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The New Generation of Rust Preventative Products Based on Renewable Materials and Incorporating Vapor Corrosion Inhibitors

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ABSTRACT

Corrosion protection was always an important part of industrial development. The use of oil- and solvent-based products in the preservation of metal has been a common practice for over one hundred years. While these products may offer good corrosion protection, they often contain hazardous ingredients and are non-degradable. A number of regulations were implemented recently for the protection of the environment. The most known among them are North Sea (UK, Norway, Denmark, The Netherlands) and US Gulf Coast lists of the chemicals environmentally acceptable in these regions, limiting the type of chemicals allowed for use in accordance with their level of biodegradability, bioaccumulation and toxicity.

Recently, the use of vegetable oils and their esters has been found to offer many similar properties to their petroleum derived counterparts. By incorporating vapor corrosion inhibitors (VCI A, VCI B, VCI C, and VCI D) in different naturally derived solvents, optimal corrosion protection or other desired properties can be obtained yielding environmentally friendly, biodegradable products.
The laboratory test results and industrial applications of these products will be discussed in this paper.

INTRODUCTION

Green chemistry is not an absolute goal or destination, but a dedication to a process for continual improvement, wherein the environment is considered along with the chemistry. Chemical products should be designed to preserve the efficiency of function, while reducing their impact on the environment.

These products should be designed so that at the end of their application, the product does not persist in the environment, and it should break down into innocuous degradation products. The development of “green” corrosion inhibitors is a process, which requires: the knowledge of the pertinent country regulations, the evaluation of the environmental performance for the environment to which the product will be exposed and the corrosion protection required in the applications the inhibitor is designed for.

Different approaches can be used to obtain an environmental profile for corrosion inhibitors utilized in a specific application. The most common method is to replace solvent- or oil-based carriers in formulations with water-based technology. These technologies provide an environmentally conscious method of corrosion protection [1], but they can be cost and time prohibitive for certain operations. In these cases, the manufacturer is left with little or no choice but to use environmentally hazardous petroleum-based products or simply do nothing. The second option is to replace petroleum-based carriers with solvents manufactured from environmentally friendly renewable resources. This has been accomplished by combining VCIs with soy-derived and canola oils to formulate anticorrosion products for many different applications. The last method commonly employed is to utilize biodegradable materials as corrosion inhibitors, in conventional solvents as carriers.

The focus of the paper will be limited to the last two approaches. The goal of this paper is to show that non-toxic products may inhibit corrosion as well or better than their more toxic traditional counterparts depending on the system.

The products in this paper will be represented as:

- VCI A – Soya methyl ester based cutting fluid
- VCI B – Soya methyl ester based all purpose lubricant
- VCI C – Canola oil based temporary coating for inside or sheltered metal protection
- VCI D – Canola oil based open atmosphere rust preventative

EXPERIMENTAL

In developing of "green" products, a battery of testing was undertaken to ensure that desired properties were achieved. These included physical properties, corrosion inhibiting properties and additional functional properties. The physical properties were established by using corresponding petroleum-based products as a baseline. Corrosion inhibiting capabilities were established using industry accepted testing. Additional functional properties were evaluated based on the similarity with petroleum-based counterparts whenever possible. For the protection of metal, the most important factor in product development was the capability to prevent the corrosion process from occurring. An assortment of standard tests was used to compare the new VCI products with products that are commercially available. Testing included humidity testing, immersion testing, cast-iron chip test, salt spray chamber test, VIA test and other tests to demonstrate the combination of the properties. Marine toxicity biodegradability and biobased content of presented products were evaluated.

ASTM D 1748-83 Rust Protection by Metal Preservatives in the Humidity Cabinet[2]: Test method for determining rust –preventative properties of metal preservatives under high humidity. Metal specimens are treated with a rust-preventative and exposed to 48.9°C +/- 1.1°C (120°F +/- 2°F) and 95% relative humidity for a given time period.. All testing was done for comparative analysis and the time period was dependent on failure mechanism.

DIN EN ISO 6270-2 [3]: Test method for evaluating rust preventative properties under high humidity[(I)]. Metal specimens are treated with rust preventative and exposed to 40°C ± 2°C and 100% humidity for 168 hours (7 days).

[(I)] Test was performed by University in Zagreb (Croatia)

ASTM B-117 Rust Protection by Metal Preservative in Salt Spray Chamber: Test method for determining rust-preventative properties of metal preservative in salt spray conditions. Metal specimens treated with the rust preventative were subjected to 35 ± 1.1-1.7°C (95±2-3°F) and 5% sodium chloride concentration in the air.

ASTM G 31-72 Half Immersion[5] and Mil-PRF-16173E Immersion[6] Corrosion: Carbon steel panels were weighed and immersed in the test solution, using DI water as control solution. The testing period was determined by the alloy used. The panels were removed after the pre-determined testing period, cleaned, and tested for weight loss. Immersion tests were done on different metals in accordance to Mil-PRF-16173E(2,3)[6]. According to this test the specimen is immersed in the solution for 1 week to at 55°C.

ASTM D 4627-86 Iron Chip Corrosion of Water Soluble Metalworking Fluids[7]: Method for evaluating the ferrous corrosion control characteristics of water-soluble metalworking fluids. In this test, class 30 gray cast iron chips are submersed in various dilutions of a water soluble (or emulsified) fluid to determine the minimum dilution that affords corrosion protection. A ladder study was used to determine the lowest concentration that would pass the testing requirements.

Vapor Corrosion Protection: Vapor inhibiting ability (VIA) was performed according to Federal Test Method Standard No 101C[8]. One gram of the inhibitor is introduced into a quart jar. The jar is sealed with the lid with the attached highly polished carbon steel specimen in it. After conditioning at room temperature for 2 hours, 3% solution of glycerin in de-ionized water is added. The sealed jar is placed into the oven at 40°C for 2 hours. After exposure the condition of the metal specimen is visually inspected and rated according to the following guidelines:

VIA Test Grades (Grade 2 or 3 are passing)

Grade 0:	Blind test No corrosion inhibiting effect
Grade 1:	Blind test Minute corrosion inhibiting effect
Grade 2:	Blind test Medium corrosion inhibiting effect
Grade 3:	Blind test Good corrosion inhibiting effect

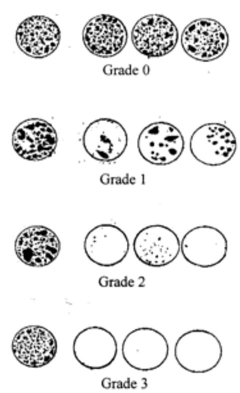

FIGURE 1 – VIA Test Grades(II)

Biodegradation[9]: The biodegradability was determined in accordance with the EPA 28-day test method. The requirement states that the ratio of Biological Oxygen Demand (BOD) to Chemical Oxygen Demand (COD) must be greater than or equal to 60%.

Biobased Content: This is the percentage of the total carbon that is modern (present day) in origin. Analyses were performed using conventional radiocarbon analytical methods(III).

(II) Modified from Figure 12 from NACE Standard TM0208-2008

(III) Tests were performed by Iowa State University.

ASTM D-4172[10]Lubricity Test: This is a Four Ball Wear test[(IV)]. ASTM D-2670[11] was used for VCI A.

Floating Coating Test: Water insoluble product (0.3%) is added to salt water (3.5% sodium chloride). The steel panel is immersed in the solution. Film-forming properties of oil-based product are evaluated by changing water a few times and visual observations of the panel.

RESULTS

In formulation of VCI A and VCI B soybean oil methyl ester was used as a carrier to give high solvency and additional lubricating properties.

VCI C and VCI D were formulated with canola oil as a carrier because: canola oil contains less saturated fatty acids - adds corrosion protection; doesn't attack coated surfaces – can be applied on top of coated metals; and has a low freezing point (-20°C, -4°F) - allowing applications in low temperatures.

Humidity Testing: Results in the humidity test varied from one test to another depending on three factors: the metal substrate, the specific VCI, and dilution in water that was used. All were factors in the length of time before failure. In each case, the VCI products outperformed the conventional water-based and petroleum based products. They also performed equally to or better than other water-based and petroleum-based VCI products. The results can be found in Tables 1-5.

Salt Spray Testing: This testing was performed on VCI D – open atmosphere corrosion inhibitor. The results are presented in Table 6.

Immersion and half-Immersion Testing: In half-immersion testing, the control panels show medium corrosion below the water line after 24 hours for carbon steel, and corrosion above the water line after 72 hours. The aluminum controls have oxidation below the aqueous line after 72 hours. In the same testing, the VCI showed no corrosion for greater than 30 days, indicating the product has both contact and vapor protection capabilities. The results of the half immersion testing can be found in Table 6. In immersion corrosion test VCI D outperformed all requirements of Military test MIL-PRF-16173E. The results are in Table 8.

Cast Iron Chip Testing: The VCI soy derived cutting fluid passed the cast iron chip testing at a lower concentration that standard water-soluble and VCI water-soluble cutting fluids. The results of this testing are in Table 9.

VIA Test : This test was performed for VCI C and VCI D. The results are compared to conventional open-atmosphere rust preventative. See Table 10, Figure 2.

Lubricity Testing: This testing was performed for VCI A and VCI B which are used as machining fluids. The results of this testing are presented in Tables 11 and 12.

Floating Coating Test: VCI C shows very good performance in this test. It forms a very persistent film on the metal surface. This film provides protection to the metal even when the salt water is changed 5 times.

[(IV)] Performed by "Petro-Lubricant Testing Laboratories, Inc.

Biodegradability Test: All tested products are 70-98% biodegradable.

Biobased Content: See Table 13

TABLE 1
ASTM D-1748-83 on 1010 Carbon Steel

Sample	Time before corrosion (hours)
VCI A	200
VCI B	300
VCI C	>500
VCI D	7000

TABLE 2
DIN EN ISO 6270-2

Sample (5%)	Results after 168 hours
VCI A	No corrosion
Conventional semi-synthetic cutting fluid	Heavy corrosion
Conventional soluble oil cutting fluid	Corrosion

TABLE 3
ASTM D 1748-83 on Heat Treated Carbon Steel Gears

Sample	Dilution	Hours to Failure
VCI A	5% in water	>108
VCI Synthetic Water Soluble Fluid	5% in water	108
Soluble Oil Cutting Fluid	6% in water	<13.5
Control (no coating)	---------	<13.5

TABLE 4
ASTM D 1748-83 on Carbon Steel Bearings

Sample	Dilution	Hours to Failure
VCI C	Undiluted	>120
VCI Water-Soluble Rust Preventative	10% in water	120
VCI Petroleum Rust Preventative	33% in Naphthenic	>120
VCI Petroleum Rust Preventative	10% in Naphthenic	>120
Commercial Rust Preventative	Undiluted	120

TABLE 5
ASTM D 1748-83 on Metal Stamped Parts (high carbon steel)

Sample	Surface Prep.	Dilution	Hours to Failure
Control 1	Methanol	----	2
Control 2	None	----	2
VCI C	Methanol	10% in water	>192
VCI C	Methanol	10% in water	24
VCI Water-based Rust Preventative	None	10% in water	16
VCI Soluble Oil Rust Preventative	Methanol	10% in water	12

TABLE 6
ASTM B-117 on 1010 Carbon Steel

Sample	Hours of protection
VCI D	500+
Conventional open-atmosphere rust preventative	168

TABLE 7
ASTM G 31-72 Half Immersion Corrosion

Alloy	Time Before Corrosion (Days) Control	Time Before Corrosion (Days) VCI C
3041 Bare Al	<1	>30
1010 Carbon Steel	<1	>30

TABLE 8
MIL-PRF-16173E Immersion Corrosion Testing (VCI D)

Specimens	Requirements (weight loss in mg/cm²)	Results (weight loss, mg/cm²)	Pass/Fail
Brass	<1.0	0	Pass
Zinc	<7.5	0.4	Pass
Magnesium	<0.5	0	Pass
Aluminum	<0.2	0.05	Pass
Steel	<0.2	0	Pass
Lead-calcium	<5.0	0	Pass

TABLE 9
ASTM D 4627-86 (Cast Iron Chip Test*)

Percent (%) of Soy-derived Cutting Fluid (in water)	Sample 2	Sample 4
5	No corrosion	No corrosion
4	No corrosion	No corrosion
2.5	No corrosion	No corrosion
1	No corrosion	No corrosion
0.5	5% corrosion	5% corrosion
0.1	80% corrosion	80% corrosion

* Conventional soluble oil cutting fluid passes this test in concentrations from 5-2.5 % only

TABLE 10
VIA TEST REUSLTS

Sample	Plug #1	Plug #2	Plug #3
VCI C	Grade 3	Grade 3	Grade 3
VCI D	Grade 3	Grade 3	Grade 2

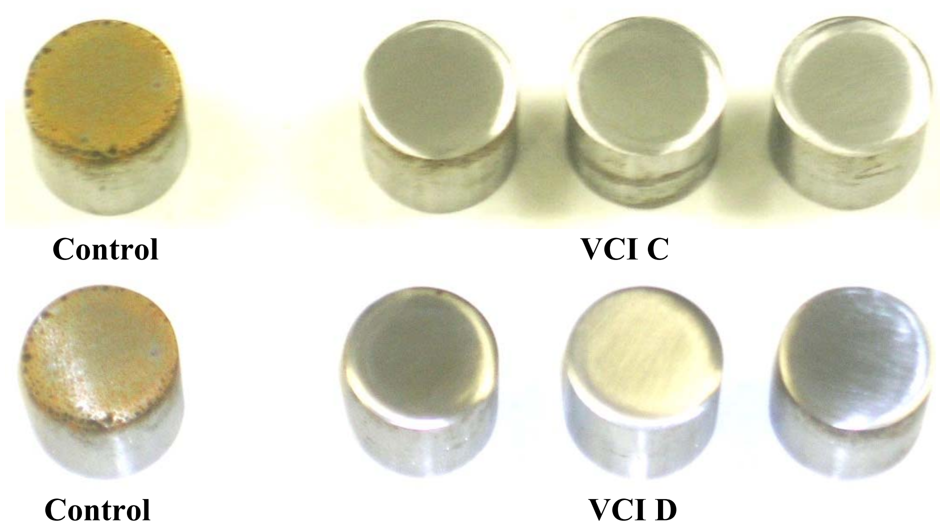

FIGURE 2- Results of the VIA Test

TABLE 11
ASTM D 4172 Lubricity Testing

Sample	Conditions	Results (scar diameter)
VCI B	40 kg, 1200 rpm, 1 hour at 75°C	0.30 mm
Conventional Lubricant	same	0.87 mm

TABLE 12
ASTM D 2670 Lubricity Testing

Sample	Conditions	Results
VCI A	Run in 5 min -159 kg, Gauge load – 408 kg	Total teeth wear 17 (2.5% solution) 10 (5% solution) Seizure (yes/no) 2.5% solution - no 5% solution - no

TABLE 13
Biobased content (modern carbon)

Sample	$\%C^{14}$
VCI A	67% (experimental)
VCI B	91% (experimental)
VCI C	95% (theoretical)
VCI D	65% (theoretical)

CONCLUSION

Following extensive testing, and field trials it is apparent that VCI biobased products will be a viable and important method for interim corrosion prevention now and in the future. These products exhibit excellent corrosion inhibiting properties both in laboratory, and real world environment. Also the most of these products demonstrate the additional functional features. Since they are biodegradable and produced from a renewable resource, they will continue to gain in market acceptance as environmentally conscious products will be preferred.

REFERENCES

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11. ASTM D-2670 Measuring Wear Properties of Fluid Lubricants (Falex Pin and Vee Block Method)