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VAPOR CORROSION INHIBITOR IN LUBRICANTS

Abstract

Incorporating of Vapor Corrosion Inhibitors in lubricating products provides a number of advantages. VCIs when added to lubricant will provide corrosion protection to machinery during the storage or transportation period and after that the same lubricant can be used in designed working application without spending extra time and money for changing the corrosion protective product for lubricating. Properly chosen combination of VCI and lubricating product also prolongs service life of machinery by minimizing the corrosive wear of the equipment. The requirements to the Vapor Corrosion Inhibitors, which will be added to the lubricants, vary considering the application condition. Usually these products should be thermostable, should not attack colored metal at high temperatures, and effect physical – chemical properties of lubricant.

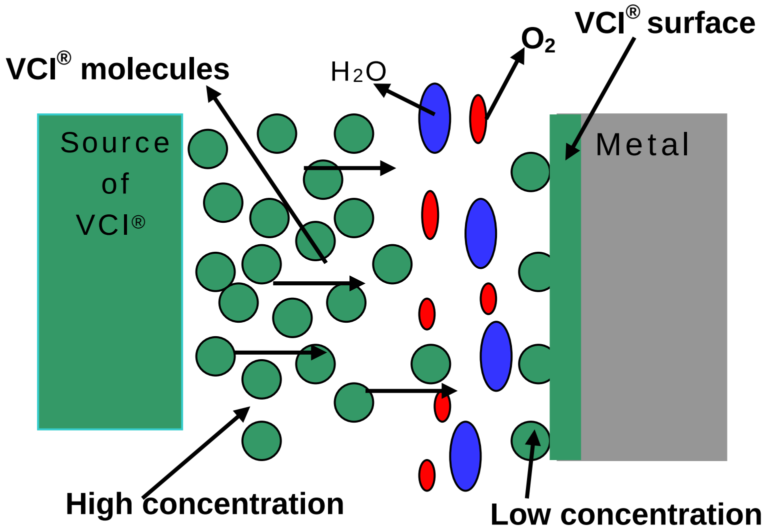
Two examples of lubricating product containing vapor corrosion inhibitor are presented in this paper.

INTRODUCTION

Vapor Corrosion Inhibitors (VCIs) are organic compounds that have appreciable pressure of saturated vapors under atmospheric conditions and inhibit corrosion by adsorption on metal / electrolyte interface. Vapor Corrosion Inhibitors change the kinetics of electrochemical reaction. The most effective are the vapor corrosion inhibitors, which have the vapor pressure in a range 10-5 – 10-7 mm Hg **[1-3,4]**. They are transported by diffusion through the gas phase and adsorbed onto metal in a thickness of a few monolayers and protect it from corrosion.

Usually vapor corrosion inhibitors form a hydrophobic protective layer on the metal. It was found that the most effective are the vapor corrosion the molecule of which consisted from amine and acid parts. The main function of the lubricants is to reduce the friction between two surfaces in rubbing contacts **[5]**. Lubrication reduces wear, save power of working equipment. The difference between the rust preventative for protection of the metal parts and machinery during mothballing or storage and the corrosion inhibitor in operating oils is that this inhibitor should not negatively affect the working properties of this oil.

Figure 1. Difusion molecules of VCI



Generally hydrocarbon based lubricant provides certain corrosion protection for the metals parts on which it is applied, but often not at the necessary level **[6]**. From other side, the service conditions of lubricated metal part can cause different kinds of corrosion mechanical damage. For example, post tensioning cables can be destroyed by stress corrosion cracking **[4]**; at the same time engines are subjected to the corrosive wear **[7,8,9,10]**. Corrosive wear caused by a chemical reaction that actually removes material from the surface. Particles of the surface are than easily removed. Water and combustion by-products are the catalysts for the chemical attack. The high operating temperatures of an engine are usually burn off most water and fuel in the engine.

However, in low-temperature operating conditions this is not the case. The water which remains unburned in engine may itself contain corrosive by-products to form acidic compounds. Foe example all diesel fuels, when combusted, leaves a small amount of sulfur. This small amount of sulfur and water in a diesel engine can react to form sulfur acid, which cause corrosive wear of engine **[9]**. It was found that ear of the rings and liner in crosshead engine caused by both corrosive and mechanical mechanisms. Also the ratio between corrosive and mechanical wear is not exactly determined, a ratio of 4:1 between the two wears is generally accepted **[10]**. Engine life span depends on the corrosion wear of piston rings, liner and crankshaft bearings. The test prove, that not the viscosity of lubricating oil, but the quality of the additives package effects the corrosive wear of engine.

Some companies suggest that alkalinity in oils (TBN) should prevent corrosive wear caused by combustion process and rust. Most lubricants contain additive packages: rust, corrosion and oxidation inhibitors that function in many ways **[8]**. Oxidation inhibitors prevent the formation of corrosive acids. Other inhibitors:

a) displace water and electrolytes from the metal surface and act as water repellent,

b) promote emulsification of free water,

c) chemically passivate metal surfaces **[8,7,4]**.

Condensation and/or water contamination is especially troublesome during lengthy shut down periods, when surfaced not continuously flushed with oil. Because of that incorporating of rust inhibitors in oils is essential for providing a protective residual film on the metal **[6,7]**. All above confirms the importance of corrosion inhibitors in preventing corrosive wear. Also one of the major advantage of adding the corrosion inhibitors in the lubricants is the possibility to illuminate the step of applying the preservative for the long term storage and removing it, when machinery should be in serves **[7]**. In case if using of vapor corrosion inhibitors for this purpose, lubricant will protect from corrosion not only the covered parts of the metal but also the surrounding surfaces **[12]**. Vapor corrosion inhibitors by their chemical nature protect metals from the combined effect of corrosion and mechanical stress on its behavior. It is reported that vapor corrosion inhibitors protect stainless steel from hydrogen embrittelment **[1-3]**.

Corrosive-mechanical destruction starts with localized corrosion, for example pitting or intergranular corrosion. This spot concentrates the mechanical tension and develops in micro crack. Micro crack acts as a very effective electrochemical cell: because of low aeration level and absence of the protective oxides, its head acts as an effective anode. At the same time the walls of the micro crack and surrounding areas become cathode. The development of crack is the self accelerating process of localized corrosion followed by growing level of mechanical tension at the head of the crack. Vapor corrosion inhibitors, being bipolar, are attracted to both: positively and negatively charged areas of the metal. When vapor corrosion inhibitor is introduced in the location of growing corrosive mechanical crack they adsorbs and forms the protective films on both cathodic and anodic areas. This action of vapor corrosion inhibitors decreases the difference in electrochemical potential of galvanic cells and prevents developing of the corrosion mechanical cracks **[4,13]**.

Vapor corrosion inhibitors were incorporated into wide variety of lubricants, including vegetable oil based lubrication products. They do not negatively effect working properties of lubricants and provide excellent level of corrosion protection **[14,15]**. This investigation will confirm that vapor corrosion inhibitors provide effective corrosion protection not only during storage and mothballing but also for the working engine.

EXPERIMENTAL

I. Incorporating of the vapor corrosion inhibitor into teflon based grease

Basic lubricant consisted from hydrotreated heavy distillate, organic polyurea thickener and Teflon (Accrolube) Corrosion inhibitor consisted from the contact sulfonate based inhibitor and aminocarbooxylate based vapor corrosion inhibitor was added to this grease at concentration level of 5% by weight. Obtained lubricant was applied on clean rust free carbon steel panels with film thickness of 7-8 mil (175-200 µm).

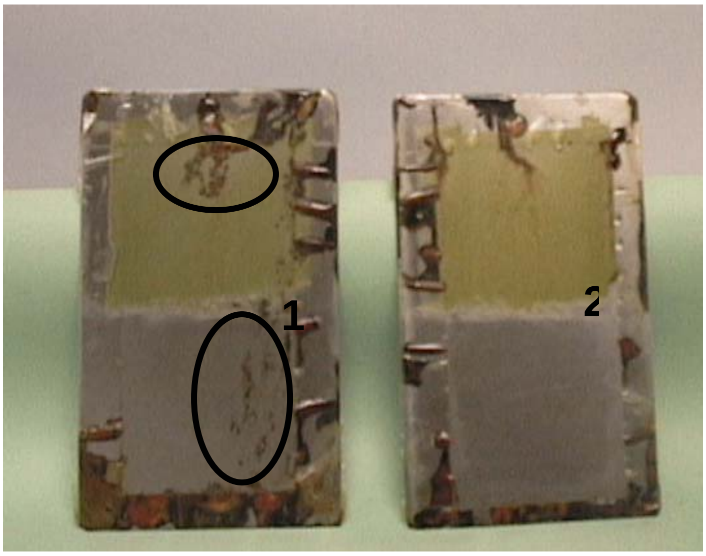
Corrosion protection was evaluated according to ASTM B 117 in salt spray cabinet. Conditions in the cabinet were: constant spray of 5% sodium chloride solution at the temperature 95˚F (35˚C). Vapor corrosion inhibiting properties were tested as follow: 50-ml of electrolyte containing 1% of sodium chloride and 1% of ammonia sulfate in de-ionized water were poured into 1-gallon (3.785L) jars. Two panels (one bare and one coated with lubricant) were attached to the lids, the jars were sealed and placed in an oven set for cycling according to the standard F-12 test procedure. The panels were inspected for any signs of corrosion after 8 days. Results are presented in Table 1 and Figure 1.

Table 1.

Material	ASTM B 117 (Salt spray) Time before Corrosion (Days)	F-12 Modified Presence of Corrosion on Bare Panel
5% Vapor Corrosion Inhibitor-1+ 95% Teflon grease	>14	No corrosion
Teflon grease	9	Corrosion
Control*	<1 hr.	Corrosion

**Bare Panel*

Figure 2: ASTM B 117 (salt Spray) test results



1. *Tefflon Grease (circled areas are where* corrosion developed)
2. *Tefflon Grease with 5% of vapor corrosion inhibitor*

As one can see Vapor Corrosion Inhibitor not only provides Teflon grease with it with vapor corrosion inhibiting ability, but also improves its corrosion protection against chlorides.

II. Incorporating of Vapor Corrosion Inhibitor Into the Engines Oil

The second investigation was conducted with the high performance engine oil grade 10W-30 and grade 15W-40. The set of laboratory tests was utilized for evaluation of corrosion inhibitor for the engine oils. It included methods of evaluation of the protection against electrochemical corrosion; effect on high temperature corrosion of the colored metals; oxidation and others physical-chemical properties of oil.

Compability test. One of the requirements to the corrosion inhibitor was that it should not cause any separation, precipitation or viscosity in original oil. During this the compability test samples of oils with added inhibitor were subjected to the temperature cycle 8 hours at 80˚C and 16 hours at -5˚C for three cycles. After that samples were evaluated for any visible change and kept for 200 days at ambient condition.

ASTM D 1748 Corrosion test in humidity cabinet. For this test samples of oils were applied on sanded and cleaned with metal carbon steel and copper panels by dipping. Those panels were placed in a humidity chamber 20 hours later and inspected for any signs of corrosion daily.

ASTM 130 (Copper Strip Tarnish Test) was performed according to the standard procedure at 80˚-95˚ for 96 hours.

The Ball Rust Test (BRT). The following acid solution was prepared:

Material	**Weight , g**
Acetic acid	6.646
HBr	4.892
HCl	103.232
De-ionized water	Fill to 1L mark

For this test the sample of oil and the acid solution were mixed at a ratio of 5:1. The BRT test was performed in a flat glass dish placed on a hotplate. The panels were washed in methanol, air-dried and immersed in 350 ml of the mixture and stirred at a rate of 300 rpm and airflow of 40 cc/min. The temperature of the test was 70˚C; the duration was 48 hours. The acid solution was added to the mixture on a regular basis: 25 ml at 8:30 a.m. and 50 ml at 40:30 p.m. each day of testing. According to the test acceptance criteria, the panels must have no corrosion after 18 hours.

Cummins High Temperature Corrosion Bench Test: 100 ml of oil were placed in a test tube. A glycerin bath was used to maintain the temperature during the test at 125˚ - 130˚C. Panels were washed in methanol, air-dried and immersed in oil being tested. An airflow of ~5L/min. was provided through the oil by an immersed atomizer made from fitted glass.

The requirements for the oil according to this test are:

1. After the test, copper specimen should not loose weight, and when visually evaluated according ASTM D 130 Copper Strip Corrosion Standards, should not be discolored more than allowed for grade 3.
2. Increase of concentration of metal in oil after the test should not exceed above baseline: for Copper – 20 ppm, for Lead – 120 ppm.

II. Multimetal Cummins Bench Corrosion Test: Copper, lead and carbon steel panels were washed with methanol, air-dried and immersed in the oil sample. The test was run at 135˚C and for 7 days. The requirements are the same as the Cummins High Temperature Bench Test.

Conducted laboratory tests indicate, that some of very effective in preventing electrochemical corrosion additives caused high temperature corrosion of copper and lead and accelerates the oxidation of the engine oil. The attempt to suppress this negative effect by adding to the oil antioxidants or anticorrosion additives did not give sufficient improvement. Among the tested for this purpose additives were Triazoles, Tiazoles, Ditiophosphates, Molybdenum containing additives, Diphenylamine and Butyl-Para-Cresol based antioxidants and their combinations.

Finally, it was found that the combination of sulfonate and aminnocarboxylate at concentration level of 2% by weight provides excellent protection against electrochemical corrosion and do not caused adverse effects on high temperature corrosion of colored metals and oxidation stability of engine oils (Table 2., Figure 2).

Table 2: Results of laboratory test of engine oils

Material	ASTM D 1748		ASTM D130	BRT*	Cummins Bench Test Copper Discoloration
	Carbon steel	Copper			
SAE 10W -30	6	5	1b	Pass/Corrosion	2c
SAE 10W-30+2% Vapor Corrosion inhibitor-2	>21	>10	1b	Pass	2c
SAE 15W-40	4	6	1b	Pass/Corrosion	2c
SAE 15W-40+2% Vapor Corrosion Inhibitor -2	>21	>10	1b	Pass	2c

**SAE 10W-30 and SAE 15W-40 provide protection to carbon steel after 18 hours of testing according to the BRT test, but fail to protect for 48 hours in these conditions.*
***Analyses of used oils: ICP (Inductively Coupled Plasma Mass Spectrometry) for metal content determination; viscosity level, % of solids and water, oxidation, Total Base and Acid Numbers (TBN and TAN) were performed by CTC Analytical Services Laboratory.*

Engine oil grade 10W-30 with 2% of vapor corrosion inhibitor containing additive was tested in a 1999 Ford Lincoln Continental with a gasoline powered V-8 engine. If was found that incorporated the corrosion inhibitor lowered copper and iron contain and did not show any adverse effects on chemical and physical parameters. (Figures 3, 4).

Figure 3

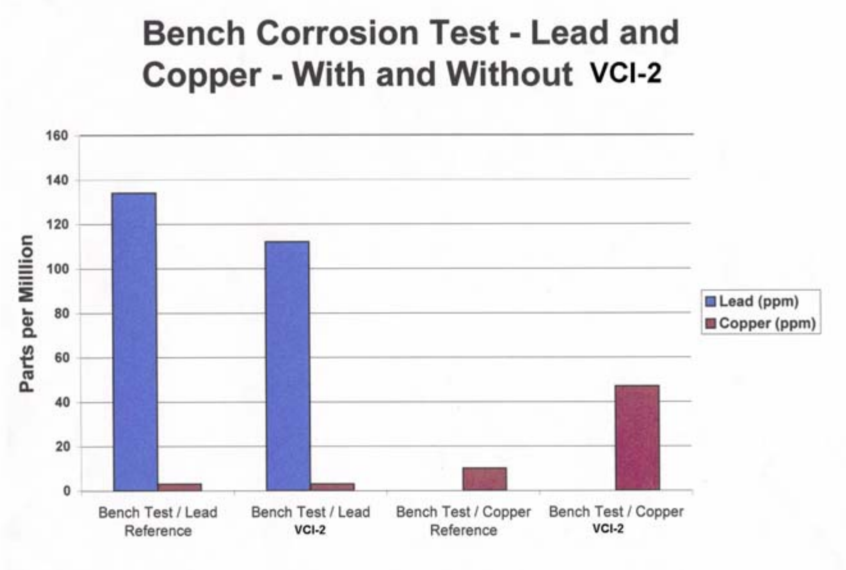


Figure 4

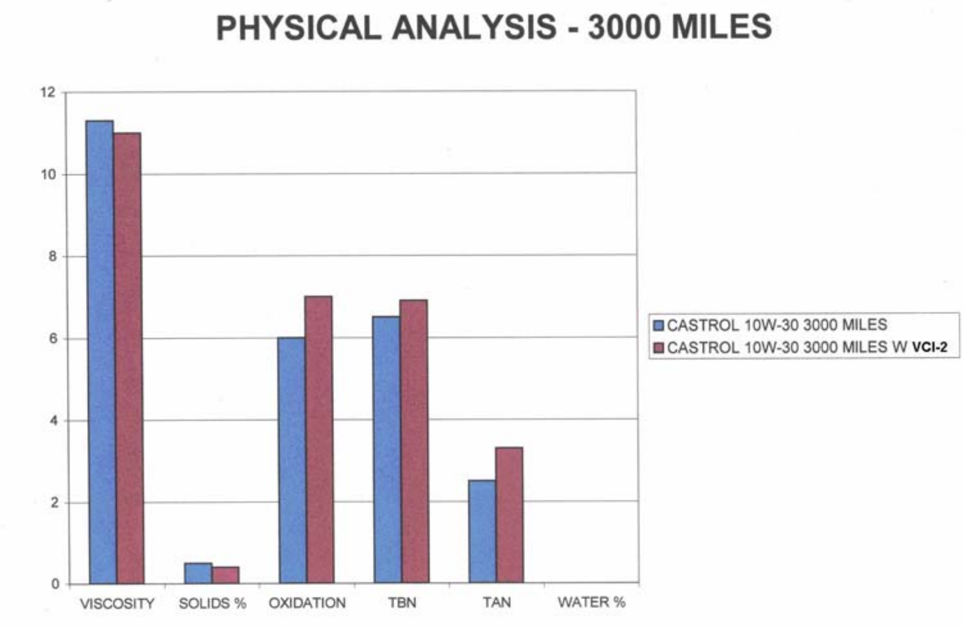
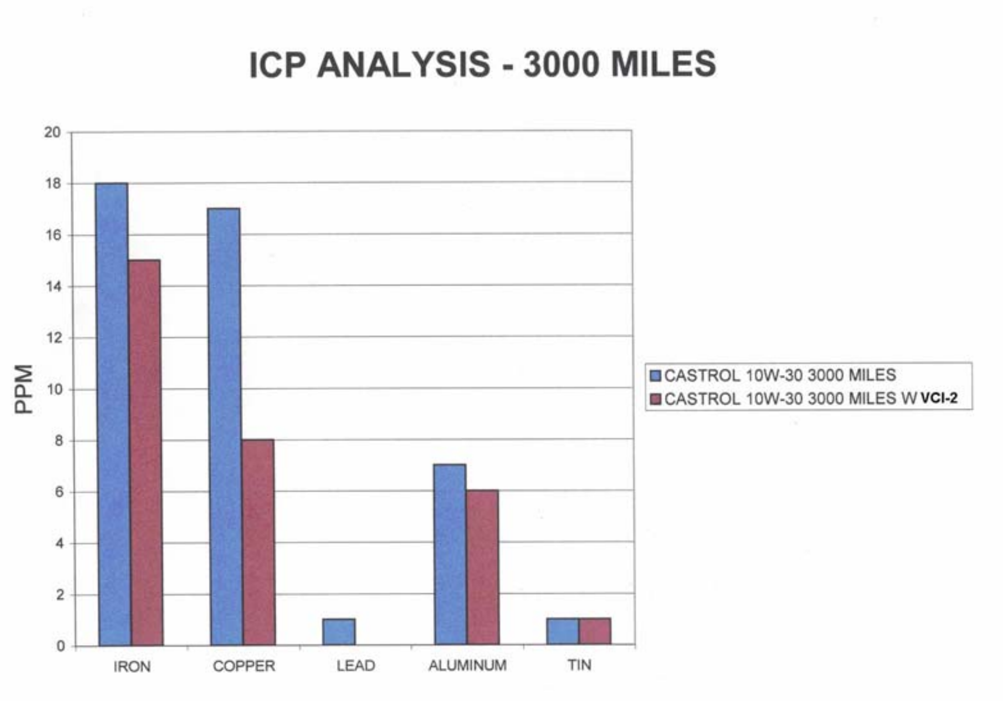


Figure 5



CONCLUSIONS

1. Vapor corrosion inhibitors combined with contact inhibitor was incorporated in lubricating Teflon based grease. Containing this additive lubricant provide excellent protection against salt spray and also protects from corrosion the metal surrounding areas coated by lubricant.
2. Additives, containing contact and vapor corrosion inhibitors can be added to the engine oil. They provide excellent protection against atmospheric corrosion during storage and shipping save time and money because illuminate the step of changing the rust preservative oil for operating engine oil, prevent corrosion by aggressive condensates and lower the corrosive wear of the operating engine.

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