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Vapor Phase Inhibitors in Functional Fluids

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ABSTRACT

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. Evaluation of the fluid with added corrosion inhibitor includes (in addition to corrosion tests) testing of the essential properties listed in the fluid specifications.

This paper 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.

Key words: vapor corrosion inhibition, tests, oil based and synthetic hydraulics and turbine fluids, lubricating oils

INTRODUCTION

In a widely-cited study[1] by the National Association of Corrosion Engineers, NACE, the direct cost of corrosion in the U.S. was estimated to equal $276 billion in 1998, approximately 3.1 % of GDP. The indirect cost of corrosion is estimated to be at least equal to the direct cost. Examination of the NACE data in 2013 indicates that total corrosion costs in the U.S. exceed $1 trillion dollars 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 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 addition of 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, corrosion inhibitor additionally should not negatively affect the specified properties of lubricants. Such requirement can be satisfied by using special formulas, limiting the dose rate, or use 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 paper presented the examples of incorporation of corrosion inhibitors in hydraulic fluids both glycol/water and oil based.

EXPERIMENTAL PROCEDURE

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 consist of 96 % of 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/descriptions identified only as “VCI-1L” apply to both formulations.

Below, in Table 1, are shown results for ash, SEM-EDS (scanning electron microscopy, SEM and energy dispersive spectroscopy, EDS(1)) analyses of these additives.

Table 1: Additive analysis

Element	EP additive 1 (% weight)	EP additive 2 (% weight)
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

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(1) Testing performed at an independent laboratory

The properties of VCI-1 and VCI-1L are shown the Table 2 below.

Table 2: Physical-chemical properties of the 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 %

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.

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

- Biodegradability: > 60 % in 28 days
- Marine toxicity: Effective Concentration, 50 % (EC_{50})/Lethal Concentration, 50 % (LC_{50}) > 10 mg/L to North Sea species
- Bioaccumulation: Log Octanol/Water Partition Coefficient (Pow) < 3

Performance testing for VCI-1 and VCI-1L includes the following tests:

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

2. *IP*⁽²⁾ *287 Cast Iron Chip Corrosion*[4] 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 sample of hydraulic fluid. The area of paper stained with corrosion was recorded after 2 hours.

3. *Vapor corrosion inhibition* was evaluated according to ASTM(3) D5534[5] *Standard Test Method for Vapor-Phase Rust-Preventing Characteristics of Hydraulic Fluids*. This test method evaluates 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 plug (coupon) inside. The plug was evaluated for the presence of rust after 6 hours of testing.

4. Multi-metal vapor corrosion test was performed on carbon steel UNS G10180 (SAE(4) 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 minutes. After that, the panel was visually inspected for the presence of corrosion.

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3

5. 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(5) 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 minute
   < 20 lb·in (2.26 N*m) at load of 500 lb (227 kg) for 30 minutes
   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 in Table 3.

Table 3: Physical-chemical properties of the 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 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. 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 strip is immersed in a sealed container with fluid, which was placed in the oven (set at 100 °C) for 3 hours. Classification of the corrosiveness was made by comparison of the appearance of the strip with the ASTM Copper Strip Corrosion classification standards.

- *Pour Point* per ASTM D97.[9]

- *Rust Preventing Characteristics* (ASTM D665[10] or IP 135, Procedure B in presence of salt water) test method covers the evaluation of the ability of inhibited fluid to prevent the rusting of ferrous parts. Rotating testing rod made from carbon steel was inserted into fluid. Artificial seawater was added to the fluid in the ratio 30 mL of seawater to 300 mL of fluid. The test was performed at 120 °F (48.9 °C) for 4 hours. After, the test rod was inspected for the presence of corrosion.

- *Acid/Base number* by color indicating titration (ASTM D974).[11]

- Viscosity @ 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 carbon steel UNS G10100 (SAE 1010)

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(5) American Iron and Steel Institute, 25 Massachusetts Avenue, NW Suite 800, Washington, DC 20001

were coated with hydraulic fluid and left in vertical position for 2 hours at room temperature. The panels were placed in humidity cabinet and inspected for the presence of corrosion at the regular basis.

RESULTS

VCI-1 and VCI-1L Test Results

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

Table 5: Falex 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 %		

VCI-2 Test Results

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

Table 6: Separability Test Results

Sample	20 min	25 min	30 min	35 min	Description of Results (tested @ 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 minutes.
ISO 32 hydraulic oil + 2 % VCI-2	35-39-6	40-40-0	-	-	Complete separation of oil and water occurred after 25 minutes.

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

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 hours @ 100 °C	ASTM D130	1a	1a
Pour Point	ASTM D97	-18 °C	-18 °C
Viscosity @ 40 °C	ASTM D2196	26 cps (0.026 Pa*s)	25 cps (0.025 Pa*s)
Viscosity @ 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 hours)	ASTM D665 (procedure A & B)	Pass	Pass
Acid Number	ASTM D974	0.2 mg KOH/g	0.4 mg KOH/g

ASTM-D1478 (humidity cabinet)
After 215 hours of testing

Figure 1: Panels at end of Accelerated Corrosion test Control (left), Sample with VCI-2 (right)

CONCLUSIONS

This work confirms that functional fluids can be satisfactorily formulated with vapor corrosion inhibitors 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.

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