Paper No.
C2020-14855

Protect and Prolong- A New Multi-functional Diesel Fuel Additive

Pavlo Solntsev
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110
USA

Brian Benduha
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110
USA

Ming Shen
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110
USA

ABSTRACT

Fuel tank interior can be exposed to corrosive environments during operation, storage, and shipping from manufacturers to dealerships or customers. The corrosion processes can be accelerated if bio-diesel fuel is used, which is known to be more corrosive for the fuel system than regular diesel. Discussed here, is a new multifunctional diesel fuel additive designed to be used during the operation, lay-off, and shipping. It provides corrosion protection in contact phase and in the vapor phase to the fuel tank interior, including headspace. It also provides anti-oxidation to diesel fuel. The additive can be easily mixed with diesel fuel in a tank during operation or fogged directly into tank space when in preparation for shipping or storage. The corrosion protection in contact phase was evaluated using ASTM D665B and ASTM D1748, corrosion protection in the vapor phase was evaluated using ASTM D5534 and a modified NACE VIA method. Compatibility to copper was tested and graded according to the ASTM D130. Fuel oxidative stability was evaluated according to ASTM D2274 and ASTM D525.

Key words: Biodiesel, Corrosion, Inhibitor, Fuel additive

INTRODUCTION

Starting from the discovery of crude oil, liquid hydrocarbons represent an essential segment of the chemical industry. The most recognizable products of this segment are fuels. According to the U.S. Energy Information Administration report for 2017, the US consumed 9.33 million barrels of fuels daily, equal to about 47% of total U.S. petroleum consumption.[1] The second most popular fuel was diesel as fuels and as heating oils with 3.93 million barrels daily consumption or 20% of the total petroleum market share. In the U.S. diesel fuel is used in the diesel engines of heavy construction equipment, trucks, buses, tractors, boats, trains, some automobiles, and electricity generators.

Moving towards more sustainable fuel sources, biodiesel becomes more and more popular. Biodiesel can be obtained by transesterification of the vegetable oils or waste cooking oils, where glycerides are converted to the methyl esters of the fatty acids, followed by purification.[2] Such produced biobased diesel is usually not used straight but blended to the regular diesel at different concentrations. For

example, in Minnesota in 2002, the state legislature passed a law that required diesel fuel to contain at least 2 percent biodiesel (B2) (Minnesota Statutes 239.77).[3] The law went into effect on September 29, 2005. The mandate increased the biobased diesel to 5 percent (B5) on May 1, 2009, and 10 percent (B10) on July 1, 2014. On July 25, 2017, the commissioners of the Departments of Agriculture, Commerce, and the Minnesota Pollution Control Agency determined that there was enough biodiesel supply, adequate blending infrastructure, and federal standards in place to require a higher biodiesel content. On May 1, 2018, the biodiesel mandate increased to 20 percent (B20).
Despite growing popularity, biodiesel has some drawbacks. Because of the high polarity of biodiesel, it is hygroscopic, more susceptible to bacteria growth,[4] and less stable towards oxidation.[5,6] All these factors lead to a higher corrosiveness of biodiesel. Additional precautionary steps should be taken to prevent the equipment failure. In the present work, we discuss lab performance data of a fuel additive VpCI-707, a new corrosion inhibiting fuel additive[†].

EXPERIMENTAL PROCEDURE

Biodiesel fuel used in this work was purchased at a local gas station in MN. According to the Minnesota regulation, the commercially available diesel fuel corresponds to the B10 type (purchased before May 1, 2018) and contains 10% of the biodiesel component. No other information is available to identify the diesel composition. The product, discussed in this work, was obtained using formulation methodology from the commercially available in the US raw materials. The untreated diesel fuel was used as a control for all tests described below.

Corrosiveness to copper

Corrosiveness to copper was evaluated using a modified ASTM D130[7] test. In this test, a copper strip was polished using the sandpaper (#240) and immersed into biodiesel fuel, with (4% by wt) or without the corrosion inhibiting additive. The test was conducted at 40°C for 300h. After the test, copper panels were removed, rinsed with hexane and dried on air.

Contact corrosion inhibition

Corrosion protection of carbon steel in the fuel was evaluated using two different methodologies: modified ASTM D1748[8] and ASTM D665B[9] tests.

ASTM D1748: Metal panels were degreased using methanol. The surface was sanded suing sandpaper #240, wiped off with Kimwipes and rinsed with methanol. The panels were then immersed into the fuel with (1.6%) or without the inhibitor additive for 1 min, let drain for 20h and placed to the humidity chamber. After the testing, the metal panels were removed from the chamber and dried on air.

ASTM D665B: Metal sample and seawater solution were prepared as described in the test procedure. The metal sample was immersed in the fuel with (1.6%) or without (control) the inhibiting additive for 30 min at 50°C. A solution of seawater was added, and the mixture was stirred for 4h. At the end of test, the metal sample was removed, rinsed with water, methanol, and dried on air.

Vapor corrosion inhibition testing

A new testing methodology was developed to evaluate the vapor phase protection of the corrosion inhibiting additive. The following setup was found to be optimal for the test. A 50ml of the fuel, with (1.6%) or without the inhibiting additive, was added to a 900 mL jar. A 50 mL beaker containing 20 mL of DI water was gently placed to the bottom of the jar. Carbon steel panels (sanded using sandpaper #240 and rinsed with methanol), were hung in the vapor phase using coated wire hooks secured to the lid of the jar. The testing panels didn't touch the fuel or water. The testing was done at 40C.

ASTM D5534[10]: Was performed according to the test standard as described.

[†] VpCI-707 is a tradename of Cortec Corporation, St Paul, Minnesota, USA

Oxidation stability

The oxidation stability test was performed according to the ASTM D2274[11] standard as described using diesel fuel with 1.6% (fuel additive?).

Elastomer compatibility

The following procedure was followed:

1. Pre-weigh the elastomer sample materials to be tested, note the dimensions, and check the hardness with a durometer.
2. Immerse the samples in solution by hanging vertically from a coated paper clip attached to the lid of the jar, and test for 120 hours at 60°C.
3. At the end of testing, the sample materials were taken out of solution, rinsed and cleaned with DI water or methanol, dried with paper towels, re-weighed, and again checked with the durometer. The materials were also visually observed for any change in color and dimensions and felt for tackiness.

RESULTS

The formulated product represents a clear low viscose liquid and can be easily prepared (formulated) from the readily available chemicals using common blending equipment. The product was developed specifically to minimize chemical and physical hazard that makes it attractive for consumer and industrial applications.

Corrosion inhibition properties were evaluated in the contact phase as well as in above fuel level space. We chose the ASTM D1748 and the ASTM D665B tests as representative tests for the contact corrosion evaluation. The ASTM D1748 test is a very common test to evaluate corrosion protection of product under relatively harsh conditions of 50°C and 100% relative humidity. Also, some OEM specifies this test for oil rust preventatives and fuel additives with the accepted performance of 300h. The humidity testing showed that carbon steel treated with diesel containing 1.6% of xxx was mostly corrosion-free when compared to the control after more than 300 hours humidity exposure, meeting the performance requirement of an OEM's specifications. Figure 1.

ASTM D665 test is another common corrosion test in the oil field area. The test standard specifies two versions of the test: ASTM D665A and ASTM D665B. A seawater solution is used to mimic a corrosive environment under the “B” version. This version is harsher compared to the version “A” where distilled water is used. We changed the test temperature to 50°C to minimize the fuel evaporation during testing. Like the ASTM D1748 test results, the untreated diesel fuel showed no signs of metal protection. In contrast, a treated diesel fuel (1.6%) showed good corrosion protection in seawater corrosive media (Figure 2).

The combined test data from the ASTM D1748 and the ASTM D665B tests demonstrated benefits of treating diesel fuel with the additive to mitigate the corrosion processes between diesel fuel and carbon steel.

Fuel additives such as carboxylate derivatives and chemicals with sulfide and polysulfide groups are known for their corrosiveness to copper and yellow metals. The ASTM D130 test is a common test to evaluate copper corrosiveness in the oil and fuel industries. In our hands, the testing temperature was reduced to 40°C but exposure time was increased up to 308h. No difference observed between treated and untreated diesel fuel sample even at the higher treating rate (up to 4%) (Figure 3).

Air space of a fuel tank can be exposed to the corrosive atmosphere which may include but not limited to saltwater and high humidity. This is especially common for oversea shipping equipment where tank filling to the top is not desired. Two tests were carried out to assess the efficacy of the fuel additive. They were the Vapor corrosion inhibiting testing” (described in EXPERIEMENT PROCEDURE) and ASTM D 5534. In ASTM D 5534, the testing fluid is opened to the atmosphere that allows any volatile components to escape from the tested system, thus higher dosages are therefore required. The Vapor corrosion inhibiting testing, Figure 4, showed that the untreated fuel (control, a) clearly exhibited rusted spots while the treated fuel containing 1.6% additive (b and c) exhibited no signs of corrosion. ASTM D 5534, Figure 5, showed that the metal plug was graded as “PASS” only when the inhibiting additive was increased to 5.6% (wt). Such a high concentration needed to pass the test can be explained by the open system used for the testing.

Different elastomers can be used in a fuel system. Therefore, it is very important to evaluate the compatibility of any fuel additive with common elastomers used in a fuel system manufacture. We choose Viton Rubber, Buna Nitrile, and Neoprene Rubber elastomers as representative samples for the compatibility testing. Compatibility test data presented in Table 1. As we can see, in untreated diesel fuel, Buna Nitrile and Neoprene showed considerable weight change and are not considered being compatible to the fuel. Only Viton Rubber showed reasonable compatibility with the untreated diesel fuel, with a weight change 0.14% after 120 hours of exposure. However, Viton rubber showed a weight change of 6.5% after 96h in diesel fuel containing 3.5% inhibiting additive, putting it into non-compatible category.

Oxidation stability testing of the diesel fuel with and without the additive was evaluated using the ASTM D2274 test protocol and data are presented in Table 2. The treated diesel fuel was found to be more stable towards oxidation compared to the untreated one.

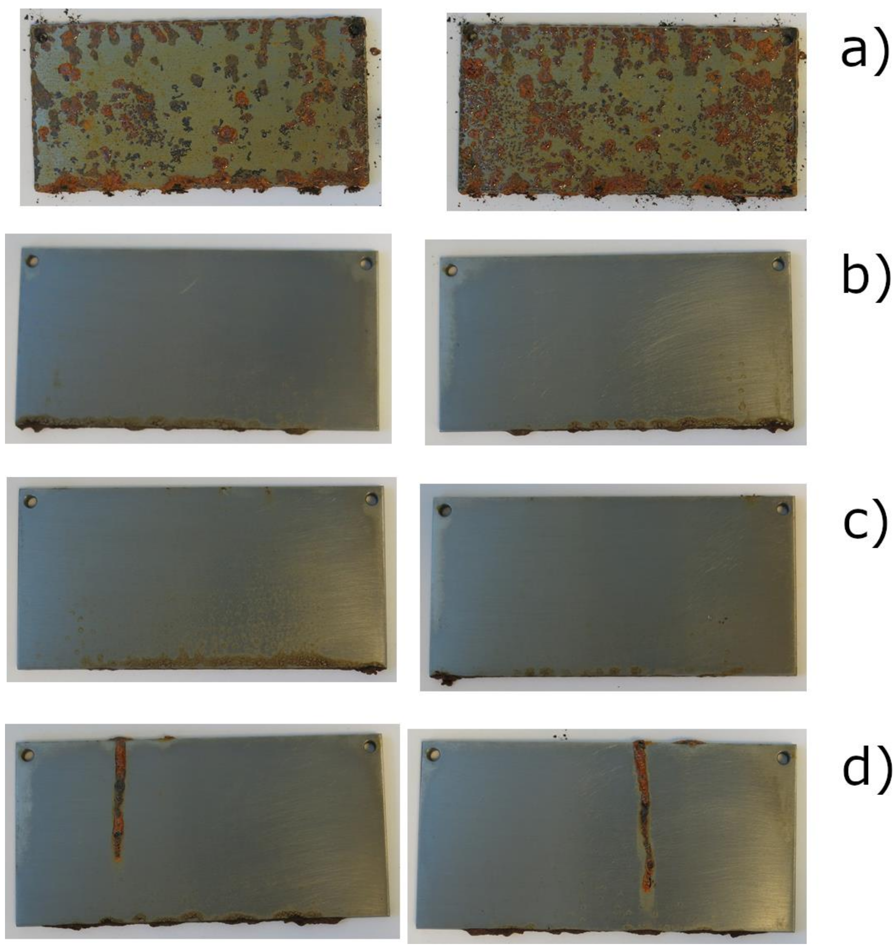

Figure 1: Contact corrosion test results per ASTM D1748 (after 310 h).
(a) –untreated fuel (control), (b) to (d) – diesel fuel with 1.6% additive (triplicate).
Two sides of the tested panels presented.

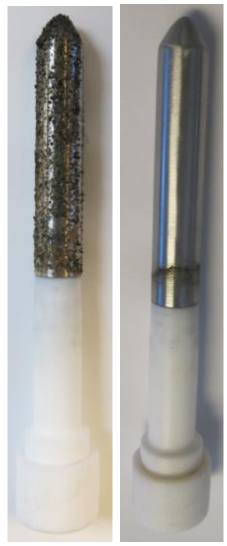

Figure 2: Contact corrosion test results per ASTM D665B.
L – untreated fuel (control), R – fuel with 1.6% additive
Test duration: 4h, temperature: 50°C

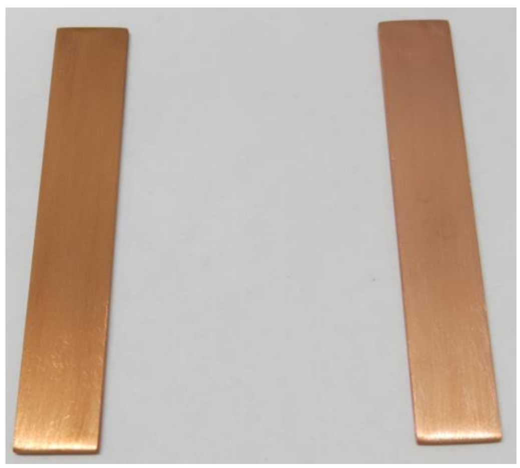

Figure 3: Corrosiveness to Copper per ASTM D130 strip test. Fuel with 4% additive.
Test duration: 308h, temperature: 40°C.

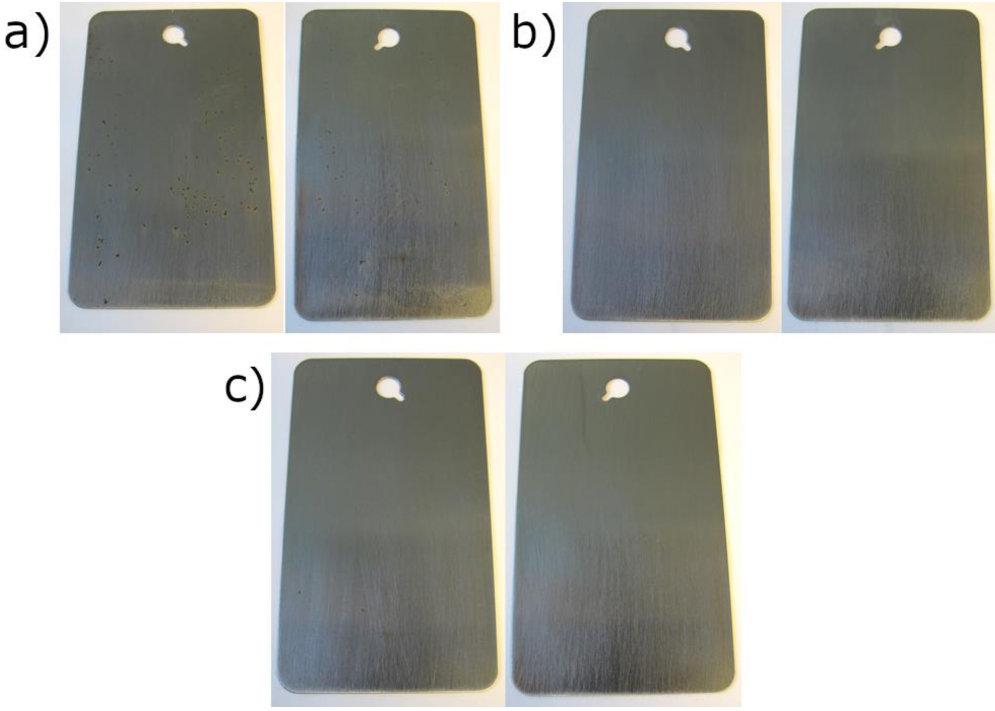

Figure 4: VIA test results.
(a) – fuel w/t additive (two sides)
(b) & (c) fuel w/ 1.6% additive (duplicate, each showing two sides)
Test duration: 720h, temperature: 40°C.

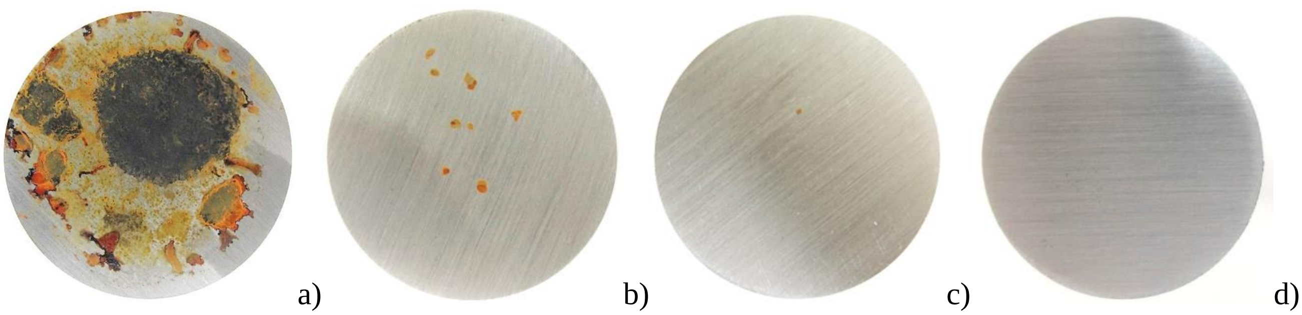

Figure 5: ASTM D5534 test results.
(a) - Untreated diesel fuel, (b) – treated diesel fuel (2.1%),
(c) - treated diesel fuel (3.5%), (d) - treated diesel fuel (5.6%)

Table 1
Compatibility testing of diesel fuel with Elastomers

	Diesel + Viton Rubber	Diesel w/3.5% additive + Viton Rubber	Diesel + Buna Nitrile	Diesel + neoprene
Start weight, g	7.3162	7.1890	5.5965	5.420
End weight	7.3264	7.7.6580	6.6236	6.860
Difference, mg	10.2	469	1027	1440
Weight change, %	0.14	6.5	18.4	26.6
Start dimensions, cm	2.54 x 5.08 x 0.32	2.54 x 5.08 x 0.32	2.54 x 5.08 x 0.32	2.54 x 5.08 x 0.32
End dimensions, in	2.54 x 5.08 x 0.32	2.69 x 5.40 x 0.32	2.79 x 5.46 x 0.48	2.86 x 5.84 x 0.40
Start hardness, creep	A79	A79	-	-

at 15 sec				
End hardness, creep at 15 sec	A79	A69	-	-
Time, h	120	96	24	24

Table 2
Oxidation stability test per ASTM D2274

	Untreated Diesel - Control	Treated diesel (1.6%)
Filtrable insolubles, mg/100mL	<0.1	<0.1
Adherent Insolubles, mg/100mL	0.2	0.1
Total insoluble, mg/100mL	0.2	0.1

CONCLUSIONS

In summary, the fuel additive discussed here can be successfully used to prevent corrosion of carbon steel in diesel fuel liquid and in vapor phase above the fuel liquid per ASTM D1748, ASTM D665B, and the Vapor corrosion inhibiting testing. The additive is not corrosive to copper per ASTM D130. It improves diesel fuel stability per ASTM D2274. The additive can be used in applications as diesel fuel additive, rust-preventative fogging during fuel vessel transportation and storage for a variety of industries.

REFERENCES

1. U.S. Energy Information Administration https://www.eia.gov/energyexplained/oil-and-petroleum-products/use-of-oil.php
2. U. Schuchardt, R. Sercheli, RM. Vargas, “Transesterification of vegetable oils: a review.” J Braz Chem Soc 9, (1998): p. 199.
3. Minnesota Department of Agriculture, https://www.mda.state.mn.us/environment-sustainability/minnesota-biodiesel
4. JA. DeMello, CA. Carmichael, EE. Peacock, RK. Nelson, Arey J. Samuel, CM. Reddy, “Biodegradation and environmental behavior of biodiesel mixtures in the sea: an initial study” Mar Pollut Bull 54 (2007): p. 894.
5. ARP. Ambrozin, SE. Kuri, MR. Monteiro, “Corrosão metálica associada ao uso de combustíveis minerais e biocombustíveis” Quim Nova 32 (2009): p. 1910.
6. M. Meira, P.M.B., Santana, A.S. Araújo, C.L. Silva, J.R.L. Leal Filho, H.T. Ferreira, “Oxidative degradation and corrosiveness of biodiesel”, Corros Rev, 32 (2014): p. 143
7. ASTM D130-19 “Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test” (West Conshohocken, PA, ASTM)
8. ASTM D1748-10 (2015) “Standard Test Method for Rust Protection by Metal Preservatives in the Humidity Cabinet”, (West Conshohocken, PA, ASTM)
9. ASTM D665-14e1 “Standard Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water”, (West Conshohocken, PA, ASTM)
10. ASTM D5534-94 (2018) “Standard Test Method for Vapor-Phase Rust-Preventing Characteristics of Hydraulic Fluids”, (West Conshohocken, PA, ASTM)
11. ASTM D2274-14 “Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)” (West Conshohocken, PA, ASTM)
12. NACE TM0208-2018-SG "Laboratory Test to Evaluate the Vapor-Inhibiting Ability of Volatile Corrosion Inhibitor Materials for Temporary Protection of Ferrous Metal Surfaces" (Houston, TX, NACE International)
13. TL 81135-002 “Testing of Anti-Corrosive Effect of VCI Auxiliary Packaging Materials”