanded and packaged by the manufacturers for shipment. After the samples were cleaned in methanol they were used to perform the Razor Blade test. The test was run in triplicate so there were three samples tested of each specific material.
The data was collected on a table and evaluated according to the prescribed method in the test standard(appendix 1). There were also photographs taken to help describe the results.

- The sample surfaces had been sanded so as to expose a fresh metal surface.
- The prepared metal samples were pre-cleaned and washed with methanol.
- They were handled with latex gloves so as not to have any oils from hands contaminate the sample surface.
- The samples were dried and then immediately put into the test sequence.

The sample group consisted of three treated samples of each material tested plus a control sample. The samples were evaluated as a pass or fail. We further identified intensities in each of the two categories.

Pass: Clear - No visible signs of corrosion
1. Clear
2. Clear - slight discoloration

Fail: Discoloration - Visible signs of corrosion
1. Discoloration
2. Severe discoloration
3. Corrosion and discoloration
4. Severe corrosion

Carbon Steel:
- 2 drops of **ionized water** were placed on each plate and then covered with a piece of test material.
- The test materials were cut to completely cover the sample metal plate 2" x 3"
- The control was a sample plate which received the same treatment of ionized water but then covered with a piece of low density polyethylene from the RIT lab stock. This polyethylene had no VCI compounds impregnated into the resin and was a food grade LDPE.
- The treated and covered samples were stored at ambient conditions indoors in the RIT labs for **2 hours** and then inspected.

RESULTS:

The table expresses the findings of the test on Carbon steel. The following are some select comments on the individual samples.
-All of the papers worked well in protecting the surface from corrosion.
-The plastic films had a more varied response. Sample numbers #1 and #3 both passed and protected the steel.
-Samples #4, #5, #7 and #8 were the worst offering virtually no protection, and allowing corrosion to be promoted.
-Sample #2, and #6 offered some protection but did allow in #2 corrosion very near the control levels.
-Sample #6 was not badly corroded and one panel observed seemed protected while the other two were in line with the control.
- All of the paper samples passed the test and provided very good protection.

Copper:
- 2 drops **of 0.05% NaCl solution** were placed on each plate and then covered with a piece of test material.
- The test materials were cut to completely cover the sample metal plate 2" x 3"
- The control was a sample plate which received the same treatment of ionized water but then covered with a piece of low density polyethylene from the RIT lab stock. This polyethylene had no VCI compounds impregnated into the resin and was a food grade LDPE.
- The treated and covered samples were stored at ambient conditions indoors in the RIT labs for **4 hours** and then inspected.

RESULTS:
The Copper had different result from the Carbon Steel. Some of the materials performed the same but others either performed worse or improved. The control panel on the copper did not discolor as expected. The group and control was tested twice and the results were the same with the control, not discoloring, but each test material behaving the same in each of the two separate tests. The validity of the test was not compromised because the positive control did not perform as expected because there were observed expected results in the regular samples which occurred in the first and second test sequence. There could be many explanations for the control not reacting as expected. The relative performance of each of the sample materials was demonstrated.(see photos)

- Sample film #1 passed and protected very well and no tarnishing or corrosion was noted
- The sample #2 failed because there was significant discoloration on one panel, medium discoloration on another and mild discoloration on the third panel.
- Samples #3 and #4 both failed because of discoloration of the test panels.
- Samples #5 and #6 both passed showing clear panels on all three test items.
- Sample #7 failed and showed the worst discoloration of the group.
- Sample #8 failed showing discoloration in several spots on all three panels.
- Paper sample #9 passed being very clear and showing no changes.
- Paper sample #10 failed showing a small discoloration.
- Sample #11 failed and showed severe discoloration.
- Paper sample #12 passed with all three panels being clear

Galvanized Steel:

- 2 drops of **3.5% CH_3CO_2 solution** were placed on each plate and then covered with a piece of the test materials.
- The test material were cut to completely cover the sample metal plate 2" x 3"
- The control was a sample plate which received the same treatment of ionized water but then covered with a piece of low density polyethylene from the RIT lab stock. This polyethylene had no VCI compounds impregnated into the resin and was a food grade LDPE.
- The treated and covered samples were stored at ambient conditions indoors in the RIT labs for **4 hours** and then inspected.

RESULTS:

Most of the plastic films failed to protect the sample metal panels. The notable exceptions were the Cortec, Fuchs and Aicello films which exhibited good protection and passed the evaluation. In contrast all of the treated papers did pass the test and protect the metal panels. The relative performance of each of the sample materials was demonstrated.(the photos were not included as their quality did not allow for discrimination)

- Samples #1- 8 all showed signs of discoloration when tested.
- Samples #2, #3, #4,# 7 and #8 showed the most severe discoloration while samples #1, #5 and #6 showed slight discoloration.
- All of the paper samples passed the test and provided very good protection.

Carbon Steel Razor Blade Test

SAMPLE #	Manufacturer	PASS / FAIL	DATA
FILMS			
1	Cortec Corp.	Pass	Clear
2	Daubert Corp.	Fail	Discoloration and corrosion
3	Northern Instruments (Zerust)	Pass	Clear
4	Brangs & Heinrich	Fail	Severe discoloration
5	Fuchs	Fail	Severe discoloration
6	Aicello	Fail	Discoloration
7	Intercept	Fail	Severe discoloration
8	SKS Corp.	Fail	Severe discoloration
PAPERS			
9	Brazil Paper	Pass	Clear
10	SKS Paper	Pass	Clear
11	Daubert Paper	Pass	Clear
12	Cortec Paper	Pass	Clear

Copper Razor Blade Test

SAMPLE #	Manufacturer	PASS / FAIL	DATA
FILMS			
1	Cortec Corp.	Pass	Clear
2	Daubert Corp.	Fail	Severe Discoloration
3	Northern Instruments (Zerust)	Fail	Corrosion and discoloration
4	Brangs & Heinrich	Fail	Corrosion and discoloration
5	Fuchs	Pass	Clear - slight discoloration
6	Aicello	Pass	Clear - slight discoloration
7	Intercept	Fail	Discoloration
8	SKS Corp.	Fail	Discoloration
PAPERS			
9	Brazil Paper	Pass	Clear
10	SKS Paper	Fail	Discoloration
11	Daubert Paper	Fail	Severe discoloration
12	Cortec Paper	Pass	Clear - slight discoloration

Galvanized Steel Razor Blade Test

SAMPLE #	Manufacturer	PASS / FAIL	DATA
FILMS			
1	Cortec Corp.	Pass	Minor discoloration
2	Daubert Corp.	Fail	Severe discoloration
3	Northern Instruments (Zerust)	Fail	Severe discoloration
4	Brangs & Heinrich	Fail	Severe discoloration
5	Fuchs	Pass	Minor discoloration
6	Aicello	Pass	Minor discoloration
7	Intercept	Fail	Severe discoloration
8	SKS Corp.	Fail	Severe discoloration
PAPERS			
9	Brazil Paper	Pass	Clear
10	SKS Paper	Pass	Clear - slight discoloration
11	Daubert Paper	Pass	Clear - slight discoloration
12	Cortec Paper	Pass	Clear - slight - discoloration

German VIA Test

The purpose of the German VIA test is to expose the test sample steel plugs to a high humidity environment and allow the VCI compounds in the plastic films and papers to elute and come in contact with the fresh metal surface.
Cortec Corporation provided the test apparatus for this test. The test Methodology is provided in Appendix B and describes the precise test methods and conditions. The test methodology also gives a full description of the test apparatus and preparation of the sample steel plugs. This test required three flasks with VCI sample materials being used and a fourth for the control with no VCI sample material.
The manufacturer names and sample numbers correspond to the Razor Blade numbers.

- 3 sample flasks were prepared for each test material.
- The sample steel plugs were sanded and prepared for exposure.
- Each sample flask received a mixture of glycerol and water a sample steel plug and two pieces of the test material.
- The control received no material samples but contained a test plug and glycerol and water.
- These sealed flasks were then stored at $(23 \pm 2)C^{\circ}$ for (20 ± 0.5)hours.
- At the end of this time period an additional fresh glycerol and water is added to the flask and then resealed.
- This newly opened and closed flask is then stored at $(23 \pm 2)C^{\circ}$ for $(2 \pm 10$ min.)hours.
- After this time the flasks are set into a $(40 \pm 1)C^{\circ}$ oven for another $(2 \pm 10$ min.)hours.
- After this last exposure time the flasks were opened and inspected.
- The bottoms of the steel plugs were covered with plastic adhesive tape and the corrosion from each plug was transferred to a test sheet for further inspection.
- The plastic adhesive tape was evaluated to determine if the sample VCI materials provided corrosion protection.
- These test strips were then examined and categorized into one of three grades as described in the Test Methodology (appendix B)
- There grades were:

0 - Worst protection
1 - Some protection
2 - Better protection
3 - Best protection

GERMAN VIA TEST

SAMPLE #	Manufacturer		GRADE	
FILMS				
1	Cortec Corp.		2	
2	Daubert Corp.		0	
3	Northern Instruments (Zerust)		2	
4	Brangs & Heinrich		0	
5	Fuchs		0	
6	Aicello		0	
7	Intercept		0	
8	SKS Corp.		1	
PAPERS				
9	Brazil Paper		2	
10	SKS Paper		3	
11	Daubert Paper		3	
12	Cortec Paper		3	

RESULTS AND DISCUSSION

The results of this test show the relative relationship between many of the VCI products on the market. Some of the test results demonstrated differences between manufacturers and other results demonstrated differences between the flexible packaging material carriers.

The results of the Razor Blade Contact test show the differences which occur in the various plastic samples. Some materials protect one metal well but fail in protection with another metal. Sample number # 3 protected carbon steel but failed to protect copper and galvanized steel. Some samples did not protect on contact at all # 2,#4, #7 and #8 failed to protect all three materials. An interesting finding occurs in sample #5 and #6 which seem to protect copper and galvanized steel but fails badly with carbon steel. The papers are prone to the metal specific variability as demonstrated in the plastic films. Sample #11 failed to protect the copper test panels, while protection was evidenced in carbon and galvanized steel. On the whole the papers seemed to exhibit better protection in the Razor Blade Contact test.

The German VIA test again showed the differences between the various plastic films and papers. The best plastic films #1 and #3 exhibited very good protection. The other films did not seem to perform well. It seems that films #1 and #3 are the superior product in corrosion protection. All of the papers protected the metal surface very well. The nature of the German test seemed to require the sample materials to elute the VCI compounds for the protective effect. The nature of polymeric films makes it difficult for many compounds to elute as the material tends to slow the transport and evaporation. The open nature of papers allows free movement of the compounds off the paper surface and allows them to move in the air and coat the sample plugs. This is evidenced in the German VIA results which have all of the paper materials exhibiting good protection.

The observation is that most of the different sample materials seem to protect at least one metal. The conclusion from this fact is to be very specific when selecting a VCI protective material and be aware how that specific material reacts with the specific metal you are attempting to protect.

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Cross Reference Chart – Nitrite Based Products.

PRODUCT	NITRITE BASED
Films	
Cortec	No
Daubert	No
Northern Instruments	Yes
Brangs & Heinrich	No
Fuchs	No
Aicello	Yes
Intercept	No
SKS	Not tested
Papers	
Brazil Paper	Yes
SKS Paper	Not tested
Daubert Paper	Yes
Cortec Paper	No