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Biodegradable VCI Building Block for Biofuels

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ABSTRACT

For years the chemical industry has relied on petroleum as the primary ingredient in thousands of products. Numerous industrial product manufacturers use petroleum-derived substances in their formulations. However, there is concern about the drastic increases in oil and gas prices, thereby increasing the cost of those products. Tighter environmental regulations continue to put pressure on oil-based product producers and their users to find safer solutions. As an alternative the use of renewable biobased products provides environmentally safe products to the manufacturers and users that offer comparable performance, economics and the added benefit of biodegradability of the final products.

Incorporation of Volatile Corrosion Inhibitors (VCI) in lubricating products provides a number of advantages. VCIs, when added to the carrier, provide corrosion protection to machinery during the operation, storage or transportation period. Properly chosen combination of VCIs prolongs service life of machinery by minimizing the corrosive wear of the fuel systems and storage tanks.

VCI Building Blocks for Biofuels (BBB) and BBB Bio are powerful corrosion inhibitors utilized to control the corrosive characteristics of biobased fuels. BBB and BBB Bio incorporate patented VCI technology to provide protection in all 3 biofuel phases: liquid, interface, and vapor phases (physical properties are listed in table 6). In addition, BBB Bio was developed with soybean oil as a carrier; allowing it to be added to a variety of biofuel and conventional fuels including diesel and gasoline during operation, storage, transport, and distribution. BBB and BBB Bio pass the rust test in accordance to MIL-PRF-25017 [1] and ASTM D-665-92 [2], These and additional laboratory tests data, photos, and field applications are presented.

INTRODUCTION

Green chemistry is not an absolute goal or destination, but a dedication to a process for continual improvements, 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 the chemicals 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 [3], 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 the petroleum-based carriers with solvents manufactured from environmentally friendly renewable resources. This has been accomplished by combining VCIs with soy-derived oils to formulate anticorrosion products for many different applications. The last method commonly employed is to utilize biodegradable materials as corrosion inhibitors.

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.

EXPERIMENTAL

For years the main part of fuels has been petroleum derivatives, but search of the renewable energy sources started in 1960s. At first, ethanol-based fuel started to be used in automotive engines instead of gasoline. At even later dates, Biodiesel was developed. In the United States Biodiesel is a fuel comprised of a mixture mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. This paper is presenting two products which recommended as anticorrosion building blocks to the fuels, including biofuels: BBB and BBB Bio.

Soybean oil is the largest source of biodiesel in the United States; however, oil from other plants is sometimes used. The resulting mixture of fatty acid methyl esters has chemical and physical properties similar to those of conventional diesel fuel. Biodiesel is registered with US EPA as a fuel additive under Section 21(b) of the Clean Air Act. BBB and BBB Bio are the building blocks for this new generation of the fuels.

Active ingredients of both products, BBB and BBB Bio, are blends of amino-carboxylates and high temperature antioxidants. BBB is the solution of the above mentioned active ingredients in mineral spirits, while BBB Bio is soybean oil methyl ester based. Soybean oil methyl ester was chosen as a carrier based on the following reasons. Soybean methyl esters provide excellent environmental and safety profile as shown by being non-toxic: the acute oral LD50 is greater than 17.5 g/kg body weight (by comparison table salt is nearly 10 times more toxic) [4]. Soya methyl esters are also biodegradable and are a very mild irritant. The chemistry of soybean oil methyl ester; being a triglyceride of the blend of saturated and unsaturated fatty acids (methyl esters) generally provides some additional corrosion protection to the metallic substrates. Due to its greater polarity than petroleum derived products the solvency of soybean oil methyl ester is similar or better when compared to petroleum-derived products.

Laboratory Tests

Compatibility Test – ASTM D-4054 B [4]: BBB and BBB Bio were added to fuels at concentration level of 0.25% by volume. Solutions were thermally cycled for 72 hours and visually observed for any changes. Additives were considered compatible with fuel if there were no changes in their appearance. [Table 1]

Immersion and *half-immersion* corrosion tests ASTM G-31-72 [5] : These tests were performed on SAE 1010 carbon steel panels at the room temperature. Deionized water was added to the solutions of fuel additive in fuel at concentration level of 5% by volume to accelerate corrosion. Panels were placed in the solutions and observed periodically. After 8 months the panels were removed and visually inspected. Results are presented in Table 1.

Rust Test of MIL-PRF-25017 (ASTM D-665) Test Method for Rust Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water, Procedure B (for synthetic seawater):
According to this procedure, BBB or BBB Bio were added to the diesel fuel at concentration of 0.25% by weight. Diesel was mixed with 5% of synthetic seawater. Specimen made from carbon steel isooctane grade 1018 was immersed into the mixture for 5 hours under the stirring conditions and the temperature 38°C. After that the test specimen was evaluated for the presence of any corrosion. Results are presented in the Table 2.

Evaluation of the performance of BBB vs widely used conventional corrosion inhibitor: BBB is an inhibitor for the Naphtha and Gas-condensate was evaluated according to the immersion corrosion test on carbon steel panels. BBB and conventional corrosion inhibitors were added to Naphtha and Gas-condensate at concentration level of 150 ppm. To accelerate the test, 5% by volume of deionized water (pH=2) were added to the solution. The pH level of the deionized water was adjusted with laboratory grade sulfuric acid. Cleaned with methanol and air dried carbon steel panels were immersed in this solution and left overnight at room temperature. Jars were vigorously shaken for approximately one minutes and left at ambient conditions for the next 72 hours. After the test, panels were removed from solutions and visually examined. Results are presented in Table 3.

Corrosion protection for non-ferrous metals: Corrosion protection for non-ferrous metals was evaluated according to DIN 50017. BBB and BBB Bio at concentration level of 1% in gasoline was applied on Solder and Terneplated panels. Panels were air-dried and placed into the testing cabinet. Test results are presented in the Table 4.

Evaluation of Corrosion Protection in the electrolytes containing Hydrogen Sulfide (H_2S) and Carbon Dioxide (CO_2): Immersion corrosion test were performed on carbon steel SAE 1010 at 45C for 24 hours. Panels were immersed in artificial seawater, prepared from the synthetic sea salt. H_2S was produced from Na_2S and Acetic Acid according to the instruction of NACE publication ID182 [6] and added to electrolyte at concentration of 1ppm. The brine was purged with CO2 for about 30 minutes. BBB and BBB Bio were tested at concentration level of 150 ppm. Weight Loss was determined and Z (% of protection was calculated according to Equation 1):

Equation 1:

$$Z=\frac{\Delta m_{cont}-\Delta m_{inh}}{\Delta m_{cont}} x100\%$$, where

Δm_{cont} – weight loss in the electrolyte without inhibitor, g

Δm_{inh} – weight loss in the electrolyte with inhibitor, g

The results are presented in the Table 5.

Corrosion protection of empty gas tank: This experiment was performed to evaluate effectiveness of BBB and BBB Bio in the applications for storage and shipment. Three five-gallon buckets were cleaned with methanol and air-dried. A 1/2 –inch hole was punched into the bottom of each bucket. One five-gallon bucket was left as the control, and the other two buckets were fogged with 20ml/0.714 oz of BBB and of BBB Bio. The lids were then crimped onto the buckets and the buckets were placed into the cycling environmental chamber for 14 days. The cycling conditions were: 50C, 100 RH, 16 hours followed by 80C, 100 RH, 8 hours. Test results are presented in the Figures: 1, 2, and 3.

RESULTS

Table 1.
Compatibility and corrosion protection of BBB and BBB Bio

Sample	Compatibility	Immersion test, presence of corrosion	Half-Immersed test, presence of corrosion
Gasoline (Control)	-	Corrosion	Corrosion
Gasoline + 0.25% BBB	Compatible	No visible corrosion	No visible corrosion
Gasoline + 0.25% BBB Bio	Compatible	No visible corrosion	No visible corrosion
Diesel (Control)	-	Corrosion	Corrosion
Diesel + 0.25% BBB	Compatible	No visible corrosion	No visible corrosion
Diesel + 0.25% BBB Bio	Compatible	No visible corrosion	No visible corrosion
Biodiesel (Control)	-	Corrosion	Corrosion
Biodiesel + 0.25% BBB	Compatible	No visible corrosion	No visible corrosion
Biodiesel + 0.25% BBB Bio	Compatible	No visible corrosion	No visible corrosion

Table 2.
MIL-PRF-25017 (ASTM D-665)

Material	Result
Diesel fuel + 0.25% BBB	No visible corrosion
Diesel fuel + 0.25% BBB Bio	No visible corrosion
Diesel fuel (Control)	Corrosion

Table 3.
Corrosion protection of BBB vs. conventional corrosion inhibitor for fuels

Material	Presence of corrosion	Material	Presence of corrosion
Naphtha + 150 ppm BBB	No visible corrosion	Gas-condensate + 150 ppm BBB	No visible corrosion
Naphtha + 150 ppm conventional corrosion inhibitor	Corrosion	Gas-condensate + 150 ppm conventional corrosion inhibitor	Corrosion
Naphtha (Control)	Severe corrosion	Gas-condensate (Control)	Severe corrosion

Table 4.
Corrosion protection of BBB and BBB Bio provided for Solder and Terneplate

Material	Solder. Time before corrosion started, days	Terneplate. Time before corrosion started, days
1% BBB, 1% BBB Bio	17 days	3
Gasoline (Control)	10	<1

Table 5.
Corrosion protection in electrolytes, containing H2S and CO2

Material	$\Delta m_{cont} / \Delta m_{inh}$	Z (%)
BBB//BBB Bio	7	86
Control		

Table 6.
Specifications for BBB and BBB Bio

Specifications	BBB	BBB Bio
Appearance	Clear yellow liquid	Clear amber liquid
WPG, lb/gal Specific gravity, g/cm^3	6.6-6.9 0.79-0.83	7.3-7.6 0.87-0.91
NVC, %	17-19	93-100
MIL-PRF-25017 (ASTM D 665 B) at 0.25% in Diesel fuel	Pass	Pass
Biobased content*	-	89**
Pour point, °C ***	-60	-59

* "Biobased content" is the percentage of the total carbon that is modern in origin. Analyses were performed using conventional radiocarbon analytical methods.
** Data provided by Iowa State University
*** Tested in the diesel fuel with pour point -60C at concentration level 0.1% by weight

CONCLUSION

BBB and BBB Bio are very effective building blocks for fuels including Biofuel. They provide exceptional corrosion protection, as shown in the Z in table 5, when added to multiple fuel types (gasoline, diesel fuel, biodiesel, etc…) and in harsh environment (H_2S, CO_2). They provide corrosion protection for ferrous and non-ferrous metals, used in automotive fuel systems and meet military testing requirements for corrosion inhibitors for the fuels listed above. Because BBB and BBB Bio are based on VCI technology they provide protection in all three phases: liquid, interface, and vapor phases above and below the fuel level and have been successfully used for lay-up applications

REFERENCES

1. MIL-PRF-25017 "Inhibitor, corrosion/lubricity improver. Fuel soluble."
2. ASTM D-665 "Test method for Rust Preventive characteristics of inhibited mineral oil in the presence of water."
3. Cracauer, C., Kharshan, M. Interim Corrosion Protection with Soy-based Products Incorporating Vapor Corrosion Inhibitors. Corrosion 2003, NACE, Paper # 03485
4. Austrian Research Center, (1991) "Toxicological Report" Seibersdorf, Austria
5. ASTM D 4054-93, part B. Standard Practice for evaluating the compatibility of additives with Aviation-Turbine Fuels and Aircraft Fuel System Materials.
6. ASTM G-31-72 Practice for Laboratory Immersion Corrosion Testing of Metals.
7. NACE ID182 "Wheel Test Method used for Evaluation of film persistent corrosion inhibitors for oil field applications."
8. ASTM-D-1748 "Standard Test Method for Rust Protection by Metal Preservatives in the Humidity Cabinet."

Figure 1: Steel Bucket protected by BBB Bio after 14 days in the Environmental Chamber with the same relative humidity and temperature as utilized for ASTM-D-1748 [8]

Figure 2: Steel Bucket protected by BBB after 14 days in the Environmental Chamber with the same relative humidity and temperature as utilized for ASTM-D-1748

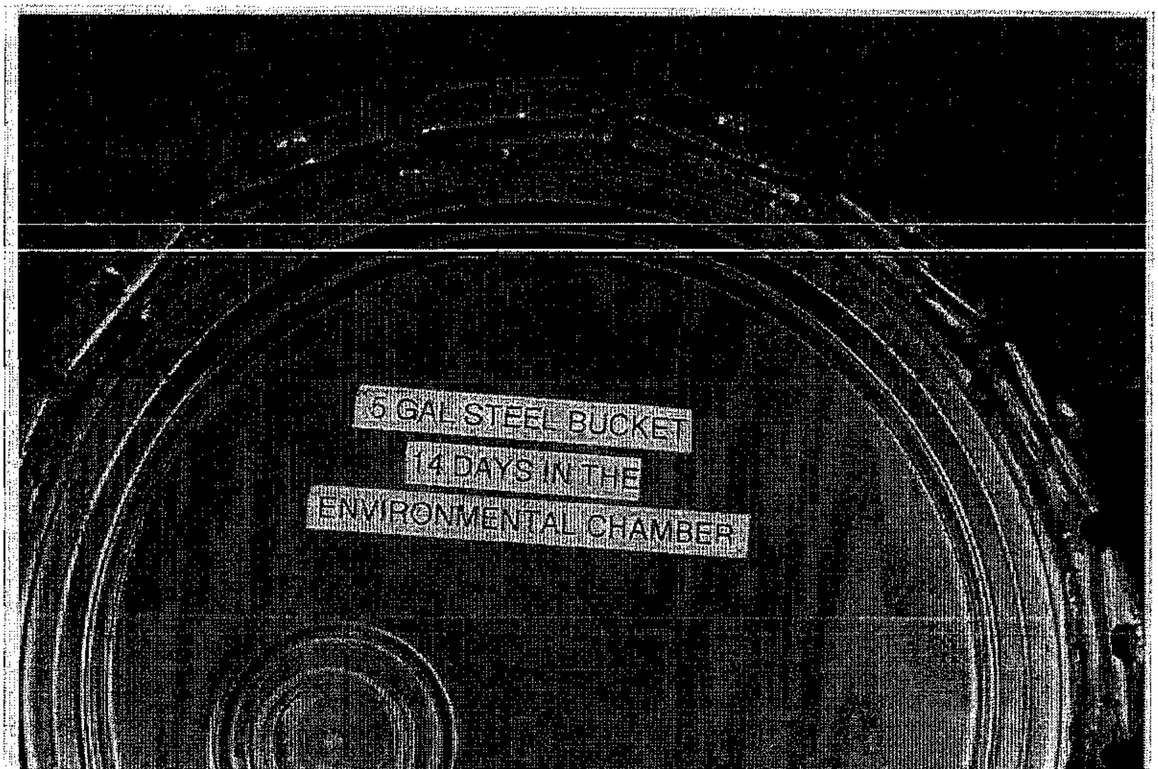

Figure 3: Unprotected steel bucket after 14 days in the Environmental Chamber with the same relative humidity and temperature as utilized for ASTM-D-1748