Vapor Phase Inhibitors in Functional Fluids

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The addition of corrosion inhibitors to lubricating compounds prolongs the service life of machinery during its working application and in storage. Criteria for selecting corrosion inhibitors for the equipment during transportation, storage, and mothballing are based on their level of corrosion protection for all metal elements while being compatible with polymers (e.g., hoses and seals) and installed lubricants. According to the application requirements, the tests for such products include evaluation of their performance in environmental chambers, including humidity and salt fog, evaluation of vapor corrosion inhibition, immersion, and other corrosion tests. In operating equipment, corrosion inhibitors added to lubricating fluids should not negatively affect their lubricity, oil-water separation, and other properties important for such fluids. In addition to corrosion tests, evaluation of the fluid with added corrosion inhibitor includes testing of the essential properties listed in the fluid specifications. This article presents the formulating approaches and evaluation of the performance of corrosion-inhibiting additives in functional fluids. The testing program is based on widely adopted standards.

In a widely cited cost of corrosion study[1] the direct cost of corrosion in the United States was estimated to equal $276 billion in 1998, approximately 3.1% of the country's Gross Domestic Product.

The indirect cost of corrosion is estimated to be at least equal to the direct cost. Examination of the data in 2013 indicates that total corrosion costs in the United States exceed $1 trillion annually.

Internal surfaces of equipment corrode during all segments of their life: operation, intermediate operation, and storage. The reasons and the intensity of corrosion vary. Usually functional liquids don't cause corrosion. Corrosion occurs because of the contaminants in functional liquids, such as the presence of moisture, salts, acidity, and other corrosive species. In the majority of cases, corrosion can be prevented, delayed, or reduced by using corrosion inhibitors.

The requirements of corrosion inhibitors for functional fluids are different for equipment lay-up vs. equipment in use. Corrosion protection of machinery during mothballing can be achieved by using special rust preventatives or adding corrosion inhibitors to working lubricating oils. For such application the most important properties of the rust preventative are the level of corrosion prevention; compatibility with all metals, plastics, and polymers used in the system; and sometimes removability.

In operation mode, the corrosion inhibitor additionally should not negatively affect the specified properties of lubricants. This requirement can be satisfied by using special formulas, limiting the dose rate, or using the inhibitor in combination with the additives, which can compensate for the negative effects of the rust preventative. Examples of successful applications of corrosion inhibitors in engine oils and fuels are described in publications.[2-3] The advantage of such products is that they can be high-performance lubricants, while at the same time possessing the ability to prevent corrosion in both storage and operation. This eliminates the necessity of changing the lubricant if equipment needs to be laid-up, returned back to operation, or used intermittently.

This article presents the examples of incorporating corrosion inhibitors in hydraulic fluids, both glycol/water-based and oil-based.

Experimental Procedures

Corrosion Inhibitor for Glycol/Water-Based Hydraulic Fluid

Two vapor corrosion inhibiting additives (VCI-1 and VCI-1L) to glycol/water-based hydraulic fluid were formulated and evaluated. The main ingredients of these additives are a blend of amine salts of saturated iso-carboxylic and aromatic acids.

Among evaluated extreme pressure (EP) additives were several types of phosphate esters and polyalkylene glycol-based products. VCI-1L consisted of 96% VCI-1 and 4% of a compatible high-performance EP lubricant. Two suitable EP lubricants were found in screening tests. Either can be used in formula VCI-1L when EP performance is required as a part of the package. When VCI-1L is made with EP additive 1, it is identified as VCI-1L1; when made with EP additive 2, it is identified as VCI-1L2. Results and descriptions identified only as VCI-1L apply to both formulations.

Table 1 shows results of the additive analysis conducted by an independent laboratory using scanning electron microscopy (SEM)-energy dispersive spectroscopy (EDS). Table 2 shows the properties of VCI-1 and VCI-1L. These products are intended to be used in subsea equipment. Besides high performance in corrosion inhibition and lubricity, their impact on the sea environment had to be evaluated.

TABLE 1. ADDITIVE ANALYSIS

Element	EP Additive 1 (wt%)	EP Additive 2 (wt%)
Ash	0.007	2.27
Oxygen	54.26	53.71
Sodium	1.96	–
Aluminum	—	1.16
Silicon	38.47	9.34
Phosphorus	4.69	31.01
Potassium	0.62	1.28
Zinc	—	3.48

TABLE 2. PHYSICAL-CHEMICAL PROPERTIES OF VCI-1 AND VCI-1L

Test	VCI-1	VCI-1L
Appearance	Clear yellowish to amber liquid	Clear yellowish to amber liquid
pH	9-8 (1% in water)	7.5-8.5 (1% in water)
Density	8.5-8.7 lb/gal (1.03-1.06 kg/L)	8.6-8.8 lb/gal (1.03-1.06 kg/L)
Non-Volatile Content	50-60%	60-70%

The components of the formulated additive were tested according to the North Sea (United Kingdom, Norway, Denmark, and The Netherlands) regulations to satisfy the criteria:

- Biodegradability: >60% in 28 days
- Marine toxicity: Effective concentration 50% (EC50)/lethal concentration 50% (LC50) >10 mg/L to North Sea species
- Bioaccumulation: Log octanol/water partition coefficient <3

Performance Tests

Performance testing for VCI-1 and VCI-1L included the following tests.

Compatibility with Seawater Test

This test was performed as follows: Hydraulic fluid samples with added 10% artificial seawater were subjected to cycling for 16 h at 80 °C and 8 h at 7 °C. Samples were subjected to seven cycles and then inspected visually for any changes.

IP 287 Cast Iron Chip Corrosion Test[4]

This test was performed as follows: The dilution of samples of hydraulic fluids with 10% and 25% of artificial seawater were prepared. Cast iron chips were placed on filter paper and wetted with a sample of hydraulic fluid. The area of paper stained with corrosion was recorded after 2 h.

Vapor Corrosion Inhibition Test

This was evaluated according to ASTM D5534,[5] "Standard Test Method for Vapor-Phase Rust-Preventing Characteristics of Hydraulic Fluids." This test method evaluates the ability of hydraulic fluids to prevent the rusting of steel in the vapor phase over the hydraulic fluid and water. A sample of the fluid was placed into the testing beaker. The beaker was heated to the temperature of 60 °C and then sealed with the lid, with an attached carbon steel (CS) plug (coupon) inside. The plug was evaluated for the presence of rust after 6 h of testing.

Multi-Metal Vapor Corrosion Test

This test was performed on UNS G10180 CS (SAE 1018) and copper. In this test, hydraulic fluid with the added corrosion inhibitor was heated to 60 °C in a wide neck conical flask. The metal panel was placed over the mouth to stand for 15 min. After that, the panel was visually inspected for the presence of corrosion.

Anti-Wear Properties Test

Anti-wear properties of the corrosion inhibitor formulation were tested (only VCI-1L2) using a Falex[†] lubricant tester with 2 V-block made from UNS G11370 (AISI 1137) steel and brass pin.[6] The target torque and anti-wear properties of the final fluid were as follows:

- 15 lb·in (1.69 N*m) at a load of 500 lb (227 kg) for 1 min
- < 20 lb·in (2.26 N*m) at load of 500 lb (227 kg) for 30 min
- Wear teeth = 5 or less

Corrosion Inhibitor for Mineral/Synthetic Oil-Based Hydraulic Fluids (VCI-2)

A vapor corrosion inhibiting additive for oil-based hydraulic fluids formula is an oil-soluble blend of calcium sulfonate and amino-carboxylates in synthetic oil. Its physical-chemical properties are shown in Table 3.

TABLE 3. PHYSICAL-CHEMICAL PROPERTIES OF VCI-2

Appearance	Brown viscous liquid
Density	0.91-0.96 kg/L
Non-Volatile Content	91-97%

The VCI additive was tested in hydraulic oil with physical-chemical characteristics conforming to ISO Grade 32.Testing procedures of ISO 32 hydraulic oil with and without VCI-2 included the following procedures:

- Water Separability (ASTM D1401[7]). This test method evaluates the ability of fluids to separate from water. Equal volumes of fluid and deionized water were mixed and placed in a graduated cylinder. The method evaluates the separated volume of fluid and water at the recommended temperature after several time intervals after mixing. Volumes are reported as oil/water/emulsion.
- Copper Strip Corrosion (ASTM D130[8]). This test evaluates the relative degree of fluid corrosivity to copper. A copper

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[†] Trade name.

strip is immersed in a sealed container with fluid, which was placed in the oven (set at 100 °C) for 3 h. Classification of the corrosiveness was made by comparing the appearance of the strip with the ASTM Copper Strip Corrosion classification standards.

- Pour Point per ASTM D97.[9]
- The rust preventing characteristics (ASTM D665[10] or IP 135, Procedure B in the presence of salt water) test method covers the evaluation of the ability of an inhibited fluid to prevent the rusting of ferrous parts. A rotating testing rod made from CS was inserted into the fluid. Artificial seawater was added to the fluid in the ratio of 30 mL of seawater to 300 mL of fluid. The test was performed at 120 °F (48.9 °C) for 4 h. Afterward, the test rod was inspected for the presence of corrosion.
- Acid/base number by color indicating titration (ASTM D974).[11]
- Viscosity at 40 °C and 100 °C per ASTM D2196.[12]
- Accelerated corrosion testing (ASTM D1748 [13])evaluates the rust-preventive properties of fluid under conditions of high humidity. Panels made from UNS G10100 CS (SAE 1010) were coated with hydraulic fluid and left in a vertical position for 2 h at room temperature. The panels were placed in a humidity cabinet and inspected for the presence of corrosion on a regular basis.

Results

VCI-1 and VCI-1L Test Results

The corrosion inhibition performance of VCI-1 and VCI-1L is presented in Table 4. The results show that the formulations provide effective corrosion protection while maintaining phase stability of the hydraulic fluid.

Table 5 shows the lubricity results obtained with VCI-1L2. The results are close to the target values, and within an acceptable range for typical customers.

VCI-2 Test Results

Table 6 shows the results of ASTM D1401, "Water Separability Test." Water separation is actually improved by the addition of VCI-2.

TABLE 4. CORROSION INHIBITION EVALUATION OF VCI-1 AND VCI-1L

Test Performed		Results
IP 287	Liquid corrosion test on neat fluid	No corrosion
	With 10% of seawater	No corrosion
	With 25% of seawater	No corrosion
Vapor Phase Corrosion Test		Pass
Compatibility with Seawater (10 % by Volume)		Clear fluid
Stability at	Room Temperature	Clear stable
	70 °C	Clear stable
	–20 °C	Clear stable
Multi-metal vapor corrosion		Pass

TABLE 5. LUBRICITY LEVEL OF GLYCOL/WATER-BASED FLUID WITH 10% VCI-1L2

Load (lb) at (min)	Torque Values (lb·in)	Load (kg) at (min)	Torque Values (N·m)
100 (1)	6.3	45.4 (1)	0.71
200 (1)	10.7	90.7 (1)	1.21
300 (1)	13.3	136 (1)	1.50
400 (1)	17.8	181 (1)	2.01
500 (1)	21.3	227 (1)	2.41
500 (30)	18.2	227 (30)	2.06
Other Lubricity Results			
Number of Teeth	6		
% Weight Loss of Pin	0.058%		

TABLE 6. SEPARABILITY TEST RESULTS

Sample	20 min	25 min	30 min	35 min	Description of Results (tested at 54 °C)
ISO 32 Hydraulic Oil (Control)	17-40-23	26-40-14	36-40-4	40-40-0	Complete separation of oil and water occurred after 35 min.
ISO 32 Hydraulic Oil + 2% VCI-2	35-39-6	40-40-0	—	—	Complete separation of oil and water occurred after 25 min.

TABLE 7. ISO 32 HYDRAULIC OIL CHARACTERISTICS

Test	Test Method	Results for ISO 32 Hydraulic Oil (Control)	Results for ISO 32 Hydraulic Oil + 2 % VCI-2
Copper Strip Corrosion Test, 3 h at 100 °C	ASTM D130	1a	1a
Pour Point	ASTM D97	–18 °C	–18 °C
Viscosity at 40 °C	ASTM D2196	26 cps (0.026 Pa*s)	25 cps (0.025 Pa*s)
Viscosity at 100 °C	ASTM D2196	6 cps (0.006 Pa*s)	6 cps (0.006 Pa*s)
Rust Prevention Test (tested at 60 °C for 4 h)	ASTM D665 (Procedures A & B)	Pass	Pass
Acid Number	ASTM D974	0.2 mg KOH/g	0.4 mg KOH/g

Table 7 shows the results of the hydraulic oil characterization tests. The results for the formulation containing VCI-2 are very close to those of the base hydraulic oil. Both samples passed the rust prevention test. However, as is seen in Figure 1, the sample with VCI-2 shows improved corrosion prevention under more aggressive conditions.

Conclusions

This work confirms that functional fluids can be satisfactorily formulated with VCI-1 and VCI-2. The final formulations provide improved corrosion resistance for glycol/water- or oil-based hydraulic fluids, while conforming to required performance specifications.

FIGURE 1 Panels at end of accelerated corrosion test; control (left) and sample with VCI-2 (right).

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This article is based on CORROSION 2016 paper no. 7506, presented in Vancouver, British Columbia, Canada.

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