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### Effects on Tribology Performance of a Reducing Additive for Automobile Lubricant

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#### ABSTRACT

We developed a unique reducing additive composed primarily of polyolester, diester, and vegetable oil-based ester compounds in order to switch from boundary to fluid lubrication and improve tribology performance, and chemically and experimentally investigated its effects on tribology performance. To confirm the lubrication effects of this reducing additive, we added it to oil and chemically investigated the cleaning and dissolving of the ultra-fine particle layer of contaminants, etc., adhering to lubrication pathways and sliding surfaces, and performed commercialization testing using actual vehicles. We found that this additive washed away and dissolved sludge, varnish, and other contaminants from lubricated surfaces, improving their lubrication properties and their tribology performance by reducing abrasion and friction.

#### INTRODUCTION

In recent years demand has grown for improved lubricating oil tribology performance in automobiles, to provide not only greater vehicle performance, but also to reduce their resource usage and environmental impact. Ester-based synthetic lubricating oil has been developed to provide greater lubrication performance, and to reduce friction and wear, in order to satisfy this demand, but there is still a great deal of room for improvement. These ester-based synthetic lubricating oils are made from organic (fatty) acids and alcohol, but attention is increasingly being drawn to the use of polyol ester-based synthetic lubricating oil<sup>(1),(2)</sup>, originally widely used in jet engines, and in automobiles as well.

This synthetic lubricating oil offers many features, such as greater low-temperature fluidity, thermal stability, and oxidation stability than mineral lubricating oils. It can be used at high viscosity levels over a wide range of temperatures. It offers excellent lubrication and is clean, dispersible, and biodegradable. However, it is prone to hydrolysis, absorbs humidity, and is limited regarding which rubber, sealing materials, resins, and paints it can be used with. It is also expensive, but it is said to offer the best tribological performance, require the least resources and energy, and be the most functional of all of the synthetic lubricating  $oils^{(1),(2)}$ .

Synthetic lubricating oils are made by mixing lubricating oil additives<sup>(3),(4)</sup>, including detergent dispersants, antioxidants, extreme pressure agents, rust-preventive agents, viscosity index improvers, pour point depressants, antifoaming agents, and friction-reducing additive. The compounds made of these additive are undergoing tremendous advances in line with the development of automobiles and their environments. The ester-based synthetic lubricating oils believed to be essential for the latest automobiles are synthetic lubricating oils which use polyolester and diester additive as their additive.

In this research, in order to develop automobile lubricating oil with improved lubrication, wear, and friction performance for use in engines, transmissions, and differentials, we developed a unique reducing additive (SOD-1) composed primarily of polyolester (POE), diester (DST), and vegetable oil-based ester (VOE) compounds as secondary synthetic additive, and chemically and experimentally investigated its effects on tribology performance.

# LUBRICATING OIL ADDITIVE TRENDS IN THE LATEST ENGINES

Looking at the trends in the lubricating oil additive used in the latest engines<sup>(3)</sup>, incompletely combusted soot (C) in diesel engines reacts with NO and SO<sub>3</sub> created by fuel combustion, accounting for the majority of deposits. Lacquer and varnish are believed to be low molecular fuel oxidation compounds formed near the end of the compression stroke. There are reports of fuel and lubrication additive contributing to reductions in the amounts of deposits in combustion chambers<sup>(5)</sup>. In exhaust gas post-processing calcium sulfate-based lubricating oil additive<sup>(6)</sup> is used in order to reduce the accumulation of DPF ash, collecting soot and ash. The presence of soot in lubricating oil in crank cases causes friction in valves and liners, so there are reports<sup>(7)</sup> of commercialization of products reducing friction for both valves and liners through the

use of appropriate lubricating additive.

The main cause of deposits in gasoline engines is said to be, at high temperatures, oxidation of base oil, and at low temperatures fuel and oxidization products. These substances form resin-like or carbon-like substances inside crank cases as components contained in blow-by gas, accumulating inside engine lubricating oil pathways and parts. Wear resistance improving additives<sup>(9)</sup>, such as new lubricating oil additives<sup>(8)</sup> extending the low friction properties for dialkyldithiophosphate gasoline enaines. zinc (ZnDTP), containing no sulfur, and phosphate ester, have also been developed. Therefore, the key attributes of lubricating oil additive required to counter deposits in both types of engines are detergent dispersal, solubility, and oxidation inhibition.

#### **REDUCING ADDITIVE**

# THE CONCEPT BEHIND THIS REDUCING ADDITIVE

Contaminants such as deposits, varnish, sludge, etc. which adhere to the lubricated and sliding surfaces of automobile engines, transmissions, and differentials, etc., accumulate over time, having a negative impact on their tribology performance (lubrication, wear, and friction). Normally this is improved by flushing them with kerosene-based cleaning agent when performing oil replacement, but as Figure 1. shows, it is not possible to completely remove all contaminants, which build up three layers of general dirt, adsorbed molecules, and oxidation film. The removed contaminants also often clog up lubricating oil pathways, so this cleaning method is not very effective, and has its own risks.

Therefore, this reducing additive, a blend of additive made primarily with POE, DST, and VOE-based compounds, is added to engine, manual transmission, power steering, and differential gear oil (10vol.% mix) and to automatic transmission oil (7vo.l% mix), lubricating while also washing off and removing contaminants. It exposes the initial processed metal surface, greatly reducing friction loss and ensuring sufficient oil clearance. This unique method improves lubrication while reducing wear and friction.

The concept behind this reducing additive is that it washes away, dissolves, and removes contaminants from lubricated sliding components, exposing their initial lubrication surfaces (the face of the processed metal), using reducing action improve its tribology performance (lubrication, wear, and friction characteristics). The main problems with this reducing additive are that it is prone to hydrolysis, absorbs humidity, and swells and hardens rubber and sealing materials. These problems have been countered by adding petroleum-based oil and grease components. This approach has been highly effective.

## CHEMICAL STATE OF REDUCING ADDITIVE AND ITS EFFECT ON ENGINE OIL

Table 1. shows the chemical state of the reducing additive and its effect on engine oil. Its kinematic

viscosity, at 40°C and 100°C, is 610 and 92.4 mm<sup>2</sup>/s, respectively. Its viscosity index is 243, its flash point is a high 170°C, and its pour point is a low -42.5°C. It offers the high viscosity, temperature-resistant viscosity, flame resistance, and low-temperature fluidity of POE and DST-based compounds. Indiana Stirring Oxidation Test (ISOT) testing found it to have a viscosity ratio of 1.06, with little viscosity change before and after oxidation. There was only a -0.80 mgKOH/g change in oxidation after heating, and its lacquer rating was found to have no deposits, indicating that there were no oxidants or sludge mixed in.

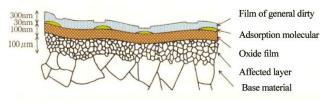


Figure1. Components of Solid Surfaces

Table 1. Oxida	tion Stability	y Test of Reducing
Addit	ve (SOD-1)	JIS K2514

Kinematic Viscosity 40°C		610.0		
100°C	mm²/s	92.4		
Viscosity Index		243		
Pour Point	С°	- 42.5		
Flash Point (PM)	С°	170.0		
Ash	mass %	2.305		
Oxidation Stability (ISOT)				
Viscosity Ratio		1.06		
Increased Oxidative	mgKOH/g	- 0.80		
Lacquer Rating		No Deposits		

### CHEMICAL STATE WHEN REDUCUCING ADDITIVE WAS ADDED TO ENGINE OIL

Table 2. shows the chemical state when 10vol.% by volume of reducing additive was added to fresh engine oil (SN5W-30). The kinematic viscosity of the engine oil without reducing additive at temperatures of 40°C and 100°C was 60.9 and 10.5 mm<sup>2</sup>/s respectively, but after adding reducing additive was 77.6 and 13.5 mm<sup>2</sup>/s, respectively, increases of 27.6 and 28.6%. Its control viscosity index of 162 rose by 10.5% to 179 after adding additive. FALEX seizure load, likewise, rose by 33.3%, from 750 to 1000 lbs. Hot tube testing, which evaluates oil heat resistance and cleaning dispersal on a 10 point scale, rose 14.3%, from 7 to 8, after adding reducing additive. Rubber swelling, likewise, rose by 46.4%, from 5.6 to 8.2%.

These results show that the reducing additive had major chemical effects. In particular, the kinematic viscosity and FALEX seizure loads improved by approximately 30%. These improvement rates indicate that the reducing additive contributed to tribology performance improvements through compound effects, such as improving lubrication, friction, heat resistance, and cleaning dispersion, and by preventing the hardening of rubber and sealing materials.

	0			
	SOD-1	SN5W-30	SN5W-30+SOD-1(10vol.%)	Progress
				Rate %
Kinematic Viscosity 40°C mm <sup>2</sup> /s	610.0	60.9	77.6	27.4
100°C mm²/s	92.4	10.5	13.5	28.6
Viscosity Index	243	162	179	10.5
FALEX Seizure Load (ASTM) lbs	-	750	1000	33.3
Hot Tube Test 289°C Mark	-	7	8	14.3
Rubber Swelling Degree vol.%	-	5.6	8.2	46.4

Table 2. Effects of Reducing Additive on Chemistry of Engine Oil (SN5W-30)

Table 3. Effects of "SOD-1" on ATF Oil Chemistry and Shear Stability (Ultrasonic Method, JPI-5S-29-88)

		New Oil (ATF)	New Oil (ATF)	Progress
			+SOD-1(7 vol.%)	Rate%
Kinematic Viscosity	40°C mm²/s	33.7	42.2	25.2
1	00°C mm²/s	7.21	8.96	24.3
Viscosity Index		185	200	8.1
Acid Value	mgKOH/g	1.72	1.48	-14.0
Shell 4-Ball Wear Test (ASTM D4	1172) mm	Seizure	0.46	—
Shear Stability (Ultrasonic	Method)			
Kinematic Viscosity 40° C mm <sup>2</sup> /s	(Before Test)	33.6	42.0	25.0
40°C mm²/s	(After Test)	30.8	36.3	17.9
Rate 40°C	%	-8.10	-13.6	—
Kinematic Viscosity 100°C mm <sup>2</sup> /s (Before Test)		7.21	8.97	24.4
100°C mm <sup>2</sup> /s (After Test)		6.50	7.59	16.8
Rate 100°C	%	-9.83	-15.4	—

# EFFECTS OF REDUCING ADDITIVE ON ATF AND SHEAR STABILITY TESTING

Table 3. shows the effects of reducing additive (7vol.% mix) on ATF oil (new oil) and the results of shear stability testing. Before adding reducing additive, the kinematic viscosity of ATF oil at temperatures of 40°C and 100°C were 33.7 and 7.21, respectively. After adding reducing additive, these increased by 31.2 and 24.3% to 42.2 and 8.96, respectively. Likewise, the viscosity index of ATF oil without reducing additive was 185, but rose by 8.1% to 200 after adding additive. The acid value fell by -14.0%, from 1.72 to 1.48 mgKOH/g. ATF oil without reducing additive seized during shell 4-ball wear testing, but after adding additive its wear diameter was 0.46mm. The reducing additive increased the kinematic viscosity of the ATF by roughly 25%, increased its viscosity index by 8%, and reduced its acid value. These property changes indicate the improvements the reducing additive made to high viscosity, heat resistance, acid resistance stability, and wear resistance.

Furthermore, shear stability testing using ultrasound was performed at temperatures of 40 and 100°C. The kinematic viscosity at 40°C was 33.6 for ATF containing no reducing additive, before testing. With reducing additive it was 42.0 mm<sup>2</sup>/s, an increase of 25.0%. After testing it was 30.8 and 36.3 mm<sup>2</sup>/s, an increase of 17.9%. Therefore, the kinematic viscosity without reducing additive at 40°C was -8.10%, but with reducing additive was -13.6%, an increase of 67.9%. Likewise, the kinematic viscosities before

testing at 100°C were 7.21 and 8.97 mm<sup>2</sup>/s. The additive increased the viscosity by 24.4%. After testing the viscosities were 6.50 and 7.59 mm<sup>2</sup>/s, with the additive increasing viscosity by 16.8%. The kinematic viscosity without reducing additive at 100°C was -9.83%, but with reducing additive was -15.4%, an increase of 57.1%.

Therefore the shear stability testing found that the reducing additive increased pre-test kinematic viscosities by approximately 25%, both at 40 and 100°C, and increased post-test kinematic viscosities by approximately 17%, for both temperatures. The kinematic viscosity increase rates at 40 and 100°C were roughly 63 and 57%, respectively. Based on this, the reducing additive can be considered to provide sufficient shear stability, since there is no reduction of the kinematic viscosity.

# EFFECT OF REDUCING ADDITIVE ON RESULTS OF ENGINE OIL SHELL 4-BALL WEAR TEST

Shell 4-ball wear testing was used to measure the friction and wear effects of reducing additive on a certain automobile manufacturer's oil 5W-30 (new oil). The testing was performed using a rotational speed of 1200 rpm, load of 40 kgf, temperature of 75°C, and time of 60 min. As Figure 2. shows, the wear scar diameter of the oil without additive was 0.46 mm, while for the oil with additive it was 0.33 mm. The reducing additive reduced the wear scar size by 0.13 mm, or 28.3%. These results show that the reducing additive is effective for improving friction and wear,

and indicates the potential for it to contribute to improved tribology performance.

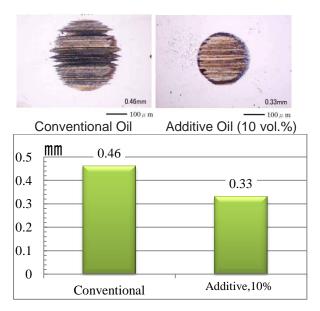


Figure 2. Shell 4-Ball Wear Test (SN 5W-30)

## EXAMPLE OF PRACTICAL APPLICATION OF REDUCING ADDITIVE

## REDUCING ADDITIVE CAMSHAFT CLEANING ACTION EXPERIMENT

In order to confirm the cleaning action of the reducing additive, a cleaning action confirmation device, shown in Figure 3, was fabricated and used to perform an experiment on a gasoline-powered automobile's camshaft (used for approx. 120,000km). As Figure 3. shows, 80cc of reducing additive were added to 720cc of engine oil (10vol.%) in an open beaker. The camshaft was then vertically suspended in the solution. The temperature was kept at 80°C±0.1°C, and a motor with an agitating blade was used to forcibly circulate the oil solution in the beaker. The results are shown in Figure 4. The camshaft end was observed at the start of the experiment, and then after 481 hours. Compared to its state at the start of the experiment, after 481 hours a great deal of the varnish and contaminants had been washed off, and the cam face was confirmed as being clean. The oil in the experiment was 1/5 heavier or more than that used in actual automobiles, but this experiment confirmed the cleaning effectiveness of the reducing additive.

#### EXAMPLE OF USE OF REDUCING ADDITIVE AS GASOLINE ENGINE WHITE SMOKE COUNTERMEASURE

A request was received from the Okinawa Prefecture Japan Automobile Service Promotion Association for minivehicle white smoke countermeasures. An automobile's valve stem shield was replaced, but it was going through approx. 1L of engine oil per 100km and producing continuous white smoke, as shown in Figure 5. Given these symptoms, it was determined that there was a possibility that the oil ring had become stuck, so the engine was disassembled. As Figure 6. shows, the compression ring and oil ring had become stuck, and there were carbon and deposits in

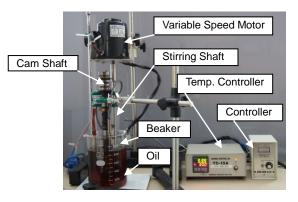


Figure 3. Cleaning Action Confirmation Apparatus



Before StartingAfter 481 HoursFigure 4. Effects of Reducing Additive on Camshaft<br/>Cleaning



Figure 5. Emission of White Smoke





Before Reducing Additive

After Driving 500 km





Removal of Carbon and Deposits in Combustion Chamber.

Figure 6. Disassembled Engine of White Smoke Car

the combustion chamber. Reducing additive was added to engine oil (10vol.% mix), and the white smoke stopped after several minutes. The vehicle was driven for approximately 500km more, and the engine was disassembled again. As Figure 6. shows, the piston ring and oil ring were no longer stuck, the carbon and deposits had been cleaned off and removed from the combustion chamber, and the plug was also cleaned. The restoration of piston ring tension also resulted, of course, in increased combustion pressure, improving oil consumption, output, fuel efficiency, and exhaust gas.

#### EXAMPLE OF USE OF REDUCING ADDITIVE FOR CLEANING OF INSIDE OF GASOLINE ENGINE

After performing vehicle inspection and maintenance on a used minivehicle, and replacing the oil with new oil, the vehicle was driven for 1,000 km, and then the engine was disassembled and inspected. The engine was then reassembled and a 10 vol.% mix of reducing additive was added to the oil. The vehicle was then driven for 5089 km at an average speed of 50 km/h. After driving, the engine was disassembled and inspected again, and the inspection results were compared against those of the initial inspection. The engine was then reassembled again and driven, under the same conditions, for another 5,032 km, for a total of 10,121 km. The engine was disassembled and inspected again, and the results of the inspection were compared against those of the previous inspections. Both inspections performed after the addition of the reducing additive found that the interior parts of the engine had been cleaned, and, in particular, that the thick sludge which had accumulated and almost clogged the cylinder body oil passage ports was almost completely washed away.

Figure 7. shows the interior of the cylinder head top and piston side after adding the reducing additive. The cylinder head top photo comparison with the second disassembly inspection results shows that the black sludge and carbon contaminants which had tightly adhered to the surface of the camshaft and cam drive were dissolved and washed away, exposing the metal surface. The 1<sup>st</sup> and 2<sup>nd</sup> disassembly inspection photos of the piston, shown in Figure 7, show that the sludge which had accumulated on the top land of the piston was significantly dissolved and washed away, the 1<sup>st</sup> and 2<sup>nd</sup> piston rings had been restored by re-exposing them, and the oil ring had been cleaned. Furthermore, comparing expanded photos of the piston ring and crown before and after testing made the extent of the cleaning results even clearer.

Table 4. shows an example of improvements to exhaust gas, comparing CO and HC measurements for a standard 1500 cc vehicle when idling, before and after adding reducing additive. As this table shows, both CO and HC were dramatically improved, CO by 0.03% and HC by 45 ppm. This evidence proves that the reducing additive can dissolve and wash away sludge, carbon, varnish, and deposits from engine interiors, restoring their initial processed metal surfaces and improving seizing.



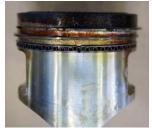


Before Test After Driving 10,121 km Camshaft Assembly in Cylinder Head



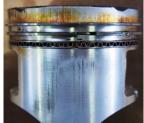


Before Test After Driving 10,121 km Enlarged View of Crown and Piston Rings



Before Test





After Driving 5,089 km

After Driving 10,121 km

Piston Side View Before Test and After Addition

Figure 7. Effects of Reducing Additive on Camshaft Assembly, Piston Side and Piston Rings

Table 4. Effects of Reducing Additive on Emission of CO, HC

	CO %	HC ppm
Before Addition	0.03	54
After Addition	0.00	9

# THE IMPACT OF REDUCING ADDITIVE ON CVT JUDDER COUNTERMEASURES

Recently there have been complaints about judder when starting a CVT automatic transmission for regular passenger vehicles of a certain manufacturer. We confirmed that adding a 7 vol.% mix of the reducing additive reduced judder. Similar complaints were received for multiple models from the same manufacturer. Table 5. shows an overview. Judder generally began after driving 47,000 to 122,000 km, and was especially common in 2002 models. The effectiveness of the reducing additive at reducing

Table 5. CVT Judder Improvement

Model	А	В	В	С	D
Model	2001	2002	2002	2002	2004
Year	2001	2002	2002	2002	2004
Mileage	122	47	113	72	57
$\times 10^3$ km				• =	0.
Symptom	Judder at CVT Starting				
After	Improvement of CVT Judder				
Addition					

judder was recognized by dealerships, and the reducing additive is now recognized by dealers as an official judder countermeasure product of the manufacturer.

The reducing additive is believed to reduce judder by dissolving and washing away built-up contaminants on the surface of the CVT clutch, which include fine metal particles, exposing their metal surfaces again, reducing slipping and restoring their friction capabilities. In this way the reducing additive has also been proven effective at reducing CVT judder.

Other examples of improvements over the past 10 years include the use of the reducing additive to effectively reduce abnormal sounds during dry engine start-up, gear shift shock, abnormal engine sounds, white smoke, excessive oil consumption, abnormal power steering sounds, and AT complaints.

## EFFECTS OF REDUCING ADDITIVE ON D1 GRAND PRIX DRIFT CAR TRANSMISSION OIL

In recent years, drift racing has gained wider recognition. Compared to conventional motor sports, drift racing is much harder on vehicles. Engines and transmissions must offer high levels of durability and wear resistance in order to withstand accelerating to 200 km/h in just 10 sec over the 500 m span after the start of the race, and then suddenly decelerating again.

Figure 8, 9 and Table 6 show the results of oil shell 4-ball wear testing and elementary analysis performed on drift cars after two hours of driving, one with standard transmission oil and one with transmission oil containing reducing additive. The car with oil that did not contain reducing additive had a wear scar diameter of 0.93 mm, where as the one which contained reducing additive had a wear scar diameter that was 59.1% smaller, at 0.38 mm. Elementary analysis found the greatest difference in the amount of Fe. The result for the car with additive-free oil was 24.9 mass%, where as for the car with oil containing mass%, an improvement of additive it was 1.2 95.2 %, indicating a significant reduction in friction and wear. Other elements were similarly affected, Cu 60.0, Al 93.5, Na 100, P 97.8 and Ca 80.0% of improvement.

The driver of the car whose oil contained additive noted that there was less shock noise when shifting up or down gear, and that shifting was smoother. The above results show that this reducing additive also greatly improves tribology performance, such as friction and wear, as well as durability, even in harsh transmission lubrication situations. In addition, other benefits can be expected to be observed in the form of reduced foreign matter by proper oil analysis techniques<sup>(10)</sup>. This could be an area of further investigation to validate these assumptions.

Table 6. Acid Dissolution Metal Analysis of Reducing Additive on Transmission Oil in Drift Car Engine (Shell 4-Ball Wear Test)

Transmission Oil	85W-250	85W-250 + SOD-1	Progress Rate %	
Diameter of Wear Scar mm	0.93	0.38	59.1	
Element Mass %				
Fe	24.9	1.2	95.2	
Pb	0.0	0.0	0.0	
Cu	0.5	0.2	60.0	
Cr	0.2	0.0	100	
AI	3.1	0.2	93.5	
Ni	0.0	0.0	0.0	
Sn	0.1	0.0	100	
Si	0.2	0.0	100	
В	0.1	0.0	100	
Na	0.4	0.0	100	
Р	4.5	0.1	97.8	
Zn	0.5	0.5	0	
Ca	0.5	0.1	80.0	
Ba	0.1	0.0	100	
Mg	0.0	0.0	0.0	
Мо	0.0	0.0	0.0	
V	0.0	0.0	0.0	





Conventional Oil

Additive Oil (10 vol.%)

Figure 8. Wear Tracks of Shell 4-Ball Wear Test

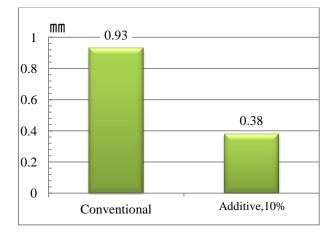


Figure 9. Shell 4-Ball Wear Test (SUNOCO 85W-250)

#### CONCLUSION

We developed a unique reducing additive composed primarily of polyolester (POE), diester (DST), and vegetable oil-based ester (VOE) compounds as synthetic additive, and chemically and experimentally investigated its effects on tribology performance. We reached the following conclusions.

- 1)The unique reducing additive composed primarily of polyolester, diester system, and vegetable oil-based ester compounds is effective at dissolving and washing away sludge, varnish, and other contaminants from lubricated surfaces, restoring them to their original conditions and improving their tribology performance by decreasing wear and friction.
- 2)The chemical and physical properties of this reducing additive have been confirmed as contributing to improved tribology performance.
- 3)The effects of this reducing additive have been proven through engine disassembly, inspection and measurement, lubricating oil durability testing, extension of interval of oil exchange and drivability testing on actual vehicles.
- 4)This reducing additive not only reduces engine friction loss, exhaust gas, and fuel consumption, but also has revolutionary tribology performance benefits for automatic transmissions, differentials, etc.
- 5)This reducing additive has been proven to offer high durability and exceptional reductions to friction and wear in drift racing, a motor sport which is punishing on cars' engines.

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#### **DEFINITIONS/ABBREVIATIONS**

ATF : Automatic Transmission Fluid
C: Carbon
CVT: Continuously Variable Transmission
DPF: Diesel Particulate Filter
DST: Diester
FALEX: FALEX Seizure Load Testing Machine
ISOT: Indiana Stirring Oxidation Test
NO: Nitric Oxide
POE: Polyolester
SO<sub>3</sub>: Sulfur Trioxide
SOD-1: Unique Reducing Additive For Automobile Lubricant Oil
VOE: Vegetable Oil-Based Ester
ZnDTP: Zinc Dialkyldithiophosphat