Boris Mikšić, Margarita Kharshan, Alla Furman, Brian Wuertz, Ivan Rogan

ISSN 0350-350X
GOMABN 46, 5, 403-418
Professional paper
UDK 620.197.7 : 665.335.2.094.942 : 621.434-632.5 : 621.436-634.9

BIODEGRADABLE VPCI BUILDING BLOCK FOR BIOFUELS

Abstract

For years the chemical industry has relied on petroleum as an ingredient in thousands of products. Numerous industrial product manufacturers use petroleum-derived substances in their formulations. However, the oil and gas are the focus of today's energy concern, and their prices are also increasing by drastically. Tighter environmental regulations continue to put pressure on oil-based products and their users. These are the reasons why the use of renewable biobased products provides not only environmentally safe alternative to the manufacturers and users, but also offers comparable performance, economics and biodegradability of the final products.

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

VpCI Building Blocks for Biofuels (BBB) and BBB Bio are the powerful corrosion inhibitors to control the corrosive characteristics of biobased fuels. BBB and BBB Bio incorporate patented VpCI technology to provide protection in all 3 biofuel phases: liquid, interface, and vapor phases. In addition, BBB Bio was developed with soybean oil as a carrier, it can be added to a variety of biofuel and regular types including diesel and gasoline during operation, storage, transport, and distribution BBB and BBB Bio are passing Rust test in accordance to MIL-PRF-25017 and ASTM D-665-92. Actual 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 the 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 excellent corrosion protection in the applications this inhibitor is designed for.

The different approaches can be used to obtain a required or improved environmental profile:

1. Replacement of solvent- or oil-based carriers in formulations with water-based technology, while these technologies provide an environmentally conscious method of corrosion protection [1], they can be cost and time prohibitive for certain operations. In these cases, the manufacturer was left with no choice but to use hazardous for environment petroleum-based products, or simply do nothing.
2. Replacement of petroleum-based carriers with the solvents, manufactured from renewable resource. This has been accomplished by combining VpCIs with soy-derived oils to formulate anticorrosion products for many different applications.
3. Use of biodegradable materials as a corrosion inhibitors.

The focus of the paper will be limited with 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

The paper is presenting two products which recommended as a anticorrosion building blocks to the fuels, including biofuels: BBB and BBB Bio.

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; later, 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.

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 the 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 mentioned above 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:

a. Excellent environmental and safety profile:
   - 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.
   - Biodegradable
   - Very mild irritant
b. Chemistry of soybean oil methyl ester: being a triglyceride of the blend of saturated and unsaturated fatty acids (methyl esters), this product provides some additional corrosion protection to the metallic substrates
c. Solvency of soybean oil methyl ester which is similar or better to petroleum-derived products.

Laboratory Tests

Compatibility Test – ASTM D-4054 B [2]

BBB and BBB Bio were added to fuels at concentration level of 0.25% by volume. Solutions were 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 [3] 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.

BBB and BBB Bio were evaluated according to the *Rust Test* of MIL-PRF-25017 [4] (ASTM D-665) [5] 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 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 with pH 2* (*pH level of the deionized water was adjusted with the laboratory grade sulfuric acid) were added to the solution. Cleaned with methanol and air dried carbon steel panels were immersed in these solution and left overnight at room temperature. Jars were vigorously shaken and left at the 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 was 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. Brine was purged with CO2 for about 30 minutes. BBB and BBB Bio were test at concentration level of 150 ppm. Weight Loss was determined and Z (% of protection) calculated according to formula:

$$Z=\frac{\Delta m_{cont}-\Delta m_{inh}}{\Delta m_{inh}} x100\%$$, 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 for the purpose 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:

50 ^{0}C, 100 RH, 16 hours

80 ^{0}C, 100 RH, 8 hours

Test results are presented in the Pictures 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

Examples of the Field Applications

BBB and BBB Bio continuously used in multiple applications in working and storage conditions.

The examples are:

- long-term lay-up of the BHP Copper Mine in San Manuel, Arizona, USA. BBB was added to gasoline, diesel, and alcohol fuels as a corrosion inhibitor fuel stabilizer and water emulsifier;
- lay-up and operation of tanks T-55 of Croatian Military;
- added as a building block to the fuel tank of pick-up trucks in the working conditions;
- and others

CONCLUSION

BBB and BBB Bio are very effective building blocks for the fuels including Biofuels.

- They provide exceptional corrosion protection when added to the fuels:
  - Different fuels
  - Harsh environment (H_2S, CO_2)
  - For ferrous and non-ferrous metals, used in automotive fuel systems
  - Passing Military requirements for corrosion inhibitors for the fuels
- Based on VpCI technology:
  - Provide protection in all three phases: liquid, interface, and vapor phases above and below the fuel level
  - Successfully used for lay-up applications

Formulated with biodegradable (BBB, BBB Bio) and renewable materials (BBB Bio) these products are continuing to gain in-market acceptance as environmentally conscious products.

References

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

620.197.7	hlapivi inhibitori korozije	vapour phase corrosion inhibitors
665.335.2.094.942	biodizelsko gorivo, metanolizat sojinog ulja	soybean oil methanolysate
621.434-632.5	benzinsko/etanolno mješano gorivo za benzinske motore	gasoline/ethanol mixed fuel for spark ignition engines
621.436-634.9	biodizelsko gorivo, metilni esteri biljnih ulja	biodiesel fuel, vegetable oil methyl esters (VOME)

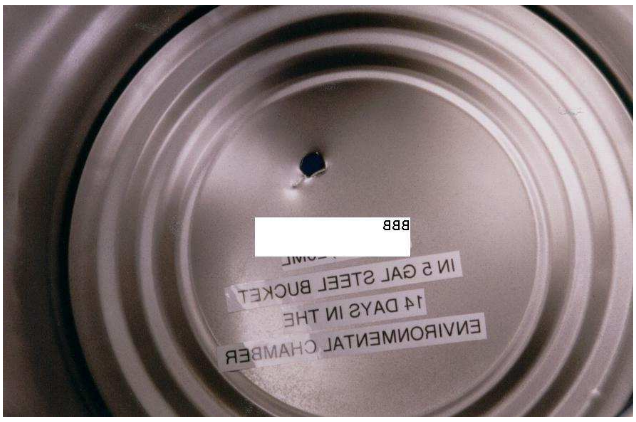
Authors

Boris Mikšić, Margarita Kharshan, Alla Furman, Brian Wuertz
Cortec Corporation, 4119 White Bear Parkway, St.Paul, MN 55110, USA
Ivan Rogan, Cortecros d.o.o. Nova Ves 57,10000 Zagreb, Croatia

Received

10.7.2006.

Picture 1



Picture 2

Picture 3