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MULTIFUNCTIONALITY OF MOLYVAN® FRICTION MODIFIERS

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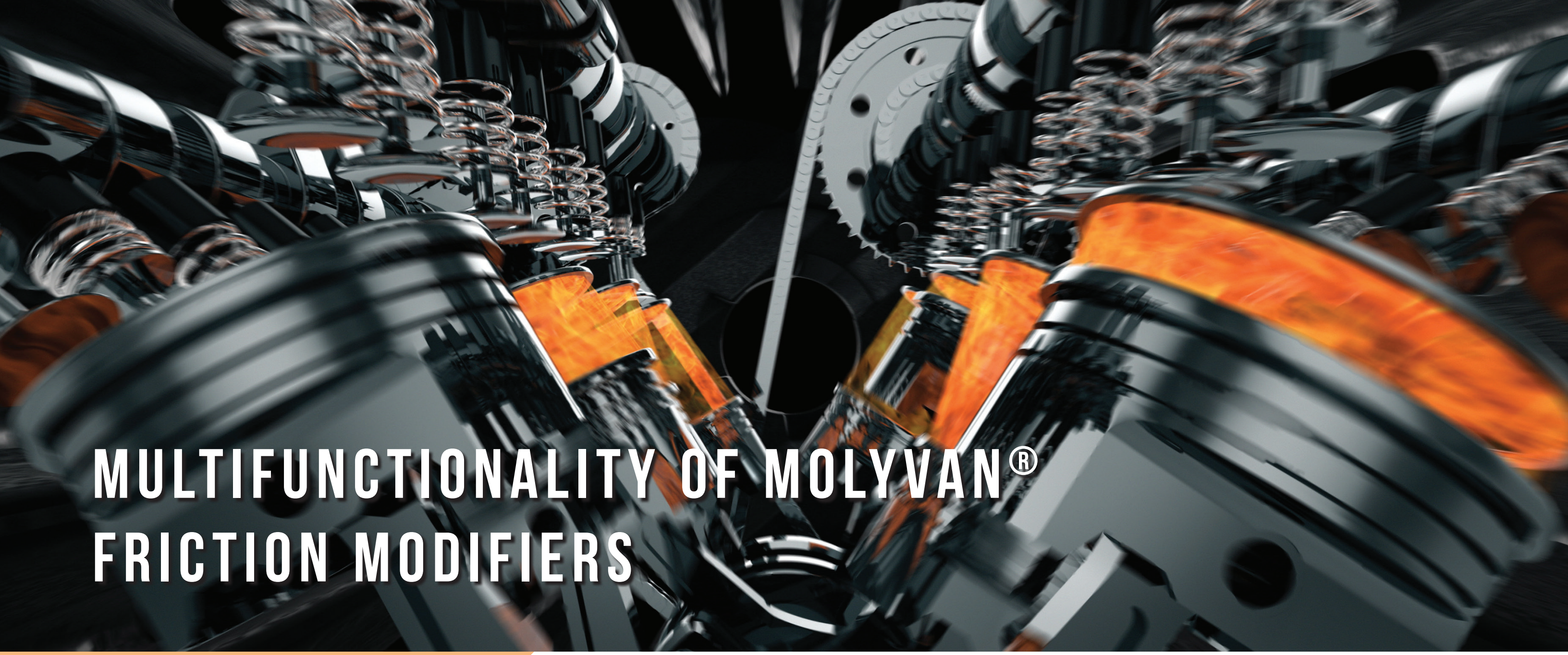

MULTIFUNCTIONALITY OF MOLYVAN® FRICTION MODIFIERS

The need for fuel efficient lubricants and additives has never been greater. Recently, the US Department of Transportation released the toughest fuel economy standards to date. The new Corporate Average Fuel Economy (CAFE) requirement for passenger cars and light duty vehicles is 49-mpg for model year 2026. This new requirement will increase the CAFE requirement by roughly 10 mpg or 36% from Model Year 2021 to Model Year 2026. Consequently, the focus on molybdenum friction modifiers has never been greater. Our separate "Friction Modifiers for Engine Oil" brochure discusses the friction reduction properties of various commercial organic and molybdenum friction modifiers offered by Vanderbilt Chemicals, LLC.

This brochure reviews molybdenum friction modifiers as multifunctional additives that bring a lot more performance to engine oil formulations than just friction reduction. Molybdenum friction modifiers impart additional beneficial properties to an engine oil such as improved wear, oxidation, piston deposits and LSPI frequency.

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DQS Inc.
VANDERBILT CHEMICALS, LLC
CERTIFIED TO ISO 9001:2015
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DISCLAIMER

MULTIFUNCTIONALITY OF MOLYVAN® FRICTION MODIFIERS

Vanderbilt Chemicals, LLC sells a wide variety of molybdenum friction modifiers into the engine oil arena. Our molybdenum friction modifiers are globally registered and used around the world. We offer three types of molybdenum friction modifiers (molybdenum dithiocarbamates, molybdenum dithiophosphates, and molybdenum ester/amides). Table 1, shown below, lists the molybdenum friction modifiers used by formulators around the world to reduce greenhouse emissions and improve vehicle fuel economy.

TABLE 1:
LIST OF COMMERCIALLY AVAILABLE MOLYBDENUM FRICTION MODIFIERS SOLD INTO THE ENGINE OIL ARENA

	MOLYBDENUM TYPE	MOLYBDENUM, %	SULFUR, %	PHOSPHORUS, %
MOLYVAN® 807NT	Molybdenum Dithiocarbamate	4.9	5.9	n/a
MOLYVAN 822NT	Molybdenum Dithiocarbamate	4.9	5.9	n/a
MOLYVAN 3000	Molybdenum Dithiocarbamate	10.0	11.5	n/a
MOLYVAN 855	Molybdenum Ester/Amide	8.0	n/a	n/a
MOLYVAN L	Molybdenum Dithiophosphate	8.0	12.4	6.3

Oxidation and Piston Deposit Control: Molybdenum Synergism with Alkylated Diphenylamine Antioxidants

Molybdenum friction modifiers are multifunctional additives that bring many beneficial properties to the formulation table. Two important supplemental properties that molybdenum additives impart to an engine oil are improved oxidation and deposit control. In addition, they are synergistic with alkylated diphenylamines (ADPAs) to reduce high temperature deposits in the TEOST™ MHT-4 and Sequence III piston deposits.

Dispersants are used by formulators to control Sequence V engine sludge and Sequence III piston deposits. The Sequence III engine test is part of the "GF" passenger car specification and is used to measure the oxidative related viscosity increase and deposit forming tendencies of a finished oil. Unfortunately, increasing the dispersant treat rate to reduce piston deposits has a negative impact on fuel economy. The molybdenum-ADPA synergism is a useful formulation tool to help reduce problematic deposits in both tests plus minimize the Sequence III percent viscosity increase while having a positive impact on fuel economy.

The TEOST™ MHT-4 is used in the "GF" passenger car specifications to measure the high temperature oxidative deposit formation tendencies of a finished oil. Aminic antioxidants such as ADPAs are well known to help control the oxidative deposit forming tendencies of a finished oil in this test. In the example below, two different GF-5 oils were formulated without any antioxidants and then top treated with either 1.6 wt.% or 2.0 wt.% ADPA and **MOLYVAN® 855**, see Chart 1. The test data for both finished oils demonstrated that the addition of **MOLYVAN 855** resulted in a dramatic deposits reduction. For example, you can get the same antioxidant performance by reducing the ADPA treat rate by 0.4 wt.% and adding 0.16 wt.% **MOLYVAN 855**. This benefit also carries over to the Oil Ring Land Deposits (ORLD) in the Sequence III engine test as shown in Chart 2.

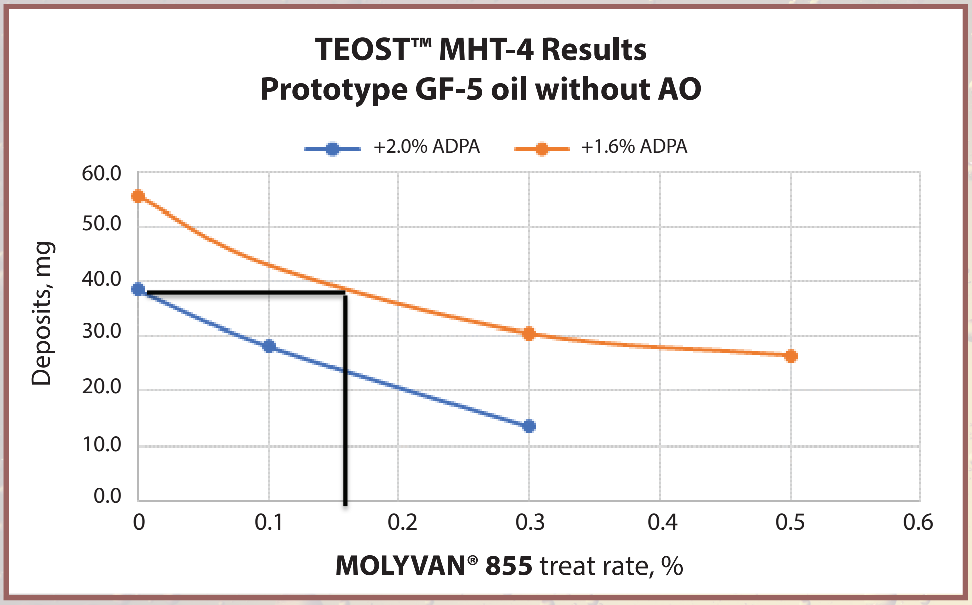
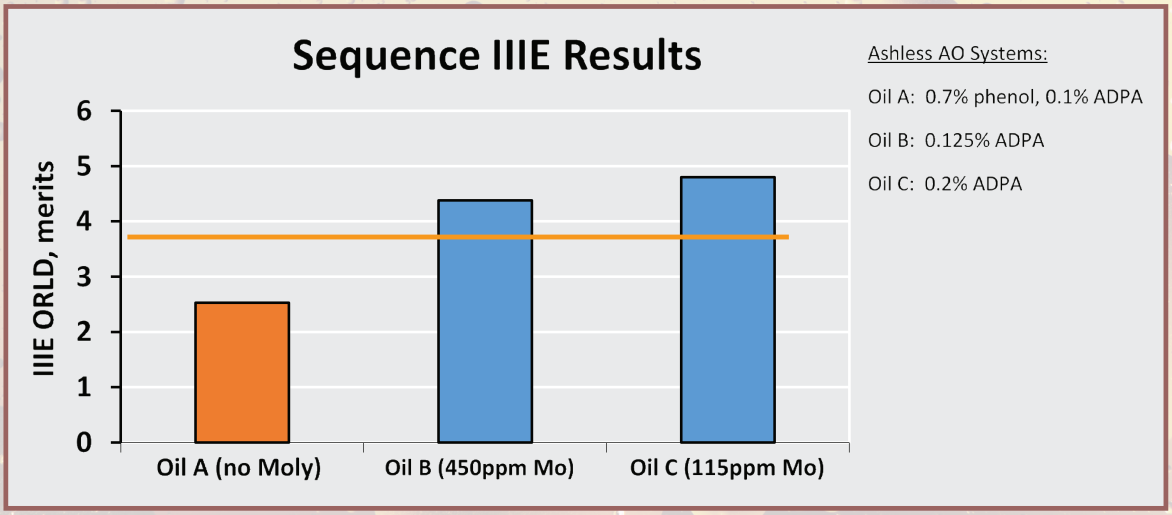


Chart 1
TEOST™ MHT-4 Deposit Results for Two Prototype GF-5 Oils Top Treat with ADPA and MOLYVAN® 855

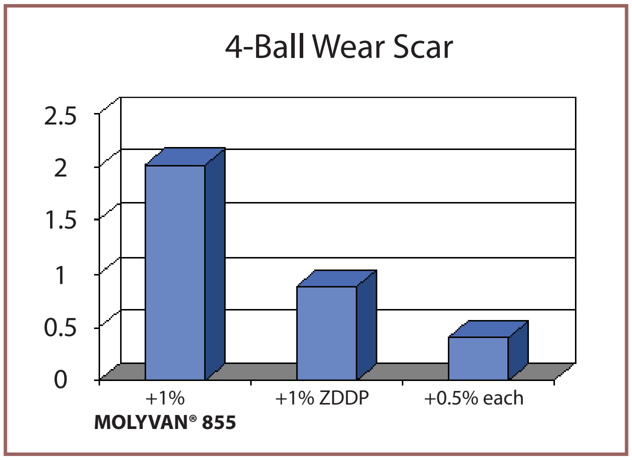
Chart 2
Sequence IIIE ORLD Merit Rating for Various API SJ formulations With and Without Molybdenum Friction Modifier

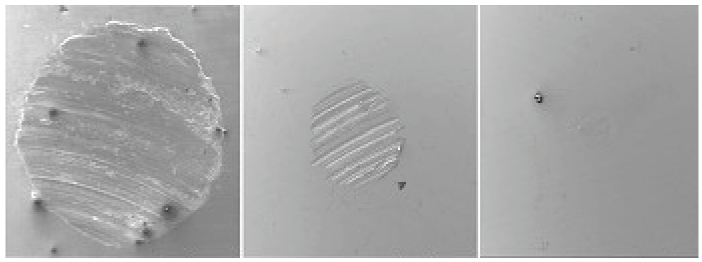


Improved Wear Control with Molybdenum Friction Modifiers

It is well known that molybdenum friction modifiers derive their wear and friction performance by decomposing and forming molybdenum disulfide. **MOLYVAN® 855** is one of our most popular molybdenum friction modifiers yet it doesn't contain any sulfur or phosphorus. Therefore, to form MoS_2, **MOLYVAN 855** first needs to complex with a sulfur source in the oil. This is unlike molybdenum dithiocarbamates (MoDTC) that can internally source the sulfur. Four ball wear testing was used to prove this important concept. Three test oils were prepared using **MOLYVAN 855**, ZDDP and Group I base oil. The first test oil contained 1.0 wt.% **MOLYVAN 855** dissolved in Group I base oil. It had the largest wear scar of all three oils tested, Charts 3A and 3B. The second test oil consisted of 1 wt.% ZDDP dissolved in Group I base oil and it had a much smaller wear scar than the test oil containing just **MOLYVAN 855**. However, the third test oil contained 0.5 wt.% each **MOLYVAN 855** and ZDDP had the smallest wear scar of all the oils tested. These test results support the concept that **MOLYVAN 855** functions as a supplemental antiwear additive when it can source sulfur from a sulfur containing additive in the formulation.

Chart 3A and 3B
Four Ball Wear Scar Test Data for MOLYVAN® 855 and ZDDP Dissolved in Group I Base Oil



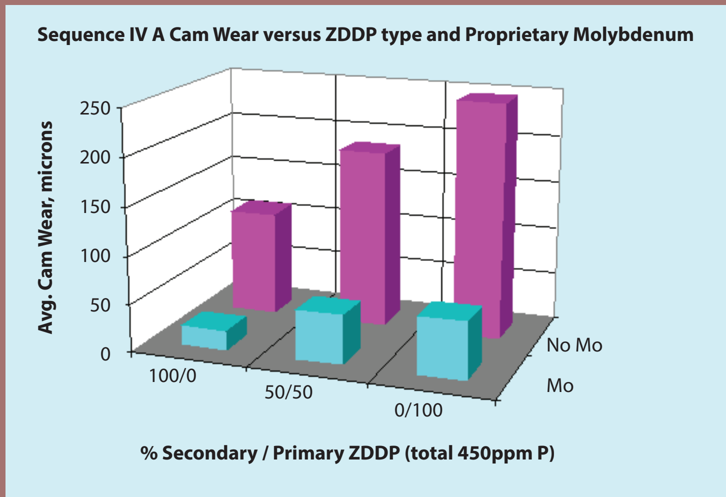


+1% **MOLYVAN® 855** | +1% ZDDP | +0.5% each

*** Test conditions: 70 KGF, 1450 RPM, 30 minutes, room temperature, Group I base oil**

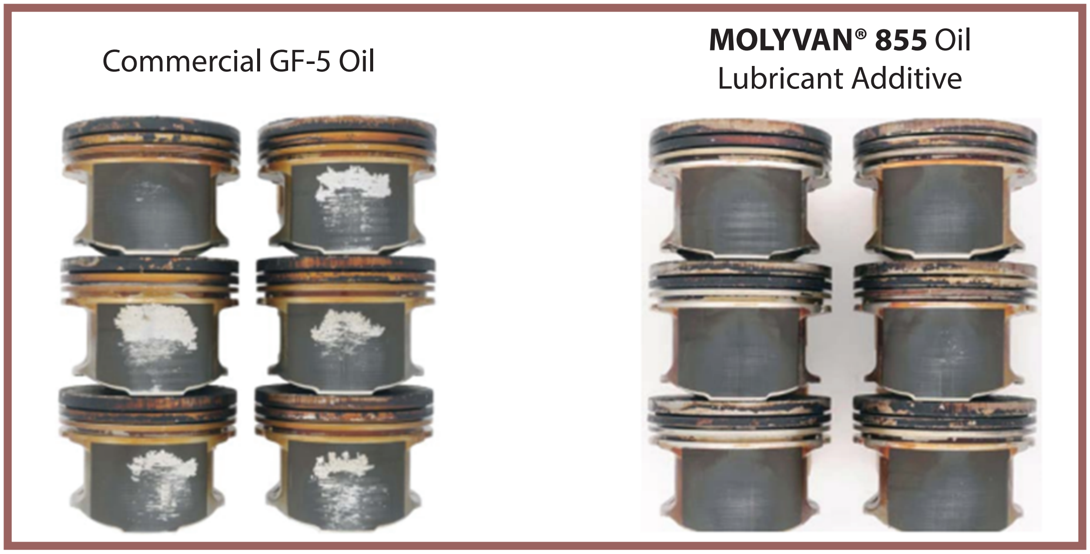
In this second example, the antiwear performance of a proprietary MoDTC was investigated using six test oils formulated with either a primary, secondary or a mixed primary/secondary ZDDP system. In the examples below, the three test oils containing 110 ppm molybdenum from MoDTC demonstrated significantly lower Sequence IVA cam lobe wear compared to three similar engine oils without the MoDTC, see Chart 4 presented by Infineum during a GF-4 ILSAC/Oil May 2003 industry meeting. The 5W-30 engine oil was a Group II fully formulated engine oil with a full complement of additives, see US Patent 6,500,786 for additional formulation details. The Sequence IVA engine test is part of the GF-5 specification and is used to measure cam lobe wear.

Chart 4
Sequence IVA Cam Wear Engine Test Data for 5W-30 Engine Oils Formulated with Various ZDDP Types With and Without Molybdenum Friction Modifier



Las Vegas Field Trial Results For MOLYVAN® FEI Plus Test Oil

A 100,000 mile Las Vegas taxi field trial was conducted on a fully formulated experimental oil containing our **MOLYVAN® 855** technology. This oil contained 700 ppm molybdenum and only 250 ppm phosphorus. The control oil was a commercial GF-5 technology with 700 ppm phosphorus and 100 ppm molybdenum. Figure 1 shows the improvement in piston scuffing for the **MOLYVAN 855** oil versus the GF-5 commercial oil.



Molybdenum Helps Reduce Timing Chain Wear

The introduction of turbocharged engines caused two unexpected performance issues:

1) Timing chain wear
2) Low Speed Pre-Ignition (LSPI)

Timing Chain Wear

It wasn't clear exactly what was causing the timing chain to wear. At the time, there were two theories used to explain the increased wear. Both theories were related to incomplete combustion. The first was corrosive wear caused by acidic blow-by, and the other was abrasive wear caused by soot formation. Industry leading work was performed by Vanderbilt Chemicals, LLC with the assistance of a timing chain OEM partner. The OEM developed and ran the bench test, demonstrating that zinc found in ZDDP was responsible for the wear.

High and low molybdenum containing test oils were run in the timing chain wear bench test (See Table 2 and Chart 5 for details). The test data showed the 700 ppm molybdenum test oil delivered much lower wear compared to the control oil with 100 ppm molybdenum. The test data was generated using a 0W-20 prototype oil whose wear performance was benchmarked and deemed comparable to a commercial GF-5 oil purchased off the shelf.

TABLE 2: ELEMENTAL PHOSPHORUS AND MOLYBDENUM IN TEST OIL

	HIGH PHOSPHORUS HIGH MOLYBDENUM	HIGH PHOSPHORUS LOW MOLYBDENUM
P, PPM	682	700
MO, PPM	684	100

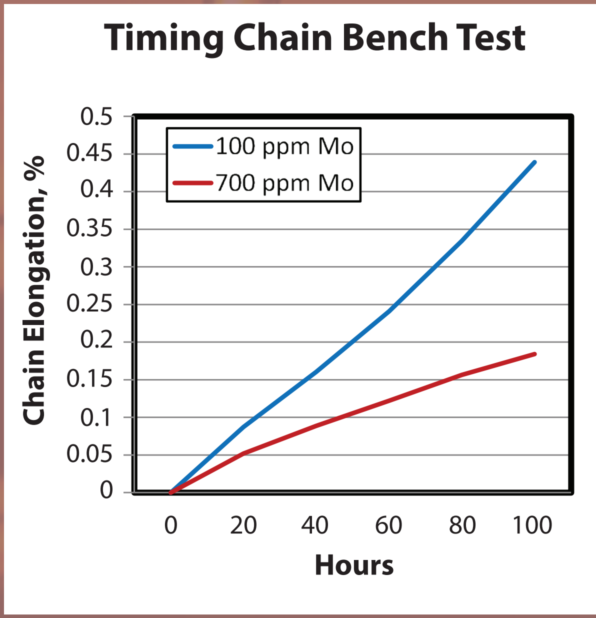


Chart 5
Timing Chain Wear Data for Low and High Molybdenum Test Oils

The ASTM Sequence X engine test is a recently developed industry test used to measure timing chain wear for the new API GF-6A/6B specifications. A developmental test oil that contained 252 ppm phosphorus, 710 ppm molybdenum and 280 ppm boron demonstrated significantly reduced timing chain wear relative to the GF-6A/GF-6B specification limits, Table 3.

TABLE 3: SEQUENCE X ENGINE TEST DATA FOR PROTOTYPE DEXOS ENGINE OIL

	SEQ. X TEST RESULT	API GF-6A LIMITS
TEST OIL	0.0246%	0.085% Max.

Low Speed Pre-Ignition

LSPI is another issue that was inadvertently created when OEMs developed more fuel-efficient turbocharged engines. Severe cases of LSPI can cause catastrophic engine failure. Once again, the root cause(s) of LSPI aren't fully understood. Industry and consortium testing have confirmed calcium sulfonate increases LSPI frequency and high group number base oil, ZDDP and molybdenum were confirmed to decrease LSPI frequency.

Two test oils, with and without molybdenum, were run in a Ford LSPI screener test. The typical Sequence IX LSPI engine test is run for 4 iterations whereas the screener test is run for only 1 iteration. The LSPI screener test allows you to screen a large number of test oils inexpensively. A representative 0W-20 Group III GF-5 engine oil formulated with an all calcium detergent system, and dispersant-PMA VI improver with reduced dispersant loading was used for the experiment. One test oil was top treated with 350 ppm molybdenum from a molybdenum friction modifier.

Table 4, shown below, summarizes the LSPI screener test data. The test data showed the molybdenum top treated oil having 3 fewer LSPI events versus the same oil without molybdenum.

TABLE 4:
LSPI SCREENER TEST EVENT FREQUENCY SUMMARY

LSPI EVENTS/ MOLYBDENUM LEVEL	350 PPM/ GROUP III	0 PPM/GROUP III
PEAK PRESSURE (PP)	0	0
MASS FUEL BURN,2 WT% (MFB2)	3	4
COMBINED PP + MFB2	7	9
TOTAL	**10**	**13**

The exact role molybdenum plays in reducing LSPI is not understood. Although industry agrees molybdenum plays a beneficial role in reducing LSPI frequency in fresh oils, they are unsure what role it plays in aged oil. There is a small group who believe molybdenum increases LSPI frequency in aged oil, but others believe this is due to a faulty matrix test design. Ultimately, additional testing will confirm what role molybdenum plays in reducing LSPI frequency.

TEOST® 33C ASTM D6335 Deposit Test

The TEOST® 33C is a bench test used to measure the turbocharger deposit forming tendencies of an engine oil and is part of the API GF-6A and GF-6B specifications. Molybdenum additives and other tribofilm formers, like ZDDP, are known to form deposits in this test.

The TEOST 33C bench test showed some correlation with turbocharger deposits for GF-2 when it was first introduced, but turbocharger and engine oil technology has evolved considerably since then and the same correlation is no longer present.

Many believe this test unfairly discriminates against molybdenum-containing additives, especially when they are needed to improve vehicle fuel economy and reduce greenhouse gas emissions.

Phosphorus is a well-known tribofilm former and is also considered a bad actor in this test. Chart 6, shown below, summarizes the test results for GF-4 engine oils that contained 600-750 ppm molybdenum and phosphorus from three different sources, including primary and secondary ZDDP. The test data showed there is a clear relationship between phosphorus level and TEOST 33C deposits in high molybdenum oils. High molybdenum oils containing less than 600 ppm phosphorus can pass the TEOST 33C at the GF-4 maximum deposit limit of 30 mgs.

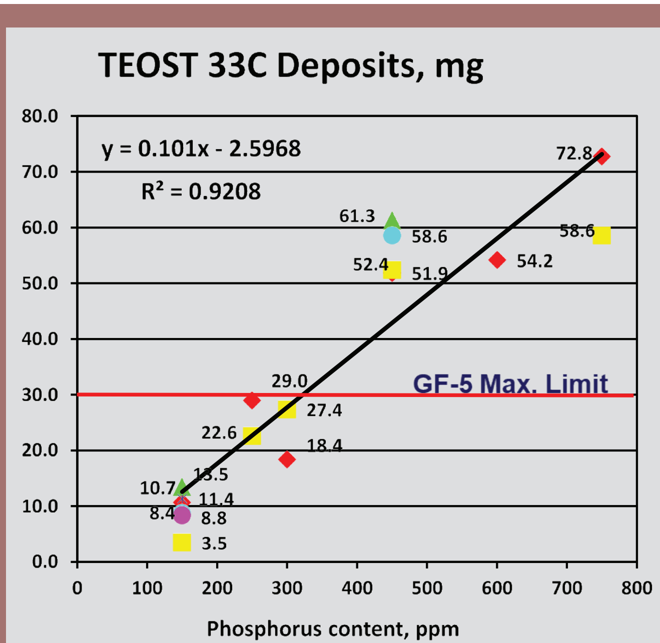
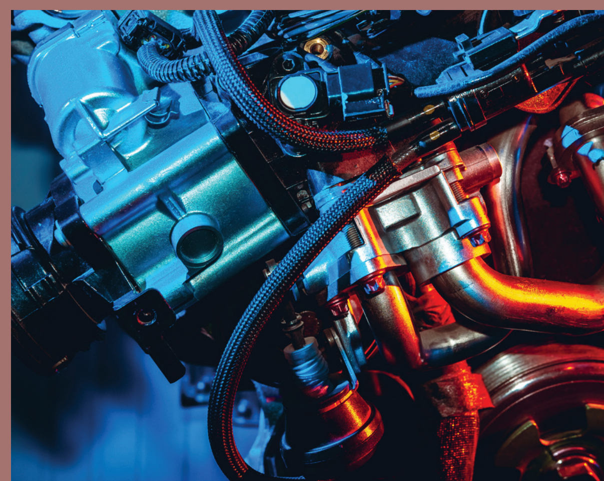
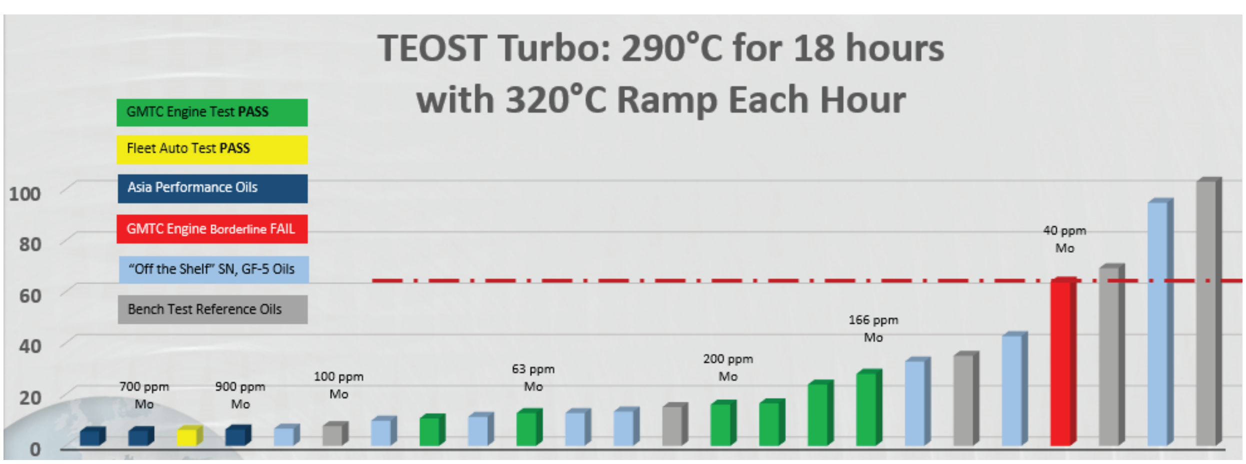


Chart 6
TEOST® 33C Test Result for Various GF-4 Low Phosphorous High Molybdenum Oils



The Savant Group has developed an alternate test method called the TEOST® Turbo Test (TEOST TT). Initial testing with various industry test oils showed this test correlates much better with modern turbocharger technology. More importantly, the high molybdenum containing oils show fewer deposits, and in some cases, lower deposits than oils that do not contain molybdenum.See Chart 7 presented by Savant at various industry meetings.

Chart 7
TEOST® TT Results for Various Molybdenum and Non-Molybdenum Containing Engine Oils



Yellow bar represents a formulation containing 700 ppm Mo from Vanderbilt Chemicals, LLC.

The need for fuel efficient lubricants and additives has never been greater. Molybdenum friction modifiers are multifunctional additives that bring a lot more to the formulation table than just friction reduction. Molybdenum friction modifiers impart additional beneficial properties to an engine oil such as improved wear, oxidation, piston deposit and LSPI fresh oil frequency reduction properties. Vanderbilt Chemicals, LLC sells a wide variety of friction modifiers into the marketplace to help lubricant formulators formulate todays and tomorrow's fuel-efficient engine oil specifications that makes the world a better place to live.

NOTES:

FOR SAMPLES, PRODUCT INFORMATION AND/OR TECHNICAL SERVICE PLEASE CONTACT VANDERBILT CHEMICALS, LLC, OR THE VANDERBILT REPRESENTATIVE IN YOUR AREA:

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