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THE DEVELOPMENT OF AN ENGINE LUBRICANT CONTAINING SOYBEAN OIL

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Abstract of Thesis

THE DEVELOPMENT OF AN ENGINE LUBRICANT CONTAINING SOYBEAN OIL

The major downfalls of vegetable oils, namely soybean oil in this research, are very detrimental to engine lubricant performance. A unique - out of the box- additive package is needed to compensate for the lubricant deficiencies. This research searched for unique additive solutions to the problems of oxidation and heat stability, low temperature pumpability, and fluid corrosiveness. The additive solutions were then tested in preliminary engine tests.

In this research, several formulations were developed that passed the main engine oil low temperature test, the mini rotary viscometer. The lubricants met the passing viscosity requirements of 60,000 centipoise and exhibited no yield stress. The formulation was tested using ASTM D 6594[1], hot tube corrosion bench test, and Sequence VIII corrosion engine test. Acceptable results were seen in both tests.

Oxidation bench tests were used to examine soybean engine oil stability. Several antioxidants showed improved performance in the TFOUT oxidation induction time bench test. A mixture of those antioxidants was tested in the Sequence IIIG engine test. All of the formulas failed the Sequence IIIG tests. However, improved test results were seen when the soybean oil was decreased from 15 wt % to 5 wt % in the formulations.

KEYWORDS: Vegetable lubricant, Soybean oil, Corrosion, engine testing, base oil

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_______July 10, 2007________

THE DEVELOPMENT OF AN ENGINE LUBRICANT CONTAINING SOYBEAN OIL

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Name	Date

THESIS

Stephanie Marie McCoy

The Graduate School

University of Kentucky

2007

THE DEVELOPMENT OF AN ENGINE LUBRICANT CONTAINING SOYBEAN OIL

THESIS

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science in the
College of Engineering
at the University of Kentucky

By

Stephanie McCoy

Lexington, KY

Director: Dr. Eric Grulke, Professor of Chemical Engineering

Lexington, KY

2007

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Table of Nomenclature

APAL	Ashland Products and Applications Laboratory
API	American Petroleum Industry
ASTM	American Society for Testing and Materials
AO	Antioxidant
CAMLIFTWEAR	Cam and Lifter Wear
CCS	Cold Crank Simulator
CLW	Cam and Lifter Wear
CRC	Coordinating Research Council
DI	Detergent Inhibitor Package
DOE	Design of Experiment
HTCBT	Hot Tube Corrosion Bench Test
HTHS	High Temperature High Shear
ILSAC	International Lubricant Standardization and Approval Committee
LH	Light Hydrogenation
KV	Kinematic Viscosity
MRV	Mini-Rotary Viscometer
OEM	Original Equipment Manufacturer
OILCONSUM	Oil Consumption
PDSC	Pressure Differential Scanning Calorimeter
PERVISINC	Percent Viscosity Increase
PPD	Pour Point Depressant
PSV	Piston Skirt Varnish
R&R	Rate and Report
SAE	Society of Automotive Engineers
SBO	Soybean oil
TFOUT	Thin Film Oxygen Uptake Test
USB	United Soybean Board
VM	Viscosity Modifier
WPD	Weighted Piston Deposits
ZDDP	Zinc dithiodiphosphate

1 Introduction

1.1 Appropriateness for the domestic industry

There are growing commercial and research interests in replacing products based on non-renewable petroleum with those derived from renewable resources. As petroleum supplies decrease, production migrates toward higher transportation fuel fractions, and geopolitical considerations affect supply, the move toward national self-sufficiency for liquid energy supplies will become even more important. This research aims to develop engine lubricants that are both derived from renewable soybean oils and are equivalent in every way to their petroleum-based counterparts. In addition to providing somewhat greater security against disruption of foreign-sourced oil supplies, they will supply the domestic industry with an environmentally friendly and biodegradable replacement for hydrocarbon lubricants.

1.2 Key barrier areas

Engine oils are the largest volume application for lubricating fluids. The functional and performance requirements of the next largest category, hydraulic fluids, are less stringent than those for engine oils. While vegetable oils have penetrated the hydraulic fluid category to some degree, they have almost no representation in the engine oil category. This is the case in spite of the superior characteristics of vegetable oils for the primary function of a lubricant - to reduce friction and minimize wear between moving parts. Vegetable oils have a built-in ability to disperse deposits and sludge generated through use and contamination, and their chemistry is conducive to providing a seal at the critical contact joints. However, vegetable lubricants do not offer good stability or performance at elevated temperatures and generally exhibit poor low-temperature characteristics, especially fluidity. Therefore, a unique - out of the box-additive package will need to be formulated to compensate for the lubricant debits.

Through this project, many key barrier areas were addressed including: oxidation and heat stability, low temperature pumpability, fluid corrosiveness, and preliminary engine testing. By vigorous examination of various additive chemistry types, solutions to bench oxidation, corrosion, and low temperature pumpability tests have been found. Preliminary engine testing was started. Oxidative stability testing has been re-evaluated in the laboratory on several different instances.

1.3 Project description

Oxidation stability is the greatest hurdle for soybean oils. Oxidative stability of mineral based lubricants is evaluated by the Sequence IIIG engine test. Once a lubricant formulation passes an engine test it is not repeated. The API monitors the development of engine test procedures and repeatability. The approximate cost to run one Sequence IIIG engine test is $34,000. Since engine testing is costly, tests have not run on “bad” bench oils.

During the first phase of work, initial evaluations of the mid-oleic soybean samples from the United Soybean Board was completed. Several basic engine oil formulations were developed and evaluated in low temperature and oxidation stability bench tests. In the second phase, more emphasis was placed on corrosion bench and engine testing along with continued oxidation bench testing. The focus for the final phase was to obtain passing engine test results in the Sequence IIIG. All the testing was completed at the Valvoline New Products Development Laboratory as well as its engine testing facilities, Ashland Product and Applications Laboratory, in Ashland, KY.

1.4 Review of existing technologies

The major constituent of a lubricating fluid is base oil. Small amounts of additives complete the lubricant formulation. The base oil provides the primary lubricant functionality and performance. The additives enhance the performance of the base oil. The amount and type of additives required in a formulation depends upon the severity of the application; usually the additives vary from 5 to 20 wt % of the total formulation.

The physical and functional properties, that both petroleum-based and vegetable lubricants exhibit, are related to their respective chemical structures. Vegetable oil by its nature provides many of desirable properties such as: good boundary lubrication, high viscosity index, and high flash point. The better boundary lubrication and load carrying capacity of vegetable oils is due to an inherent chemical structure that orients itself with the polar ester region on the metal surface and non-polar hydrocarbon region away from the metal. However the oxidative stability and low temperature properties still limit their use for lubrication applications.

Due to vegetable lubricants being naturally derived, cold temperature pumpability issues arise. Low temperature pumpability is an issue in cold winter conditions. During cold temperature wax crystals can form which inhibit oil from being distributed to various engine locations at start-up. This can cause metal to metal contact, which is damaging to an engine.

Oxidation stability and cold temperature pumpability are vital properties of engine lubricants. Unfortunately, the double bonds found in the soybean oil are much more susceptible to oxidation, with the oxidative stability decreasing dramatically with the number of double bonds per fatty acid chain. Oxidation leads to both polymerization and degradation. Polymerization increases the viscosity and reduces functionality. Degradation leads to breakdown products that are volatile, corrosive, disintegrate the structure and reduce the properties of the lubricants. Before vegetable oils can be considered as base oils for severe applications like engine oils, the two major limitations, oxidative stability and low temperature behavior, need to be further improved. With the right combination of lubricant additives the oxidation, as well as cold temperature pumpability issues involved with natural lubricants can be stabilized.

1.5 Product development

Motor oil is a very demanding lubrication application. It was mentioned earlier that the currently available commodity vegetable oils (soybean, corn, canola, and sunflower) display numerous deficiencies in lubrication products as a consequence of their fatty acid composition.

To develop a competitive engine oil formulation incorporating significant quantities of vegetable oil based components, the following skills, capabilities, and technologies are required:

- Access to commercial quantities of high stability vegetable oils (as starting material)
- Knowledge of additive functionality and interactions
- Engine and lubrication testing capabilities and knowledge
- Intimate knowledge of engine oil technology
- Knowledge of the ever-changing market requirements.

2 Literature Survey

2.1 Soybean oil in lubricants

The literature for engine oils containing soybean oils is very limited. Vast amounts of literature can be found for different types of bio-based lubes and additives derived from them [2-4]. Sharma et al. investigated greases with improved oxidation stability. They used an epoxy vegetable oil as their base fluid. The tests used to measure oxidation stability were the pressure differential scanning calorimeter and a rotary bomb oxidation test [5].

One thing common with all literature is the lack of any type of testing besides bench tests. Most of the fluids were not as complex as engine oils and may be able to be effectively evaluated in bench tests. When it comes to engine oils, engine tests and fleet studies are critical when introducing a product “new” to the industry.

2.2 Cold temperature properties

Cold temperature properties of engine lubricants have always been of interest to oil manufacturers, original equipment engine manufacturers, and base oil producers. One paper that had a general review on the subject was written by M. K. Mishra at Texaco R&D. The review evaluates the different type of polymer additives that can be used to control cold temperature viscosities in non-soybean engine lubricants [6].

Very little literature can be found on the cold temperature properties of engine lubricants which contain soybean oil. One article by Erhan et al. discusses the inferior cold temperature properties of vegetable-based lubricants. They state that cold temperature and oxidation stability are the two most critical concerns with vegetable lubricants. They tested pour points and cold temperature storage of vegetable oils. The conclusion to their work was that lubricant additives will help with some of the problems with vegetable lubricants. However, they also suggest that vegetable base oils must be modified to produce products that are oxidatively stable and can perform in cold temperature [7].

2.3 Corrosion inhibitors

Little corrosion work on vegetable engine oils has been published. Sharma el at investigated the corrosion resistance of bio-based grease [5]. The group of Jayadas et al. [8] evaluated the corrosion mechanism of industrial vegetable-based lubricants. They evaluated the lubricants using ASTM D130, the copper strip test and ASTM D665, the rust prevention test. The corrosion properties were analyzed using quantum chemical calculations. The work compared the anti-corrosive properties of ZDDP (zinc dialkyldithiophosphate) with other additives. They concluded that leading cause of corrosion in vegetable oil containing lubricants was moisture. The problem can be fixed by use of ZDDP and moisture control [8].

2.4 Oxidation of lubricants

The instability of vegetable base oils when it comes to oxidation is well known in the literature [3, 9-12]. Erhan and Adhvarya noted that the oxidative stability and low temperature properties of vegetable oils must be improved before they are considered for universal applications [10]. Birova et al. [13] evaluated oils made with chemically modified vegetable oils. They modified vegetable oils by epoxidizing the double bonds which resulted in the formation oxirane rings. The rings were then opened by the use of hydrogen donor.

Wagner et al. [14] worked on chemical reactions on vegetable fatty compounds that would generate more marketable vegetable lubricants. They tested their reactions in both the lab and on plant scale level.

Lal and Carrick at Lubrizol [15] also suggest that advances in breeding techniques might be able to generate vegetable lubricants that are more oxidatively stable and have better cold temperature properties.

The food industry has had an interest in the oxidative stability of vegetable oils for years. Although much of the research does not directly apply to lubricants, some of the basic oxidative principles are the same. The work done by Zambiazi and Prybylski [16] found that the fatty acid compound in vegetable oils is not the only reason for its oxidative instability. It was found that the minor endogenous components also affect the stability of the oils. The amount and types of compounds can play a large role in oxidation stability of oil. If this is true, there could be multiple issues if engine oil was made with different samples of vegetable oils grown in different locations or during different growing seasons. Engine oils might have to be retested every time a new batch of vegetable base oil is used. This would be very costly and would ensure that no lubricant marketer or additive company would be willing to make the investment required.

Fox and Stachowiak [17] evaluated the autoxidation mechanisms of vegetable oil. They also monitored and analyzed the oxidation products and looked at their impact on the lubrication properties of vegetable oil.

No literature existed specifically about vegetable engine oils and the extensive oxidation testing required to produce an API certified engine lubricant. Therefore, the research completed in this project is needed to determine the ability for vegetable base stocks to be used in practical applications.

3 Research Objectives and Tasks

3.1 Technical feasibility and targets

The primary target of this work is the development of a commercially feasible, renewable resource soybean oil-based lubricant that can be used as a partial or complete replacement or substitute for petroleum-based oils. There is likelihood that special benefits will be demonstrated from a renewable resource based lubricant. Soybean oil is readily available, well-characterized and well-understood, and is an appropriate choice for a pilot study. Three areas that have been ignored or only cursorily examined in the past for natural lubricants are:

- Corrosion
- Engine testing
- Biodegradability and mutagenicity of new and used engine oil.

This study focused on the first two areas, corrosion and preliminary engine testing.

3.1.1 Project plan

A key element of the project plan was to develop a lubricant system that performed well enough to warrant engine testing. Low levels of soybean oil addition would lead to one type of product (5-10 wt %), while higher levels of soybean oil would have significant marketing value.

3.1.2 Product development constraints

One test formulation will contain the United Soybean Board (USB) supplied mid-oleic oil at a concentration of 15 wt%, one with 5 wt%, and the other will be the same formulation with the mid-oleic oil replaced with 5 wt% of the USB high-oleic oil sample. If either of these engine tests shows promising results, not necessarily a complete pass, it is recommended that the project be carried on as described below. If the tests do not show promising results, then it is recommended that the engine oil development project not carry on any further until more bench work is completed.

3.2 Project goals and objectives

Table 1. Engine Test Hurdles

Oxidation stability	Oil consumption
Emissions	Corrosion durability
Engine wear and durability	Seal compatibility
Fuel economy	Catalytic converter compatibility and preservation

The major project goal was to develop an engine lubricant that uses a partial blend of soy and performs as well as conventional motor oil. The oil formulation should also be economically feasible.

A second goal was to interest end users and automotive manufacturers in the properties and potential for replacing petroleum derived engine oils with oils that consist partially of naturally derived base oils.

3.2.1 Specific objectives

1) Optimize the vegetable oil formulation for passenger car engine oil
2) Develop formulation that shows positive results in screening bench tests
3) Perform screening engine tests to evaluate performance under actual use conditions

4) Find a feasible solution to problems that arise due to engine testing.

4 Typical Passenger Car Engine Oil Formulation

Engine oil serves many purposes in a motor. Some of the functions such as friction and wear reduction are very apparent. Other functions such as cooling of engine parts, an anti-corrosion agent, a cleaning agent, and a sealing agent are less known to the typical consumer [18].

Engine lubricants are composed of both base oils and a complex system of chemical additives. The chemical additives are carefully formulated so that the lubricant can perform all the functions mentioned above. The chemical additives that may be included in an engine oil include detergents, dispersants, antiwear agents, antioxidants, viscosity modifiers, pour point depressants, foam inhibitors, anticorrosion agents, antirust agents, seal swelling agents, biocides and demulsifiers [19].

There are many test requirements engine lubricants must meet. In the United States, vehicle manufacturers determine what type of engine oil they want to be used in their automobiles. Typically the oils they specify are certified under the American Petroleum (API) and/or International Lubricant Standardization and Approval Committee (ILSAC) systems. As technologies have become more complex, so have the series of tests required to certify engine oils.

A series of laboratory bench tests and stationary engine tests are required to be able to meet current API and ILSAC certifications. Vegetable based lubricants will not gain acceptance if they are not able to meet the stringent requirements to which mineral based products are held. Today the evolution of new engine oil certifications are driven by the demand for improved emissions control. Because of the emissions demand, the original equipment manufacturers have increased the operation severity of many of their engines. This has resulted in field problems that are addressed by increase in lubricant quality [18].

Engine oils are classified into viscosity grades by SAE J300 [20]. The standard determines engine oil viscosity grades based on several tests including kinematic viscosity (D445, [21]), cold cranking simulator (ASTM D5293, [22]), low temperature pumpability (ASTM D4684, [23]) and high temperature high shear viscosity (ASTM D4683, [24]). The test requirements can be seen in Table 2.

Table 2. SAE J300 Viscosity Classification [20]

Vis Grade	Cold Crank Simulator (cP)	MRV TP-1 (cP) Cold Temp Pumping	Kinematic Vis 100°C, (cSt)	HTHS @ 150°C (cP)
0W	< 6200@-35°C	60,000 @ -40°C	> 3.8	-
5W	<6600@-30°C	60,000 @ -35°C	> 3.8	-
10W	<7000@-25°C	60,000 @ -30°C	> 4.1	-
15W	<7000@-20°C	60,000 @ -25°C	> 5.6	-
20W	<9500@-15°C	60,000 @ -20°C	> 5.6	-
25W	<13000@-10°C	60,000 @ -15°C	> 9.3	-
20	-	-	$5.6 < v < 9.3$	> 2.6
30	-	-	$9.3 < v < 12.5$	> 2.9
40	-	-	$12.5 < v < 16.3$	>2.9*
40	-	-	$12.5 < v < 16.3$	> 3.7**
50	-	-	$16.3 < v < 21.9$	> 3.7
60	-	-	$21.9 < v < 26.1$	> 3.7

* For 0W-40, 5W-40, and 10W-40 grades.
** For 15W-40, 20W-40, 25W-40 and 40 grades.

Engine oil performance is almost entirely measured by engine testing. This testing can take place over the road but the majority of the time takes place on test stands. The engine size can range from a single cylinder to a full sized many cylinder commercial type engine. The tests are run according to a specific procedure. The procedures involve variations in load and speed and can require continuous or intermittent operation. The engine tests are designed with great care to mimic engine conditions and applications that are important to lubricant performance. Typically test protocols are developed to be more severe than actual on-road conditions. This allows for the lubricant to age quickly so testing time is reduced [18].

API 1509 [25] defines the procedure used to develop and implement new engine tests in the lubricant industry. Typically a company or group will propose a new test to API. Then a task force containing members from various organizations is formed. The task force is responsible for coordinating test development activities and analyzing test data. When deemed ready by the task force, the engine test will then be subjected to industry precision matrix testing. The task force also establishes criteria to determine if the engine test is reproducible, discriminative, and precise. Once these criteria have been met, the task force formalizes the test procedure. After the test procedure has been formalized, an American Society for Testing and Materials (ASTM) committee is formed to draft an official ASTM standard.

Engine tests evaluate many performance characteristics of lubricants. Test measurements may be physical measurements or controlled visual ratings. The visual rating scale was developed by the Coordinating Research Council (CRC). Independent “raters” are trained and certified to rate different engine parts based on the CRC manuals [18].

5 Materials and Methods

5.1 Methods

Multiple test methods were used to guide the development of these lubrication systems. Sets of physical property methods, often ASTM tests, were used to identify additives that might address known lubrication problems. Once improved packages were developed, engine tests were completed to identify problems that might occur in the field. Typical lubricant test methods include physical and rheological property measurements. Low temperature and high temperature physical properties were measured on each sample. All tests were performed by the author except those for which a special lab/operator exists at Valvoline. These conditions are specifically noted for each case.

Oxidative properties were measured using the Thin Film Oxygen Uptake Test (TFOUT) (ASTM D4742, [26]) and Pressure Differential Scanning Calorimeter (PDSC) (ASTM D6186, [27]). The TFOUT is a pressurized bomb immersion oxidation test that is run using a specialized additive trio. The trio consists of water, fuel, and a catalyst mixture. The trio represents liquids present in the engine when operating. The catalyst mixture was developed to mimic the materials that are found in a passenger car engine. It includes a lead source which is present in the components used in the engine. Originally the trio was developed to mimic the oxidative performance of a lubricant in the Sequence IIID oxidation engine test. The TFOUT is run at 160 ºC and measures time in minutes to oxidation. A 1.5 g sample is required. TFOUT testing followed the ASTM procedure.

When samples were run on the PDSC, air was used in place of the nitrogen specified by the ASTM procedure requires. This was for the purpose of laboratory safety. The PDSC also measured induction time to oxidation. A 3.2 mg sample is required. Prior to installation of the PDSC, some samples were sent to Savant (Midland, MI) for PDSC testing. This firm used nitrogen rather than air in their methods. Test results were only compared when the same gas was used.

Lubricant cold temperature properties were measured by ASTM D5293 [22], cold cranking simulator (CCS), ASTM D5950 [28], pour point determination, ASTM D4684 [23], mini-rotary viscometer (MRV), and ASTM D5133 [29], scanning Brookfield testing. All tests were completed per ASTM procedure, including the number of repetitions.

The main bench test used to determine if a lubricant will have satisfactory cold temperature performance is the MRV. The mini-rotary viscometer test was run at different temperatures for different oil grades. The MRV was run at -35 C for SAE 5W grades and -30 C for SAE 10W grades. The MRV is about a 48 hours test. During the test time there is a heating and cooling cycle. The cycle was developed to mimic the temperature transitions that an automobile sitting out in the cold might go through in a cold climate. At the beginning of the test a sample is inserted into a test cell. A spindle with a string wrapped around the top is then inserted into the sample. The cooling/heating cycle begins. At the end of the test, the viscosity and yield stress of the oil are measured. A weight is attached to the string and the viscosity is determined by how fast the string unwinds. Yield stress is determined the movement when the weight is attached. When the viscosity is under 60,000 cP and no yield stress existed, the lubricant was considered passing.

This test suite gave a good overall characterization of various oil formations. Table 3 lists some of the details about the typical tests used. Table 4 shows typical properties for a GF-4 engine oil, which was taken as a typical reference material.

Table 3. Test Methods

Test	Equipment	Comments
Kinematic Viscosity	ISL (Houston, TX) VH series	• Measures viscosity of Newtonian fluids • Run at 100 °C and 40 °C • Calibrated glass capillary viscometer • Measure the time required for a specific volume of liquid to flow through by the force of gravity.
Thin film oxygen uptake test (TFOUT)	Tannas Company (Midland, MI), Model TF951212-1-1	• Pressurized bomb immersion test • Measures time (minutes) to oxidation as detected by a rapid decrease in the plot of cell pressure vs. time • 160 ºC, catalyst/ fuel package used • Correlated to Sequence IIID
Hot tube corrosion bench test (HTCBT)	In-house built per ASTM method	• 7 day test, 135 ºC • Evaluate metal composition in fluid at EOT, copper strip varnish • Designed to evaluate diesel engine oils
Mini rotary viscometer, (MRV)	Cannon (State College, PA) CMRV 4000 series	• ~48 hour heating/ cooling cycle • Low temperature, low shear
Cold cranking simulator (CCS)	Cannon CCS 2000 series	• ASTM D5293 • Low shear rate viscometer that predicts oil's ability to flow in a cold engine • Different test temps defines by SAE J300
NOACK	ISL	• Measures % volatility of oil after it is heated to 150 °C for one hour
Pressure Differential Scanning Calorimeter (PDSC)	TA Instruments (New Castle, DE) 2920 Modulated DCS w/ PDSC attachment	• Measures time to oxidation

Table 4. Typical values for GF-4 SAE 5W-30 engine oil

Test	Typical Results SAE 5W-30 passenger car oil
Kinematic viscosity, cSt	10.0- 11.0
TFOUT, minutes	~ 300
HTCBT	
Lead, ppm	300 ppm
Copper, ppm	15 ppm
Tin, ppm	0 ppm
Strip rating	2 max
MRV	
Viscosity, cP	<30,000
Yield stress	No yield stress
CCS @-30 C, cP	6000
PDSC, minutes	50
NOACK, % wt	15

5.1.1 Engine test methods

All engine test methods were done by Ashland Products & Applications Laboratory (APAL, Ashland, KY). Before a lubricant can claim API or ILSAC credentials, a series of bench and engine tests must be completed. API and ILSAC are the governing arm of lubricant specifications in the United States. The two organizations are made up of original equipment manufacturers (OEM's), additive companies, base oil producers, and oil marketing representatives. Engine oil and other fluid specifications are set by API and ILSAC committees.

Engine tests procedures are made into ASTM procedures after they are developed. The tests of interest in this work are the Sequence VIII test and the Sequence IIIG test.

The Sequence VIII test is used to determine an engine lubricant's ability to withstand corrosion in the copper lead alloy engine bearings. The test involves a single cylinder Labeco research engine that is run at high speed steady state for forty hours. A weight loss measurement in the engine bearings determines the quality of the lubricant. The lubricant is also required to remain in its original viscosity grade.

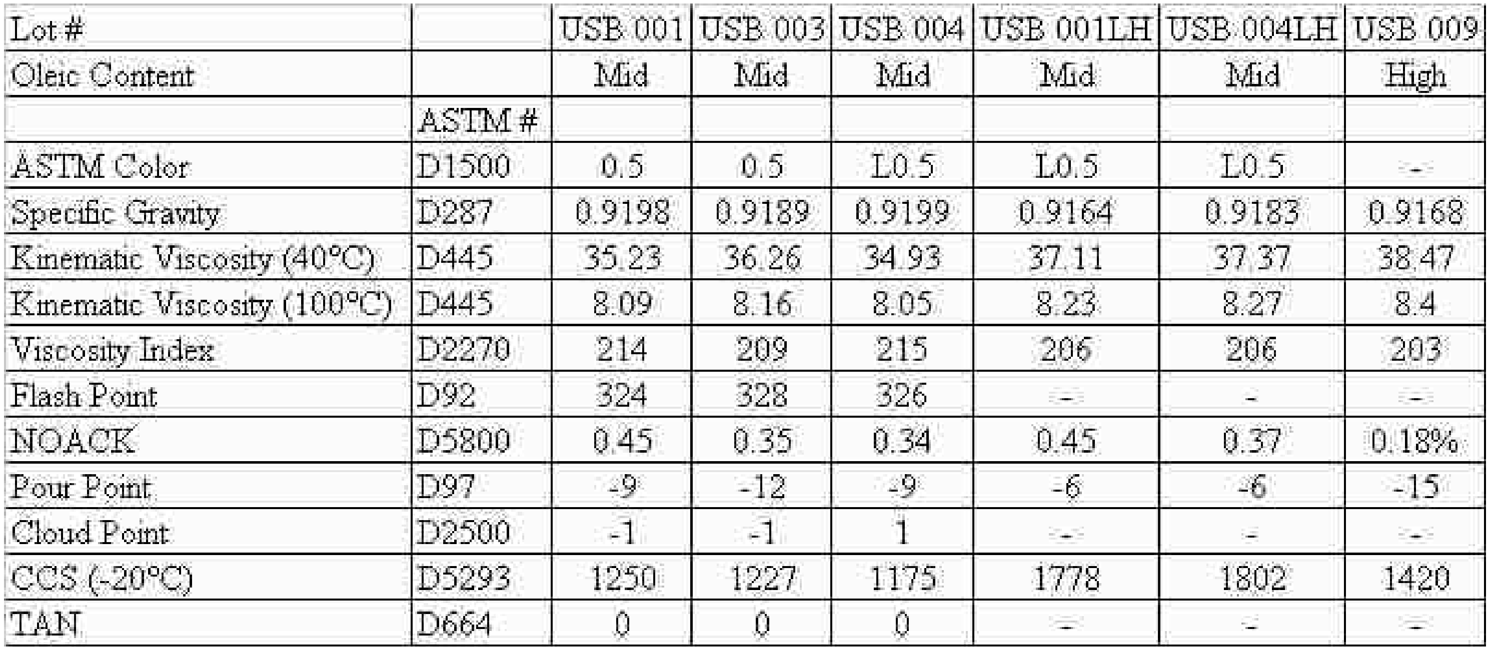
The Sequence IIIG is an oxidation engine test that runs for 100 hours at a temperature of 150 °C. The test uses a General Motors V-6 engine. Measurements taken include percent increase of the lubricant viscosity at 40°C, weighted piston deposits, piston skirt varnish, oil consumption, and the number of stuck rings. A pass or fail rating is assignment to the lubricant based on the results of the measurements mentioned. The Sequence IIIG test has recently been developed and is currently in an ASTM committee under final review.

5.2 Materials

All of the materials used in the bench tests are per ASTM standards. TFOUT oxidation induction time tests were completed using a catalyst 3D package from Tannas Company. PDSC tests used zero grade compressed air.

Base oils that were involved in testing included Mobil P43, (ExxonMobil Chemical, Houston, TX), group I Marathon 100 N (Marathon Oil Company, Findlay, OH), group II Motiva Star 4 (Motiva Enterprises LLC, Houston, TX), group III Yubase 4 (SK Corporation, Seoul, Korea), group IV Durasyn 4 (Innovene, Naperville, IL), and treated bio oil AP 560 (Cargill, Minneapolis, MN). Several different soybean oil samples were used during the course of the research. See Table 5 for details.

Table 5. Samples of Soybean oil obtained from the United Soybean Board



Lot #		USB 001	USB 003	USB 004	USB 001LH	USB 004LH	USB 009
Oleic Content		Mid	Mid	Mid	Mid	Mid	High
	ASTM #						
ASTM Color	D1500	0.5	0.5	L0.5	L0.5	L0.5	-
Specific Gravity	D287	0.9198	0.9189	0.9199	0.9164	0.9183	0.9168
Kinematic Viscosity (40°C)	D445	35.23	36.26	34.93	37.11	37.37	38.47
Kinematic Viscosity (100°C)	D445	8.09	8.16	8.05	8.23	8.27	8.4
Viscosity Index	D2270	214	209	215	206	206	203
Flash Point	D92	324	328	326	-	-	-
NOACK	D5800	0.45	0.35	0.34	0.45	0.37	0.18%
Pour Point	D97	-9	-12	-9	-6	-6	-15
Cloud Point	D2500	-1	-1	1	-	-	-
CCS (-20°C)	D5293	1250	1227	1175	1778	1802	1420
TAN	D664	0	0	0	-	-	-

6 Results and discussion

6.1 Initial screening

Initially a soybean oil sample was received from the United Soybean Board (USB 001). The sample was generated from other non-lubricant related projects the United Soybean Boards was funding. There was no control over the sample selection or soybeans used to produce the sample. The soybean base oil sample was run through physical property tests. The results for these tests can be seen in Table 5, USB 001.

After the physical property evaluation of the soybean base oil was completed, fully formulated engine oils were made containing various amounts of the soybean oil. The soybean oil was used at three different treatment levels: low (10 wt %), medium (35 wt %) and high (60 wt %). The test results for the blends revealed several benefits and downfalls when using soybean oil in a lubricant formulation. The benefits included a decrease in NOACK volatility, and a lower cold crank simulator (CCS) result. Some of the downfalls were failing low temperature pumpability MRV tests and decreased oxidative stability. The results for these initial blends can be seen in Table 6.

Table 6. Heavy Duty SAE 5W-40 engine oil blends

OIL	LOW	MIDDLE	HIGH
% SB OIL	10%	35%	60%
Vis (100 C)	14.35	14.4	14.4
CCS (-30 C)	6500	6300	6200
MRV			
Yield Stress	35- 70	35	105- 140
Viscosity	48500	50550	57540
Specific Gravity	0.880	0.880	-
Pour Point	-45	-45	-
TFOUT	80 min	25 min	-

6.2 Cold temperature testing

Multi-grade lubricants perform at both high and low temperatures. Cold temperature properties of a lubricant are important because of wax formation that may occur. If waxes form, a fluid may become too thick to properly lubricate engine parts when a vehicle is starting. If wax crystals collect around the oil pick-up tube, no fluid will flow to areas of the engine that need to be lubricated. This can lead to future wear and damage to an engine. Pour point depressants (PPDs) are polymeric components used in engine oil formulation to modify the formation of wax crystals [18]. Different base oil structures require different PPD types to prevent crystal growth that may harm the engine during cold temperature start-up. The test used to evaluate wax crystal growth is the MRV.

Initial MRV tests were run using a blend of Mobil P43, a synthetic ester, mid-oleic soybean oil from the USB, and PPD1 or PPD2. These blends were run at -35 C. Only one blend was able to pass the MRV. A passing MRV result is obtained when the viscosity is below 60,000 cP and no yield stress exhibited. This blend included 30 % synthetic ester, 0.80 % PPD2, and 69.2 % mid-oleic soybean oil. All percentages are in weight. The test results can be seen in table 7. The testing also revealed several trends. Lower amounts of the soybean oil in the blend led to lower fluid viscosities at the end of the test.

Table 7. MRV results for various SBO's with ester and pour point depressants

SBO, %	Ester, %	PPD 1, %	PPD 2, %	Yield Stress, Pa	Viscosity, cP
99.2	-	0.8	-	>350	>>>10E6
94.2	5	0.8	-	>350	>>>10E7
79.2	20	0.8		>350	>>>10E8
69.7	30	-	0.3	>350	114400
69.2	30	-	0.8	<35	13270

Once a passing viscosity below 60,000 cP and no yield stress were achieved in the MRV test with the base oil and PPD mixtures, fully formulated passenger car engine oils were developed. When a detergent inhibitor package and viscosity modifier was added to the mixture, the results changed. Use of the PPD2 no longer gave passing MRV results. The viscosity numbers were passing, but the test failed based on yield stress. The results can be seen in table 8.

Table 8. SAE 5W-30 blends with failing MRV results

SAE Grade	5W-30	5W-30	5W-30	5W-30
SBO %	15	30	15	30
PPD2	0.3	0.3	0.8	0.8
Yield Stress, Pa	>70	>70	>70	>70
Viscosity, cP	28,290	29,150	31,870	32,260

Next formulations for engine oils were developed that incorporated several different pour point depressants. The oils were developed as SAE 10W-30 grades. MRV viscosity and yield stress test protocols for 10W oils are run at a temperature 5 °C warmer than 5W grades. This allows a better chance of the passing test results. Passing viscosity and yield stress results were with all of the pour point depressants that were evaluated (Table 9).

Table 9. MRV results for various pour point depressant chemistries

SAE Grade	10W-30	10W-30	10W-30	10W-30
PPD 3	0.3	X	X	X
PPD 4	X	0.3	X	X
PPD 5	X	X	0.3	X
PPD 6	X	X	X	0.3
Yield Stress (Pa)	<35	<35	<35	<35
Viscosity (cP)	20540	20410	19870	24640

Another pour point depressant was used to blend several different SAE 5W-30 engine oils. The treatment level of the pour point depressant was varied from 0.20 to 0.87 wt%. MRV tests were run. The MRV results showed the pour point depressant was successful at helping the formulation pass the MRV at all levels. However, it was seen at a higher pour point depressant treatment level, the viscosity measurement decreased (Table 10). This proved the pour point depressant was interacting with the lubricant formulation at cold temperatures. The amount of pour point depressant in the formula was indirectly proportional to the end test viscosity. This is desirable since it indicated that the lubricant would be less viscous after sitting in a cold atmosphere. The lubricant would be able to more effectively lubricant the engine at start-up.

Table 10. SAE 5W-30 grades

SAE Grade	5W-30	5W-30	5W-30	5W-30
PPD 7	0.2	0.53	0.87	GF-3 Typical
Yield Stress (Pa)	<35	<35	<35	<35
Viscosity (cP)	28016	29266	27707	60000

6.3 Oxidation

6.3.1 Typical formulations tested

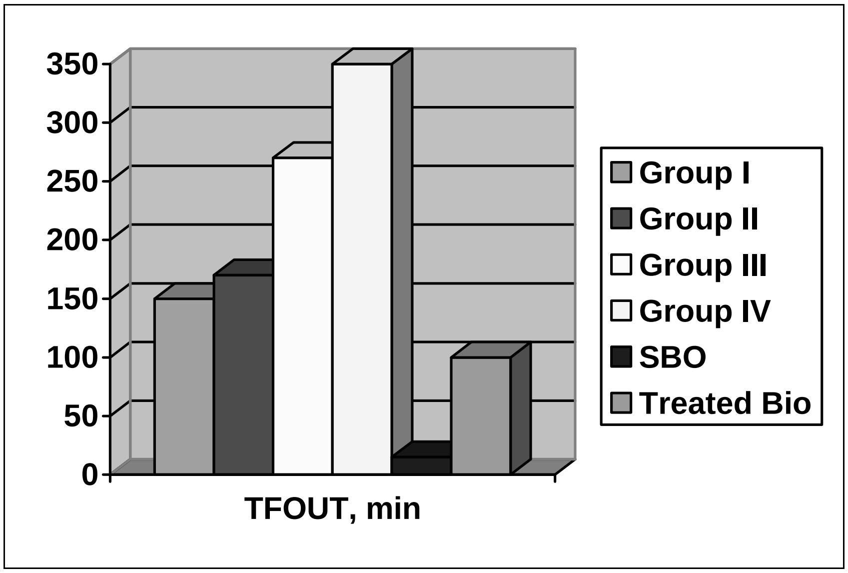
Initial test results indicated oxidative stability of the soybean oil formulations to be a large issue. Once passing MRV results were observed, the next hurdle observed in the in initial testing was oxidation stability.

6.3.2 Oxidation inhibition

The oxidative stabilities of lubricant base oils increase with their quality. Figure 1 shows TFOUT oxidation induction time results when several different blends with varying base oils were tested. The oils were formulated with the same additive package and different base oils. The lubricant which contained Group 1 oil lasted about 150 minutes in the TFOUT oxidation induction time test. The Group II-based lubricant lasted slightly longer. The Group III oil was more stable in this test, with a failure time of 270 minutes. The longer time to failure may be a result of the higher saturates content. The same phenomenon occurred for the Group IV oil which lasted 350 minutes until oxidation induction in the TFOUT oxidation induction time test.

The TFOUT oxidation induction time for the soybean oil sample was less than a third that of Group I oil. The soybean oil has a high degree of unsaturation, which is known to lead to rapid oxidation. Several companies market vegetable base oils that have been processed to remove some of the unsaturated sites. One of the treated vegetable oils was tested. The TFOUT oxidation time was better than the soybean oil but still not as good as the Group I oil. In the passenger car engine oil market today, many lubricants must incorporate Group II or III base oils to be able to meet the stringent oxidation requirements. Based on the current formulations, it will be very hard to incorporate any soybean oil into passenger car motor oil and meet the current industry standards.

Figure 1. TFOUT results for blends with various base oils



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6.3.3 DOE to determine optimum concentrations in base oil

After screening the engine oils made with different base oil Groups with the TFOUT test, it was realized that blends with SBO were going to need additives to boost their oxidative stability. When lubricants do not meet the desired oxidation stability hurdles, antioxidants are added to the formulation to improve performance. This approach was used with the soybean lubricant, but a much wider spectrum of chemicals were evaluated as potential antioxidants than typical for a passenger car engine oil. Multiple additives were evaluated in the TFOUT oxidation induction test. The additives which showed promising results were evaluated further. Some potential additives evaluated were AO1, AO2, AO3, AO4, AO5, and AO6. The additives represented a wide array of chemistries from amines to molybdenum to napthanates. See Table 11 for additive details.

Table 11. Initial additives used to improve oxidative stability.

Additive	**Description**
AO1	Diphenylamine
AO2	Naphthylamine
AO3	Diphenylamine
AO4	Naphthylamine
AO5	Organic molybdenum compound
AO6	Copper napthanate

Since the additives had promising results in TFOUT oxidation induction time testing when used alone, they were then evaluated in combination with other promising additives to determine if any synergies existed. A design of experiment (DOE) was made using ECHIP software. The parameters of the design allowed for the interaction of the additives in Table 11 to be tested. The design also set a limit on the total wt % of additive that could be added to the blend. Two different maximum treatment level were tested, 1.2 wt% and 2 wt%. These levels were set based on previous TFOUT oxidation induction testing and with a final formulation cost in mind. The ECHIP software also randomized the trial in the matrix and added several repeat blends to help eliminate inaccurate data points and test bias. See Table 12 for details of the blends.

Table 12. Oxidation stability blends tested based on ECHIP DOE.

TRIAL	**12**	**5**	**7**	**13**	**11**	**5**	**2**	**2**	**1**	**14**	**6**	**4**	**4**
AO1	0	0.6	0	0	0	0.6	0.6	0.6	0	0	0.6	0.6	0.6
AO2	0.6	0	0.6	0.6	0.6	0	0	0	0	0	0	0	0
AO3	0.6	0.6	0	0	0	0.6	0	0	0	0.6	0	0	0
AO4	0	0	0	0.6	0	0	0	0	0	0	0.6	0	0
AO5	0	0	0	0	0.6	0	0	0	0	0.6	0	0.6	0.6
AO6	0	0	0.6	0	0	0	0.6	0.6	0	0	0	0	0
Level	1	1	1	1	1	1	1	1	1	1	1	1	1
TRIAL	**9**	**8**	**10**	**3**	**1**	**3**	**15**	**20**	**15**	**28**	**23**	**16**	**21**
AO1	0	0	0	0.6	0	0.6	0	0.6	0	0	0	0	0.6
AO2	0	0	0	0.6	0	0.6	0	0	0	0.6	0	0	0.6
AO3	0.6	0	0	0	0	0	0	0.6	0	0	0	0.6	0.6
AO4	0	0	0.6	0	0	0	0.6	0.6	0.6	0	0	0.6	0
AO5	0	0.6	0	0	0	0	0.6	0.2	0.6	0.6	0	0	0
AO6	0.6	0.6	0.6	0	0	0	0	0	0	0.6	0.6	0	0.2
Level	1	1	1	1	1	1	2	2	2	2	2	2	2
TRIAL	**25**	**17**	**27**	**24**	**22**	**26**	**16**	**19**	**17**	**18**	**19**	**18**	
AO1	0	0.6	0	0	0	0	0	0.6	0.6	0.6	0.6	0.6	
AO2	0.2	0.2	0.6	0.2	0.6	0.6	0	0.6	0.2	0	0.6	0	
AO3	0	0	0.6	0.6	0.6	0	0.6	0	0	0.2	0	0.2	
AO4	0.6	0.6	0.6	0.6	0	0	0.6	0.2	0.6	0	0.2	0	
AO5	0.6	0	0.2	0	0.6	0	0	0.6	0	0.6	0.6	0.6	
AO6	0.6	0.6	0	0.6	0.2	0	0	0	0.6	0.6	0	0.6	
Level	2	2	2	2	2	2	2	2	2	2	2	2	

The results from these tests were used to select three multi-component antioxidant packages for further work.

A mix of soybean oil, Group II base oil, and antioxidants were tested in the TFOUT. The amount of base oils and the chemistry of the antioxidant packages were varied. The DOE software (ECHIP) was used to optimize the TFOUT results with the concentration of soybean oil in the lubricant blend.

Table 13 shows the results from some of the trials. AO package 3 was an optimized version of packages 2 and 3. It was found that the optimum concentration to obtain a TFOUT result of at least 300 minutes was 24% soybean oil with AO package 3 treated at 2.6%.

Table 13. TFOUT results for different antioxidant packages

Soybean Oil, wt%	Group II BO, wt%	AO Package 1, wt%	AO Package 2, wt%	AO Package 3, wt%	TFOUT, min
15.0	82.1	2.9	X	X	320
30.0	67.1	2.9	X	X	120
45.0	52.1	2.9	X	X	50
15.0	83.1	X	1.9	X	100
30.0	38.1	X	1.9	X	30
24.0	73.4	X	X	2.6	330
45.0	52.4	X	X	2.6	150
60.0	37.4	X	X	2.6	115

6.3.4 Optimization of DOE additives with DI package

After several DOE's were completed, further TFOUT oxidation induction time testing was performed to optimize the antioxidant package with the detergent-inhibitor package used in the engine oil. The testing evaluated the additives shown in Table 14.

Table 14. Additives evaluated in fully formulated engine oil.

Additive	**Description**
AO2	Phenyl-alpha-naphthylamine
AO 7	di-t-butylhydrocinnamate acid ester w/ a C8 group
Zinc	Secondary zinc-dithiodiphosphate
Moly1	Organic molybdenum dithiocarbamate
Moly2	Organic molybdenum amine

The additives in Table 14 were blended in several different formulations. Additive treatment levels were kept constant. Treatment levels were selected based on previous DOE work with base oils and antioxidants. Table 15 shows the detailed blend formulations as well as TFOUT oxidation induction times and kinematic viscosities.

One of the blends that was tested contained only antioxidants and base oils. This blend had an induction time of over 440 minutes. Ideally formulated engine oils would be able to achieve the same oxidation induction time result. However, this is rarely the case. The use of other additives in formulations tends to cause a decrease in oxidation stability. The extensive amount of formulas tested evaluated the individual effects of each component in the soybean engine oil formulation.

Nineteen blends were tested, including a baseline blend that contained everything but the soybean oil (base oils, DI additives, viscosity index improver, pour point depressant, and antioxidants). The blends are shown in Table 15.

A baseline blend was made that did not contain any soybean oil. An oxidation induction time of 320 minutes was seen for the baseline. When soybean oil was added to the baseline, the TFOUT oxidation induction time decreased to 125 minutes.

Table 15. Blends made to determine optimal oxidatively stable formulation.

Blend #	1	2	3	4	5	6	7	8	9	10
Base Oil	69.2	70.1	69.2	84.2	70.3	85.3	68.7	70.1	85.1	85.3
Soybean Oil	15	15	15	-	15	-	15	-	15	-
Dispersant	4	4	4	4	4	4	4	4	4	4
Detergent	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Old Zinc	-	-	1	1	1	1	1	1	1	-
New Zinc	1	1	-	-	-	-	-	-	-	1
AO2	0.6	-	0.6	0.6	0.6	0.6	0.6	-	-	0.6
AO7	0.3	-	0.3	0.3	0.3	0.3	0.3	-	-	0.3
Moly1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Moly2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
VM + PPD	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
Inhibitor 1	1	1	1	1	-	-	0.5	1	1	-
Inhibitor 2	0.05	0.05	0.05	0.05	-	-	0.05	0.05	0.05	-
Inhibitor 3	0.05	0.05	0.05	0.05	-	-	0.05	0.05	0.05	-
Inhibitor 4	-	-	-	-	-	-	1	-	-	-
KVis (100 °C)	10.23	9.45	10.18	9.42	10.13	9.45	10.11	10.17	9.39	9.5
CCS (-30 °C)	5897	5608	5942	5969	6066	6157	5976	5687	5873	6130
TFOUT, min	130	80	135	335	125	130	130	95	170	320

Table 15. (continued)

Blend #	11	12	13	14	15	16	17	18	19
Base Oil	71	86	71.3	86.3	86.2	72.9	87.9	89.3	91
Soybean Oil	15	-	15	-	-	15	-	-	-
Dispersant	4	4	4	4	4	4	4	-	-
Detergent	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	-
Old Zinc	-	-	-	-	-	-	-	-	-
New Zinc	1	1	-	-	1	-	-	1	1
AO2	0.6	0.6	0.6	0.6	-	-	-	0.6	0.6
AO7	0.3	0.3	0.3	0.3	-	-	-	0.3	0.3
Moly1	-	-	0.5	0.5	0.5	-	-	0.5	0.5
Moly2	-	-	0.2	0.2	0.2	-	-	0.2	0.2
VM + PPD	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
Inhibitor 1	-	-	-	-	-	-	-	-	-
Inhibitor 2	-	-	-	-	-	-	-	-	-
Inhibitor 3	-	-	-	-	-	-	-	-	-
Inhibitor 4	-	-	-	-	-	-	-	-	-
KVis (100 °C)	10.09	9.41	10.02	9.42	9.46	10.19	9.4	8.1	7.89
CCS (-30 °C)	6064	6018	5703	5950	5905	5840	5640	4335	4199
TFOUT, min	115	325	30	115	155	5	-	220	440+

6.3.4.1 Manufacturer change in zinc additive

During the course of the investigation, one of the additive manufactures introduced a new secondary ZDDP additive. Several blends were tested to determine whether the new additive had any adverse effects on the oxidative stability of the engine oils. Blend 1 used the new ZDDP component in place of the older version. Blend 3 contained the older version. The TFOUT oxidation induction time results of the two blends were 130 and 135 minutes respectively. From these results, it was concluded that there is little difference in oxidative stability between the two additives when incorporated in engine oil containing soybean oil.

The new ZDDP additive was also tested in a baseline formulation that did not contain soybean oil. Blend 4 used the new ZDDP in the formulation, while blend 10 used the old chemistry. The new ZDDP blend had a TFOUT oxidation induction time of 335 minutes versus an induction time of 320 minutes. These results confirmed that there was no impact on oxidative stability when substituting the new ZDDP chemistry.

Blend 2 was made with the new ZDDP minus any antioxidants. This blend had a TFOUT oxidation induction time of 80 minutes. Using the new ZDDP additive alone will not compensate for the inadequate oxidative stability of soybean oil.

6.3.4.2 Effects of soybean oil

Blend 3 was made using the antioxidant package developed through vigorous TFOUT oxidation time testing. Blend 4 was made using the same formula as blend 3 minus the soybean oil. The TFOUT oxidation induction time difference was 200 minutes

(135 vs. 335). The use of a small amount of soybean oil is very detrimental to oxidative stability of a lubricant.

6.3.4.3 Effects of corrosion inhibitors

The corrosion inhibitors used in the engine oil formulation with soybean oil are not typical engine lubricant additives. Several blends were made to determine the role, if any, that corrosion inhibitors played on the oxidative stability of the soybean engine lubricant. Blend 3 included the corrosion inhibitor package developed during extensive HTCBT testing. Blend 5 used the same formulation minus the corrosion inhibitor package. The TFOUT oxidation induction times for blends 3 and 5 were 135 and 125 respectively. The corrosion inhibitors did not inhibit the oxidative stability of the lubricant and might have even slightly helped. Another blend, 7, investigated the use of slightly different corrosion inhibitor package. A new component was added while the treat level of an existing component was decreased. The TFOUT oxidation induction time was 130 minutes which was very close to blends 3 and 5. Neither corrosion inhibition package showed ill effects on the TFOUT oxidation induction time of the engine oil made with soybean oil.

6.3.4.4 Effects of antioxidants

The impact of antioxidants on the soybean oil was great. The antioxidant packages developed through extensive DOE’s increased the oxidative stability of the engine lubricants. This impact can be seen when comparing blends 3 and 8. Blend 3 contains an antioxidant package along with 15% soybean oil. Its TFOUT oxidation induction time is 135 minutes. Blend 8 contains 15% soybean oil as well, minus the antioxidant package. The TFOUT oxidation induction time of blend 8 is 95 minutes. When the engine oil contained the antioxidant package, the TFOUT oxidation induction time was increased by over 40%.

Blend 9 was formulated without soybean oil or antioxidants. The TFOUT induction time was 170 minutes, demonstrating large impact the soybean oil plays in oxidative stability.

When the corrosion inhibitors, soybean oil, and antioxidants were removed, blend 15 has a TFOUT oxidation induction time of 150 minutes. This result again shows that the corrosion inhibitors are not detrimental to oxidative stability. When compared to the result of blend 9, it appeared that the corrosion inhibitors aided in oxidative stability.

6.3.4.5 Effects of Zn and Mo with oxidation inhibition

Zinc and molybdenum compounds can impart oxidative stability in a lubricant. Several blends were made to investigate the oxidative stability contribution of the zinc and moly components in the soybean oil formulation. Blend 11 did not include any moly in the formulation. It has a TFOUT oxidation induction time of 115 minutes. Blend 13 did not incorporate a zinc component. It has a TFOUT oxidation induction time of 30 minutes. Blend 5 contained the moly and zinc components in the formulation. It had a TFOUT oxidation induction time of 125 minutes. When the moly components were removed from the blend containing soybean oil, a slight drop in oxidative stability was observed. When the zinc component was removed from the blend, a significant drop in TFOUT oxidation induction time was observed, 30 minutes versus 125 minutes. The moly and zinc components were also separately removed from the blend that did not contain soybean oil. Blend 12 without the moly components had a TFOUT induction time of 325 minutes. Blend 14 without the zinc component had a TFOUT oxidation induction time of 115 minutes. Blend 4 which contained the moly components had a TFOUT induction time of 335 minutes. Including the moly components in the formulation slightly increased the TFOUT oxidation induction time. However, both of these comparisons show that the role the zinc component plays in the TFOUT oxidation induction time is large. When removing the zinc component from the blends tested a very large drop in the TFOUT oxidation induction time was seen.

The TFOUT oxidation induction time when removing anti-oxidants and zinc components in the soybean oil formulation dropped drastically. Blend 16 illustrated that point. The TFOUT oxidation induction time for blend 16 was 5 minutes. The blend did not contain any zinc or antioxidant components. This result proved that zinc and antioxidant components play a major role in the oxidative stability of engine lubricants. Since the TFOUT oxidation induction time result for blend 16 was so low, blend 17 was not run.

6.3.4.6 Effects of dispersants and detergents

The effect of dispersants on TFOUT oxidation induction time stability was quickly evaluated. In blend 18 the dispersant and soybean oil were removed. The TFOUT oxidation induction time was 220 minutes. When compared to blend 5, which had a TFOUT induction time of 330 minutes, there is a large difference between the blend with and the blend without dispersant.

The combined effect of dispersant and detergent was also evaluated. Blend 19 did not include soybean oil, detergent, or dispersant. The TFOUT oxidation induction time was over 440 minutes.

Detergents and dispersants play a role in the TFOUT oxidation induction time stability. However, for a lubricant to function properly, detergents and dispersants must be incorporated into the formulation. Lubricants technology must try to minimize the negative effects additives can provide in one area, while maximizing their performance in others. A fine balance is needed when formulating additives. Formulators must work to achieve this balance so lubricants cam perform successfully in their environments. When formulating soybean oil, detergents and dispersants must be chosen that will maximize the oxidation stability while still performing their intended duties as dispersants and detergents.

6.3.4.7 Bench testing versus engine performance

The longest induction time seen with the soybean oil present in the formulation was 135 minutes. This time was nowhere near the baseline oxidation induction time of 320 minutes. The soybean oil was very detrimental to the oxidation induction time measured by the TFOUT.

A large difference is seen when testing antioxidants that have been blended with base oils versus testing blends of fully formulated engine oils. Initial DOE work showed that blends of base oils, soybean oil, and antioxidants gave TFOUT oxidation induction times up to 320 minutes. Fully formulated blends that included soybean oil and the same antioxidants were only able to achieve TFOUT oxidation induction times of up to 135 minutes. Several groups have shown promising results when blends in antioxidants and vegetable oils together, but few address the fact that for lubricants to perform in their desired function, other additives must be present[30]. Lubricants must not only be oxidatively stable, but also must provide antiwear, corrosion, and deposit protection as well as guarantee suitable cold temperature performance.

6.3.5 Correlation between bench and engine oxidation tests

After all the bench oxidation testing was completed, the first Sequence IIIG oxidation engine test was run. The test failed miserably and had to be aborted before the test time was complete due to rapid thickening of the lubricant. Since the bench test result did not predict engine test results, a study was completed to determine if oxidation bench tests such as the TFOUT and PDSC were able to predict performance in the Sequence IIIG oxidation engine test. Oxidation stability in engine oils was measured by the Sequence IIIG engine test. The test evaluated lubricant viscosity increases as well as deposit and wear performance. Typically, oil candidates were tested in oxidation bench tests before being subjected to the longer more expensive engine test. Since the bench tests used to screen lubricants for oxidative stability obviously did not accurately predict engine test performance in the case of the soybean lubricant, it was decided to take a further look at correlating the bench tests with engine test results.

Data from two common oxidation bench tests, TFOUT and PDSC were used to try to correlate with Sequence IIIG engine test results. With the help of Gail Evans at Lubrizol (Wickliffe, OH), nineteen different engine oil samples that had been run in the Sequence IIIG were obtained. A diverse group of samples were obtained. The samples were made with different additive chemistries, SAE grades, base oil combinations, and run at different engine test laboratories. When using bench tests to predict engine test behavior, it is important that the correlation be valid over a variety of different lubricant properties. The same engine tests are run in all different product grades, from monogrades, to the whole spectrum of multi-grades (SAE 0W-20's to heavier SAE 20W-50's), and product types, from passenger car to heavy duty diesel. The samples were sent with blind codes and the engine test results were sent after all the bench testing was completed.

All of the samples were run in the TFOUT and the PDSC. As can be seen from Table 16, the bench test results varied greatly. The minimum TFOUT test time was 150 minutes seen in sample number ten. The same sample also had the lowest PDSC result at 36.7 minutes. Sample number 15 lasted the longest on the PDSC and the TFOUT.

Table 16. Bench test results

Sample Number	TFOUT, min	PDSC, min
1	245	45.9
2	240	42.6
3	235	51.6
4	300	56.9
5	265	56.0
6	310	55.3
7	270	40.9
8	310	50.6
9	270	54.1
10	150	36.7
11	215	48.2
12	170	44.1
13	290	46.3
14	210	44.5
15	500	95.8
16	450	50.2
17	220	47.2
18	290	78.0
19	435	50.7
20	350	50.3

After the bench tests were completed, the data along with the engine test results were evaluated using SYSTAT II statistical analysis software. The software was used to try to correlate the bench test results with the engine test data. There are many parameters measured when running an engine test. Some parameters are used to determine if a lubricant passes or fails a test while others are just reported. The results that are just reported can be used to make sure a test run was valid or as an indicator for future lubricant problems that may not have shown up in the immediate test measurements. Some parameters that are evaluated are cam and lifter wear (CLW), weighted piston deposits (WPD), piston skirt varnish (PSV) average over the six cylinders, percent viscosity increase of the lubricant, oil consumption during the test, and the number of hot and cold stuck rings. Table 17 shows the measurements that are taken after the engine test is complete. The passing parameters values are listed in Table 17. The other parameters are rated and reported (R&R) in the test report. Many other measurements are taken when running an engine test. The test temperature, power output, coolant flow, and engine speed are just a few things that are monitored.

Table 17. Sequence IIIG Engine Test Specifications

Measurement	ILSAC GF-4 Specifications
Test length, hours	100
Viscosity increase, %	150, max
Average cam+ lifter wear, µm	60, max
Average weighted piston deposits, merit	3.5, min
Average piston skirt varnish, merits	R&R
Number of hot stuck rings, total	0, max
Number cold stuck rings, total	R&R
Oil consumption, L	R&R

Initially all of the data was copied from an MS Excel file into a SYSTAT II data file. See Appendix 1 for all engine and bench test data. The software can evaluate data using many different statistical methods. The method concentrated on in this paper is the Pearson correlation matrix. The Pearson correlation is used to indicate the linear correlation between two variables. The correlation calculates a Pearson Product Moment. The Product Moment ranges from -1 to +1. If the moment is +1 there is a perfect positive linear correlation between the variables. If the value of the moment is negative, the variables are inversely related. Values closer to +1 or -1 indicate greater influence between the variables. The closer the number is to zero, the less the two variables influence each other[31].

Using SYSTAT II, a Pearson Correlation matrix was run using the inputted variables. The software rated the statistical dependence of each variable to the other variables in the list. Each variable was assigned a product moment that indicated the degree of correlation with the other single variable. The Pearson correlation matrix also generates a scatterplot so correlations can be visually evaluated.

Initially all the variables listed in Appendix 1 were used in the correlation matrix. Since there were some duplicates, such as viscosity increase % and viscosity increase final %, they were eliminated. When reporting engine test results a severity factor is used based on the engine test stands previous run of a designated reference fluid. This is one of the many ways engine test calibration standards ensure lab to lab differences are minimized.

There are a lot of results reported for the engine test that may not be directly influenced by the oxidative properties of the lubricant. Variables such as completion date, test length, and test lab were not deemed important to this study. The variables that were used in the Pearson correlation matrix were TFOUT, PDSC, percent viscosity increase (PERVISINC), cam plus lifter wear (CAMLIFWEAR), weighted piston deposit (WPD), piston skirt varnish (PSV), and oil consumption (OILCONSUM). When the results from all twenty of the samples were evaluated in the matrix, the only significant correlation was between the TFOUT and PDSC results. Since this defeated the purpose of the work, all of the future matrices were generated with each of the bench tests separately.

When the bench test results were modeled separately using all the samples data, only a few weak correlations existed, none of which were between the bench test and a measured engine test parameter. There were several correlations within the engine test data itself. The percent viscosity increase showed a relatively strong (around -0.6) negative correlation with the WPD and PSV. This correlation could have been predicted prior to modeling. As the viscosity of a lubricant rises due to oxidative thickening, it is not going to be able to lubricate the metal parts in the engine properly. When the engine parts are not lubricated properly, hot spots may develop in the engine. These spots can lead to the formation of varnish and deposits. So as the percent viscosity increase gets larger, the WPD and PSV will get more severe. The WPD and PSV are measured by a professional rater on a merit scale. The closer to 10 the rating, less the piston deposits of skirt varnish are present. This caused an inverse relationship between the variables. See Appendix 2 for details.

The WPD and the PSV showed a high positive correlation of 0.737. If a lubricant has been oxidized, it can lead to deposit formation in the ring lands and varnish on the skirt of the piston. Therefore, the WPD and PSV should be positively correlated with one another. When looking at the PDSC correlation matrix, no correlation existed with CAMLIFWEAR and OILCONSUM. TFOUT correlations did not exist for any of the parameters.

Since there was not any evidence of the bench tests results correlating with the engine test parameters, the data was filtered several different ways. First the data was divided into the 5W-XX's and 15W-XX's formulations. The procedure described before was then repeated.

There were 13 data points that were 5W-XX's lubricants. When the Pearson correlation matrix was run using the PDSC bench results, several modest correlations were evident. The PDSC results were slightly correlated to the PERVISINC and PSV. The correlation for the PSV and PERVISINC was nearly identical to the matrix that included data for all the viscosity grades. However, the correlation for the WPD dropped. When looking at the TFOUT matrix for the same 5W-XX's data points, no correlations were evident. One interesting point to note was that the correlation between the engine test parameters themselves was very similar to the first case when all the samples were included in the matrix. See Appendix 3.

The set of data that included 15W-XX's oils had five data points. The PDSC correlation showed different results than all those that had been previously run. The correlation between PDSC and PERVISINC jumped up to 0.573, while OILCONSUM jumped to 0.635 and WPD to -0.568. The PDSC correlation with OILCONSUM can be explained by the use of heavier base oil incorporated in the 15W-XX's blends. Heavier base oils do not volatilize as rapidly as their lighter counterparts. Therefore, it is expected that oil consumption would be less when running in the same engine at the same conditions.

The correlation between PDSC and PSV dropped to 0.219. The TFOUT correlation matrix showed that relationships existed with PERVISINC, CAMLIFWEAR, and PSV. This was the first time any significant relationship existed with the TFOUT data. See Appendix 4 for details.

There were several conclusions drawn from the data modeling. Data analysis for all samples showed that there is little or no correlation between lubricant performance in oxidation bench tests and the Sequence IIIG engine test. The PERVISINC is negatively correlated to WPD and PSV. The WPD and PSV are positively correlated to one another.

As a group, the higher viscosity grade lubricants showed stronger relationships between oxidation bench tests and the Sequence IIIG engine test. When the data for the 15W-XX's was evaluated, a correlation between the PDSC and OILCONSUM existed.

The current bench tests used for engine test performance prediction are not adequate. Bench test factors needing improvement include:

- accurate prediction of lubricant performance in the engine test,
- accurate prediction of performance of lubricants based on non-traditional chemistries,
- accurate prediction of oxidative stability of vegetable lubricants, and
- accurate prediction of oxidative stability for blends of traditional and non-traditional lubricants. In the United States, 757 gallons of passenger car lubricants are produced. If those fluids could use 10% of soybean oil that would save 757,000 barrels of base oil a year.

6.4 Re-Screening

Over the course of the research, several different experiment soybean base oils were sent from the United Soybean Board for evaluation. One particular set of samples included two oils that had been lightly hydrogenated. The hydrogenation procedure would have added hydrogen to double bonds that may have been present in the soybean oil. The process completed was referred to as “light” because little hydrogen took place so as not to drastically increase raw material costs and to allow the soybean oil to retain most of its physical and chemical properties. The two samples were evaluated in bench tests both alone and in fully formulated engine oils. The bench test results for these samples USB001 LH and USB 004 LH can be seen in table 5. No significant difference was seen when the results were compared to the non-hydrogenated samples.

Once satisfactory MRV and TFOUT oxidation induction time testing was completed, corrosion bench test work was started.

6.5 Corrosion

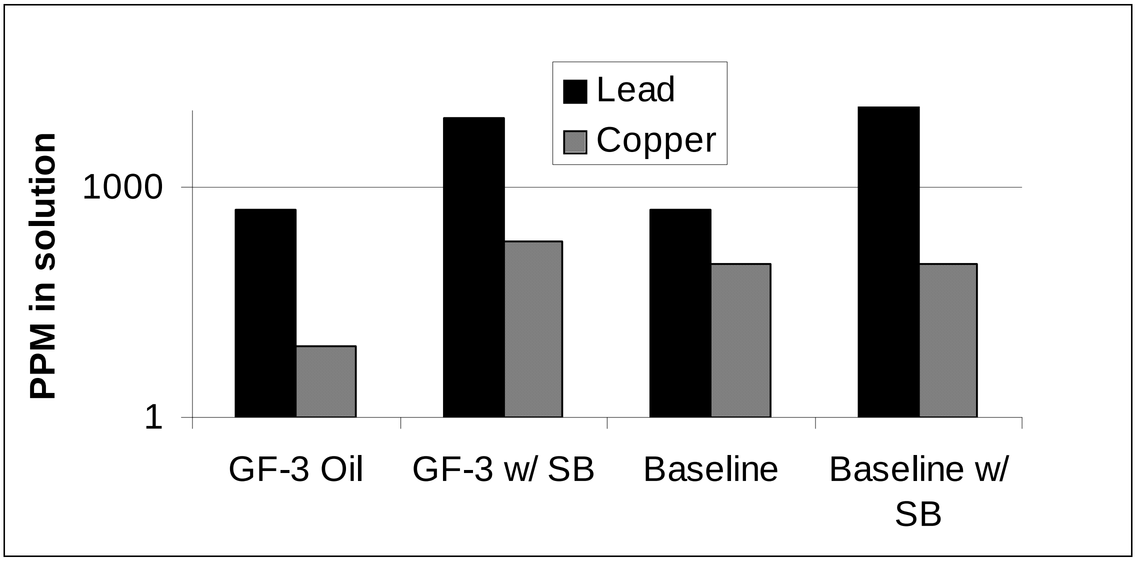
Lubricants are used in atmospheres where there are high temperatures in the presence of various metals and water. Corrosion of metals is always a concern in places where lubricants are used. Potential lubricants must be tested to determine whether they are able to protect metals in corrosive environments. The soybean oil was subjected to corrosion testing on both the bench and engine test levels. The bench test used to evaluate the soybean engine oils was ASTM D6594 [1], the hot tube corrosion bench test (HTCBT). The hot tube corrosion bench tests runs for seven days at 135 C. Several different metal coupons are suspended in the test lubricant and air is bubbled through the glass reactor at a flow rate of 5 liters per hour. Metal analyses on the test candidate are performed by ICP after the test. The ICP results for copper, tin, lead are reported.

The copper coupon is used in the test is rated based on the ASTM D130 [32] color scale. The coupon color may or may not relate to corrosion inhibition. Additives may react with the copper surface, change its color, but provide protection. On the other hand, additives may dissolve the copper surface, but maintain its original appearance. Therefore, both coupon rating and copper levels in the solution must be reported.

The corrosion inhibition requirements for diesel engine oils are greater than those of passenger car gasoline engine lubricants. The HTCBT was designed to test diesel engine lubricants. However, the HTCBT is a good bench screening test for gasoline lubricants.

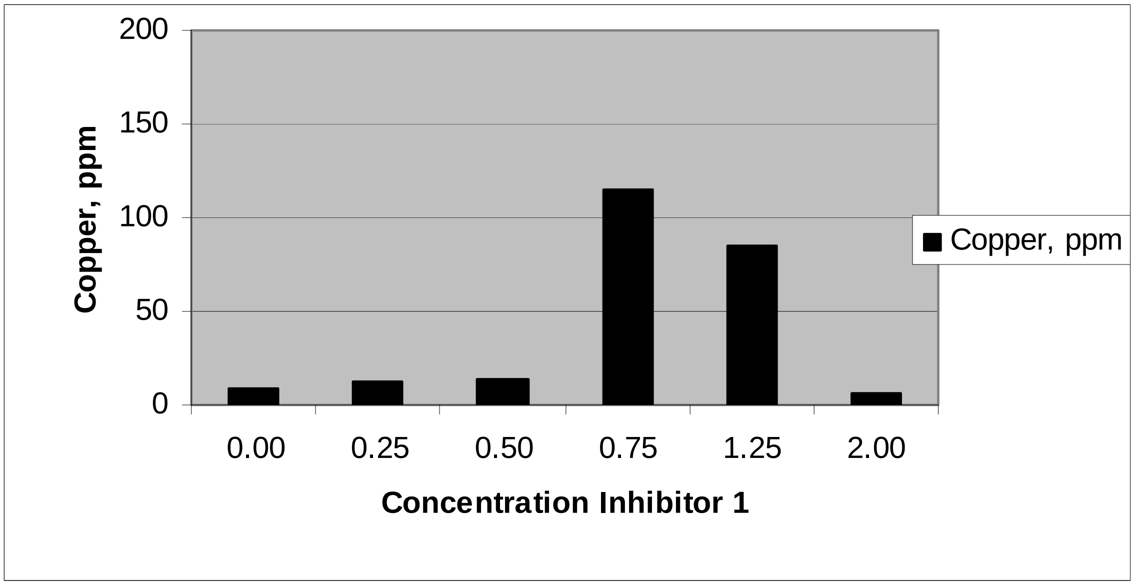
Since this was a development project, the formulation was subjected to all the typical lubricant bench tests. Two different soybean engine lubricant chemistries were evaluated along with a baseline for each. Some of the results for a few of the test parameters can be see in Figure 2. None of the samples tested showed any tin in the ICP metal analysis, a key measurement in the test protocol. This was typical for all of the corrosion testing that was completed. However, significant differences were seen in the lead and copper concentrations between the baselines and the soybean engine oils, especially the lead. The formulations that included soybean oil had over 5000 ppm of lead in solution, caused by corrosion of the lead block in the test. The baselines contained about 500 ppm lead. The fully qualified GF-3 oil showed a much lower concentration of copper in solution than the soybean lubricants. Since the GF-3 oil was fully API certified and had passed a Sequence VIII corrosion engine test, its data was used as the desired targets.

Figure 2. HTCBT results for SAE 5W-30 oils with and without SBO.



Since the initial hot tube corrosion bench test did not show adequate corrosion protection with the soybean engine oil, further testing was completed. Over fifty different corrosion additives were evaluated. Of these, four were selected for further evaluation. The first screening test for these was the hot tube corrosion bench test. Several were found to impact the soybean engine oils corrosion inhibition. One inhibitor that showed a positive effect on the hot tube corrosion bench test was inhibitor 1. The chemical make up of this inhibitor was a borated ester. Several patents were developed by Valvoline using this chemistry in engine oils in the past [33, 34]. This inhibitor also showed promising results when incorporated into the engine oil containing soybean oil. In the hot tube corrosion bench tests the treat levels of inhibitor 1 was varied from 0.25 wt% to 2.0 wt%. The results for the amount of copper in solution can be seen in Figure 3.

Figure 3. HTCBT copper results when varying Inhibitor 1 treat level

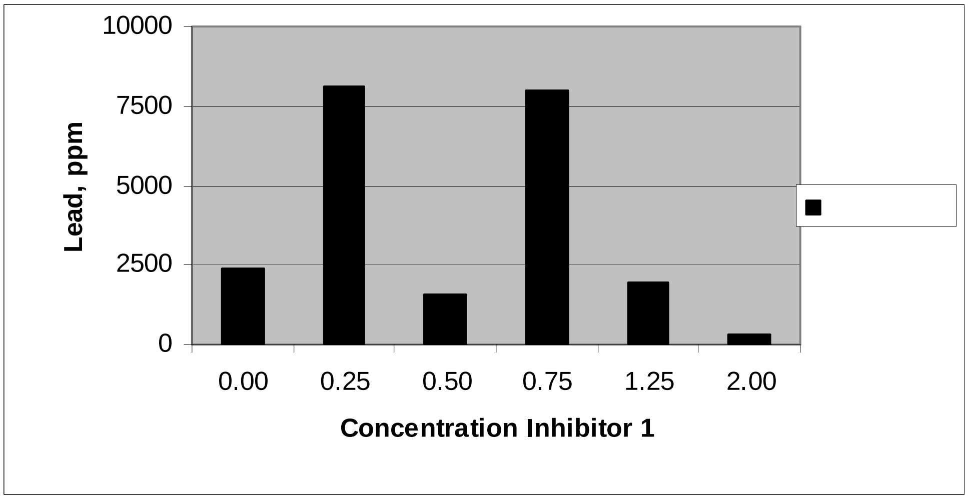


The first blend did not contain any soybean oil. The amount of copper in solution for that blend was less than 25 ppm.

Overall, the soybean lubricants were not as aggressive towards copper as they were towards lead. Until the treat level of 0.75 wt% was tested, the copper level in solution remained low. In the blends that contained 0.75 and 1.25 wt% inhibitor 1, the amount of copper in solution increased to 115 ppm and 84 ppm respectively.

The results for the amount of lead in solution can be seen in Figure 4. The lead results did not follow the same trend as the copper results. The blend treated with 2.0 wt% inhibitor 1 had the lowest amount of lead in solution at 325 ppm. The blends treated with 0.25 wt% and 0.75 wt% inhibitor 1 has the highest amounts of lead in solution at over 8000 ppm. It is believed that when levels of lead in solution in the tested oils reached a high level, test results were no longer repeatable. When the lead coupon in the test started to corrode, the reaction took place very quickly and uncontrollably. This might explain the lack of trend when increasing the concentration of inhibitor 1.

Figure 4. HTCBT lead results varying concentration of Inhibitor 1



The copper strip ratings are based on color of the copper coupon from the hot tube corrosion bench tests where inhibitor 1 concentrations were varied can be seen in Table 18. There was an inverse relationship between the amount of copper in solution and the rating of the strip. In the blend that contained 0.75 % inhibitor 1, the copper strip had a passing result of 2B. However, for that same blend, the amount of copper in solution was 115 ppm, the greatest of all the blends tested. The blends that contained 0.25 wt% and 0.5 wt% had a copper strip rating of 4A, a failing result. These same blends had less than 25 ppm of copper in solution. The soybean oil in the lubricant may have had a polishing effect on the copper. The strip ratings were failing when there was not a lot of copper in solution. The strip ratings were passing when the amount of copper in solution were greater. However, after a certain concentration of inhibitor 1 was reached, 2.0 wt %, this relationship did not hold true. It was noted with blends that contained a treatment level approaching 2.0 wt % solubility issues were seen. This could be one reason that the blend with the treat level of 2.0 wt% inhibitor 1 did not follow the trend of the other blends.

Table 18. HTCBT Copper Strip results when varying Inhibitor 1

Inhibitor 1, wt%	0	0.25	0.50	0.75	1.25	2.0
Copper Strip Rating	4A	4A	4A/4B	2B	2A	4A

After the extensive evaluation of inhibitor 1, mixtures of inhibitors found promising from the initial screening test were evaluated. The lead levels for the best three inhibitors all exceed the test standard of 500 ppm for diesel, and Valvoline's internal standard of 1000 ppm for screening purposes. The copper levels are below 50 ppm (diesel standard) and 100 ppm (Valvoline screening standard). The evaluation of the copper strip should result in a maximum qualitative rating of 2, and three of the four recipes met this criterion. The first formulation is the baseline. It contained 15 wt% soybean oil without any corrosion inhibitors. The baseline had 11,496 ppm in solution, 139 ppm of copper in solution and a copper strip rating of 4B. These results are failing by both the diesel engine oil and the Valvoline internal standards. All of the blends made with the different inhibitor mixtures showed improvements in all test parameters. The last formulation minimizes lead, has low copper in the oil and an acceptable copper strip rating, and was the preferred system based on the hot tube corrosion bench test. Table 19 shows these results.

Table 19. HTCBT results for SAE 5W-30 oils with various corrosion inhibitor packages

Additive pack	85.0	84.15	84.44	83.94	83.90
Inhibitor 1	-	0.75	0.50	1.00	1.00
Inhibitor 2	-	-	0.01	0.01	0.05
Inhibitor 3	-	0.10	0.05	0.05	0.05
HTCBT					
Lead, ppm	11496	7283	10176	7071	6576
Copper, ppm	139	90.1	54.9	61.9	62.4
Cu strip	4B	4A	2C	2C	2C

6.6 Engine Tests

Once an engine oil was formulated that showed acceptable bench test results, an initial engine test was run. In order to certify lubricants based on the API specifications that are used in the automotive industry, a series of engine tests must be completed. The series of tests have been modeled form real world automotive scenarios. The tests can range from a test time of 40 hours up to several hundred and can cost over $40,000 each. The engine test requirements for commercial passenger engine oils will be a major factor in the progression of the development of a bio-based lubricant that can be marketed on a large scale.

The first engine tests run during the course of this research were the Sequence VIII bearing corrosion test. These tests were run first because it the cheapest, shortest, and the hot tube corrosion bench test results were seen as promising. Engine tests were completed on two samples: the baseline and the baseline plus inhibitor package. The two samples contained the same base oils, detergents, dispersants, viscosity modifiers, and pour point depressants. These samples tested were SAE 5-W30’s. The baseline package did not contain any of the corrosion inhibitors that were screened using the hot tube corrosion bench test. The test results can be seen in Table 20. The API SM certification test limits are a maximum of 26 mg weight loss in the bearing and the lubricant must start and end the test being the same grade. The baseline blend without the corrosion inhibitors had a bearing weight loss if 108.6 mg. This is over four times the test specification requirement of 26 mg.

Table 20. Sequence VIII engine test results

	Weight Loss, mg	Stripped Viscosity, cP @ 10 hours
GF-4 Spec Limits	26	Stay in grade
Baseline	108.6	11.51
Baseline + Inhibitors	4.0	11.09
Baseline + Inhibitors w/ lead alloy bearings	19.1	11.86

The Sequence VIII is typically not a difficult test to pass if the lubricant chemistry is balanced well. The impact to the chemistry balance when only a treatment level of 15% soybean oil is added to the sample is monumental. Figure 5 shows the bearings from the baseline Sequence VIII test. Multiple wear rings can be seen on the surface. Heavy varnishing can also be seen.

Next a Sequence VIII was run on the sample that contained the baseline formulation with the corrosion inhibitors. This formulation had a bearing weight loss of four mg. This was considered an excellent passing test. The four mg of bearing weight loss is over six times less than the Sequence VIII test specification. The bearings from this test can be seen in Figure 6.

Figure 5. Sequence VIII bearings from baseline test

These bearings look drastically different from the bearings in Figure 5 because the lubricant formulation provided much better corrosion protection when the inhibitors were added in the second test. The copper color indicated that little varnish was present. Very few wear markings can be seen in Figure 6 compared to Figure 5.

Figure 6. Sequence VIII bearings from Baseline + Inhibitors

Because these formulations were aggressive with respect to lead corrosion, an additional engine test was run using a special engine configuration in which the copper bearings were replaced with lead alloy bearings to specifically evaluate lead corrosion in the engine. Older engine technologies utilized bearings that contained lead. When developing a lubricant, engines of all manufacturers must be considered. Even though it was proven that the soybean lubricant would not cause any harm to the more modern bearings made with copper, lead bearings were also tested. Consumers keep their vehicles for long periods of time so lubricants must adequately address all materials with which they could come in contact.

The lead alloy bearing test was run using the same Sequence VIII procedure. The weight loss of the lead alloy bearings was 19.1 mg. Since the bearings are not in the engine test protocol, no test specifications exist. However, with a weight loss less than 20 mg, the lubricant would provide adequate corrosion protect if it would be used in an engine that utilized lead bearings. Figure 7 shows the lead alloy bearings after the Sequence VIII test. Very few scar or wear marks were seen.

Figure 7. Sequence VIII lead alloy bearings

After the passing Sequence VIII result, oxidation engine work was started. The oxidation engine test is called the Sequence IIIG. The test is run for 100 hours and it goes through various loads and cycles. An engine oil sample containing soybean oil and a baseline sample were the first two tests run.

Test results can be seen in Table 21. The baseline formula did not contain any soybean oil. The formulation was a near pass with the viscosity increase barely over the test limit at 168%. The average weighted piston deposits also failed. With slight modifications of the baseline formulation a passing Sequence IIIG would be obtainable.

Table 21. Initial Sequence IIIG results

	GF-4 Specs	Baseline	SB Oil
KVis (40°C), %	150 max	168	18,065
Average weighted piston deposits, merits	3.5 min	2.31	0.98
Hot stuck rings	None	0	16
Average cam + lifter wear, µm	60 max	15	14.41
Test length, hours	100	100	57

The soybean oil sample exhibited much worse performance than the baseline. The soybean oil formulation, which showed good results in the thin TFOUT oxidation induction time test was the first sample tested. The sample was not even able to withstand the engine conditions for the duration of the 100 hour test. The soybean oil sample was run for 57 hours. The test was aborted when a rapid increase in oil viscosity caused the oil to become too thick to flow and coat the engine parts. After the test was aborted, the engine was torn down and the parts were evaluated. Figure 8 shows the pistons from the Sequence IIIG test. Heavy varnish along the piston skirts and deposits in the ring land area were found. The parts showed the lubricant performance was far from adequate. Figure 9 shows the piston pins from the test. The heavy varnish coating on pins four and five indicated that the lubricant inadequately protected the engine.

Figure 8. Pistons from Sequence IIIG test

Figure 9. Piston pins from Sequence IIIG test

After the first soybean oil formulation failed the Sequence IIIG, bench tests were re-evaluated. The TFOUT oxidation induction time test was revisited. This time the soybean formulation was based off a passing Sequence IIIG chemistry. Additives that were found to be beneficial in the TFOUT oxidation induction time test were added to the formulation. Two more Sequence IIIG tests were run. The concentration of the soybean oil in the formulation was dropped to 5 wt%. The first test contained 5 wt% mid-oleic soybean oil. The second test used 5 wt% high-oleic soybean oil. At this treat level, many of the beneficial properties of the soybean oil, such as volatility, cold crank simulator values, and viscosity index, still aid in the oil properties. The TFOUT oxidation induction times of the mid-oleic and high-oleic blends were 220 and 290 minutes. Test results for the engine oils containing 5 wt% of the mid and high-oleic soybean oil can be seen in Table 22.

Based on the results, not much difference was seen between the mid and high-oleic soybean oils, even though there was a difference in the TFOUT oxidation induction time of 70 minutes. However, when compared to the first Sequence IIIG test with soybean oil a lot of progress was made. Both of the formulations that contained 5 wt% oil were able to last the duration of the whole test. When the soybean engine lubricant that contained 15 wt% oil was evaluated, the test had to be aborted at 57 hours because of the thickening on the oil. Half the number of hot stuck rings was seen with the decrease of the treatment level of the soybean oil.

Table 22. Sequence IIIG results for engine oils containing 5% soybean oil

	GF-4 Specs	Mid-oleic	High-oleic
KVis (40°C), %	150 max	308	325
Average weighted piston deposits, merits	3.5 min	3.18	2.59
Hot stuck rings	None	5	4
Average cam + lifter wear, µm	60 max	26.41	20.9
Test length, hours	100	100	100

7 Conclusions and recommendations

Cold temperature performance is an area of concern for engine lubricants formulated with soybean oil. In this research, several different formulations were developed that passed the main engine oil low temperature test, the mini rotary viscometer test. The used of specialized pour point depressants allowed for engine oils containing various amounts of soybean oil. The lubricants met the passing viscosity requirements of 60,000 cP and exhibited no yield stress.

An area in the vegetable lubricant field where little work has been reported is metal corrosion. This project measured metal corrosion, namely lead and copper, using conventional ASTM methods. It was discovered that lead corrosion is an issue for lubricants that incorporated the soybean oil. Samples that included soybean oil showed worse performance in the hot tube corrosion bench test than their respective baselines. Testing was done to determine an optimized inhibitor package for the oil. When the optimized inhibitor package was used, the soybean lubricants showed improved performance in the hot tube corrosion bench test. This optimized package was tested in a Sequence VIII engine test. The test results proved that the optimized inhibitor package was capable of performing in engine as well as bench test conditions.

Vegetable base oils are notorious for their poor oxidation and heat stability. This research looked at various antioxidants that could be used to improve oxidation stability. Several different antioxidants showed improve performance in the TFOUT oxidation induction time bench test. A mixture of those antioxidants was tested in a formulation in the Sequence IIIG engine test. All of the samples failed the Sequence IIIG tests.

However, improved test results were seen when the amount of soybean oil was decreased from 15 wt % to 5 wt %.

A significant difference was seen between the formulations that used the same additives with the mid vs. high-oleic soybean base oils in the TFOUT oxidation induction time test. However, when those same formulations were run in the Sequence IIIG engine test, no significant difference was seen.

A part of this study looked at the ability of oxidation bench tests to predict performance in the Sequence IIIG. No strong correlations were seen in the formulations evaluated. With engine tests costing so much and taking so much time, a bench test that can reliably predict engine test performance would be valuable. When this research was started, no other oxidation bench tests existed. However, at its conclusion, Degussa RohMax (Horsham, PA) has designed a test, the ROBO, which is currently undergoing repeatability studies and will be developed into an ASTM method.

Preliminary engine test work was started. Two of the major Sequence test results were discussed. A Sequence VIII corrosion engine test was run with a soybean formulation. The test result was a strong pass. This indicated that corrosion issues associated with soybean oils can be overcome with the right combination of inhibitors. Several Sequence IIIG oxidation engine tests were run. None of the formulas run were able to pass the test. Improvement was seen when decreasing the concentration of the soybean oil in the formulation. Much more work is needed in this area. When the ROBO bench test is fully up and running, it should be a good screening test to use when trying to formulate a soybean engine lubricant.

Much research still needs to be completed to be able to commercialize engine oil that contains some soybean base oil. With additional R&D, genetic development of new soybeans, and improved catalyst and oil processing technologies, there is a possibility that a soybean engine lubricant will exist in the future.

8 Appendices

8.1 *Engine test Results*

Sample Number	Book Number	Vis Grade	Location	Completion Date	TEST LENGTH hr	VISCOSITY INCREASE ORIG UNITS %	AVERAGE CAM + LIFTER WEAR ORIG UNITS µm	AVG WEIGHTED PISTON DEP.ORIG UNITS MERIT	AVGRAGE PISTON SKIRT VARNISH ORIG UNITS MERIT
1	7185-26-1	5W-30	R AUTOMOTIVE RESRCH	10/7/2003	100	67.08	25.6	4.97	9.4
2	7185-26-2	5W-30	R AUTOMOTIVE RESRCH	12/05/2003	100	106.77	14	3.94	9.34
3	7185-26-3	5W-50	R AUTOMOTIVE RESRCH	1/11/2004	100	6737.61	30.1	2.84	8.5
4	7185-26-4	15W-40	WICKLIFFE	2/6/2004	100	100.47	21.2	5.93	9.01
5	7185-26-5	5W-50	WICKLIFFE	2/1/2004	100				
6	7185-26-6	5W-50	WICKLIFFE	2/13/2004	100	20.3	22.8	3.8	8.03
7	7185-26-7	5W-30	WICKLIFFE	3/12/2004	100	115.28	16.8	4.14	9.16
8	7185-26-8	5W-30	R AUTOMOTIVE RESRCH	5/14/2004	100	87.2	10.6	3.99	9
9	7185-26-9	5W-40	WICKLIFFE	5/20/2004	100	0.1	17	4.69	9.09
10	7185-26-10	15W-40	WICKLIFFE	6/1/2005	100	105.6	23.1	5.9	8.88
11	7185-26-11	5W-30	WICKLIFFE	8/25/2004	100	116.43	19.2	4	8.46
12	7185-26-12	15W-40	WICKLIFFE	12/14/2004	100	55.01	15.4	6.46	9.13
13	7185-26-13	15W-40	WICKLIFFE	12/28/2004	100	352	24.2	4.29	9.22
14	7185-26-14	15W-40	WICKLIFFE	3/8/2005	100	78.61	13.8	5.42	9.39
15	6776-189-2	5W-30	ASHLAND	10/25/2004	100	167.49	25.5	2.31	7.56
16	6776-191-2	5W-30	ASHLAND	09/12/2004	56	18065.12	14.4	0.98	6.92
17	7185-25	5W-30	ASHLAND	08/29/2005	100	308.4	26.4	3.18	9.55
18	7185-47-3	5W-30	ASHLAND	03/23/2006	100	325.83	20.9	2.59	8.28
19	7185-64-1	5W-30	ASHLAND	04/20/2006	100	123.98	15.6	6.12	9.9

Sample Number	NUMBER OF HOT-STUCK RINGS - TOTAL	OIL CONSUMPTION L	VISCOSITY INCREASE FINAL TRANS RESULT	VISCOSITY INCREASE FINAL ORIG UNIT RESLT %	AVERAGE CAM + LIFTER WEAR FINAL ORIG UNI µm	AVG WEIGHTED PISTON DEP. FINAL ORIGINAL MERIT	MAXIMUM CAM + LIFTER WEAR ORIG UNITS µm	NUMBER OF COLD-STUCK RINGS - TOTAL	Pass/ Fail
1	0	3.54	4.205886	67.1	25.6	5.32	34	0	P
2	0	4	4.670677	106.8	14	3.94	21	0	P
3	0	4.08	8.815461	6737.6	40.8	2.84	51	4	F
4	0	2.88	4.810893	122.8	21.2	5.59	34	0	P
5	0	4.74		8045	65.9	2.26		0	F
6	0	2.22	3.211655	24.8	22.8	3.46	29	0	P
7	0	3.16	4.948398	140.9	16.8	3.8	22	0	P
8	0	3.7	4.468204	87.2	13.7	3.99	17	0	P
9	0	1.81	-2.105134	0.1	17	4.12	24	0	P
10	0	2.78	4.847278	127.4	23.1	5.37	32	0	P
11	0	3.48	4.94491	140.5	19.2	3.47	27	0	P
12	0	2.03	4.007515	55	15.4	6.09	20	0	P
13	0	3.58	6.102946	447.2	24.2	4.29	36	0	F
14	0	3.05	4.603814	99.9	13.8	5.42	26	0	P
15	0	2.44	5.120924	167.49	25.5	2.31	30	0	F
16	16	3.97	9.801738	18065.1	14.4	0.98	28	0	F
17	0	3.33	5.731333	308.4	26.4	3.18	37	5	F
18	4	3.74	5.786376	325.8	20.9	2.59	33	4	F
19	0	3.29	4.82012	124	15.6	6.12	43	0	P

8.2 SYSTAT II analysis for all data points.

The following is an analysis completed using the SYSTAT II software.
The initial list below shows the variables used in the analysis.

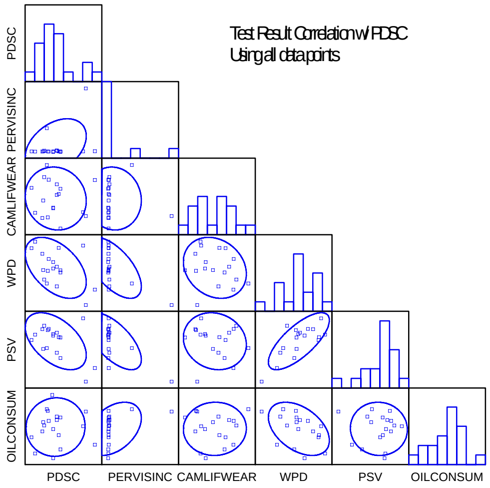
```
SYSTAT Rectangular file I:\IIIGSamples.syd,
created Wed Aug 02, 2006 at 15:52:54, contains variables:

        VAR(1)   BOOKNUMBER$     VISGRADE$    LOCATION$         DATE   TESTLENGT
     PERVISINC    CAMLIFWEAR           WPD          PSV    HTSTCKRNG   OILCONSUM
      VISTRANS   VISINCFINAL    CAMLIFTFNL       WPDFNL   MAXCAMLIFT   PASSFAIL$
        TFOUT$          PDSC      VAR00022
```

The table below shows the Pearson correlation of each variable to the other variables used in the model. Values range from -1 to 1. The higher the absolute value of the value, the more significant the interaction between the variables. If a value is negative the variables have an inverse relationship. If the value is positive the variables have a direct relationship.

Pearson correlation matrix

	PDSC	PERVISINC	CAMLIFWEAR	WPD	PSV	OILCONSUM
PDSC	1.000					
PERVISINC	0.378	1.000				
CAMLIFWEAR	-0.078	-0.063	1.000			
WPD	-0.470	-0.612	-0.201	1.000		
PSV	-0.489	-0.646	-0.121	0.737	1.000	
OILCONSUM	0.061	0.404	0.019	-0.438	-0.032	1.000

The scatterplot matrix below shows the relationships of the data points in the model. The ploy shows the histogram of the variables on the diagonal. The other boxes show the scatterplot of each variable versus each other. When two variables show a good correlation, the plot will have a narrow distribution of points that can be encircled in a small area.

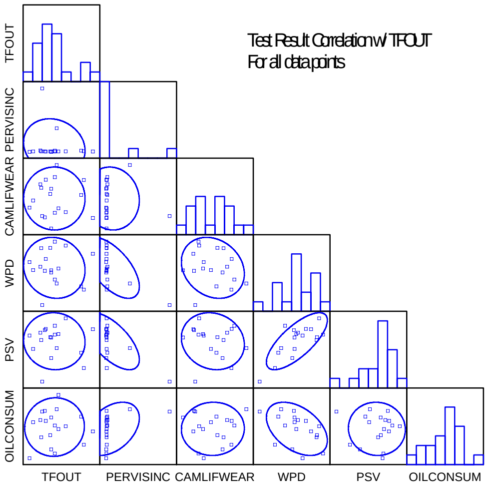


Number of observations: 18

Pearson correlation matrix

	TFOUT	PERVISINC	CAMLIFWEAR	WPD	PSV
TFOUT	1.000				
PERVISINC	-0.153	1.000			
CAMLIFWEAR	-0.004	-0.063	1.000		
WPD	-0.080	-0.612	-0.201	1.000	
PSV	-0.033	-0.646	-0.121	0.737	1.000
OILCONSUM	0.002	0.404	0.019	-0.438	-0.032

	OILCONSUM
OILCONSUM	1.000



```
Number of observations: 18

***WARNING***
The file
     I:\IIIGSamples.syd
was read for processing, and its contents have been replaced by saving
the processed data into it.

  21 cases and 21 variables processed and saved.
```

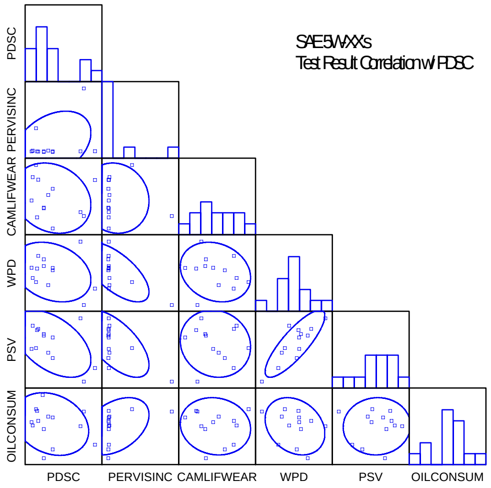
8.3 SYSTAT II analysis for all 5W-XX's data points

SYSTAT Rectangular file I:\IIIGSamples_5W.syd,
created Wed Aug 30, 2006 at 08:32:50, contains variables:

```
VAR(1)        BOOKNUMBER$   VISGRADE$     LOCATION$     DATE          TESTLENGT

PERVISINC     CAMLIFWEAR    WPD           PSV           HTSTCKRNG     OILCONSUM

VISTRANS      VISINCFINAL   CAMLIFTFNL    WPDFNL        MAXCAMLIFT    PASSFAIL$

TFOUT         PDSC          VAR00022
```

Pearson correlation matrix

	PDSC	PERVISINC	CAMLIFWEAR	WPD	PSV	OILCONSUM
PDSC	1.000					
PERVISINC	0.358	1.000				
CAMLIFWEAR	-0.192	-0.082	1.000			
WPD	-0.268	-0.669	-0.192	1.000		
PSV	-0.488	-0.635	-0.094	0.833	1.000	
OILCONSUM	-0.195	0.401	-0.097	-0.253	0.032	1.000



Number of observations: 13

Pearson correlation matrix

	TFOUT	PERVISINC	CAMLIFWEAR	WPD	PSV
TFOUT	1.000				
PERVISINC	-0.177	1.000			
CAMLIFWEAR	0.299	-0.082	1.000		
WPD	-0.222	-0.669	-0.192	1.000	
PSV	-0.140	-0.635	-0.094	0.833	1.000
OILCONSUM	0.043	0.401	-0.097	-0.253	0.032

	OILCONSUM
OILCONSUM	1.000

SYSTAT Rectangular file I:\IIIGSamples_15W.syd,
created Wed Aug 30, 2006 at 08:33:46, contains variables:

VAR(1) BOOKNUMBER$ VISGRADE$ LOCATION$ DATE TESTLENGT

PERVISINC CAMLIFWEAR WPD PSV HTSTCKRNG OILCONSUM

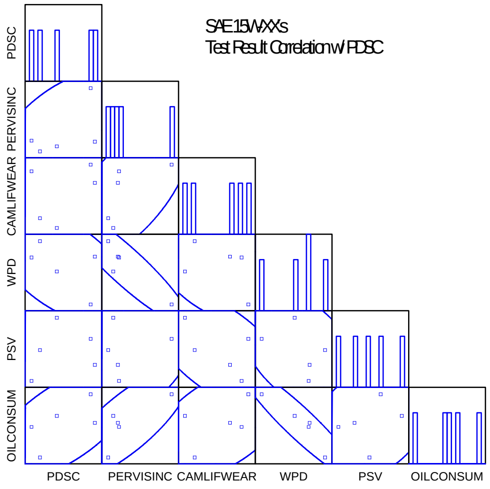
VISTRANS VISINCFINAL CAMLIFTFNL WPDFNL MAXCAMLIFT PASSFAIL$

TFOUT$ PDSC VAR00022

Pearson correlation matrix

	PDSC	PERVISINC	CAMLIFWEAR	WPD	PSV
PDSC	1.000				
PERVISINC	0.573	1.000			
CAMLIFWEAR	0.371	0.665	1.000		
WPD	-0.568	-0.915	-0.458	1.000	
PSV	0.219	0.174	-0.593	-0.436	1.000
OILCONSUM	0.635	0.788	0.522	-0.932	0.302

	OILCONSUM
OILCONSUM	1.000

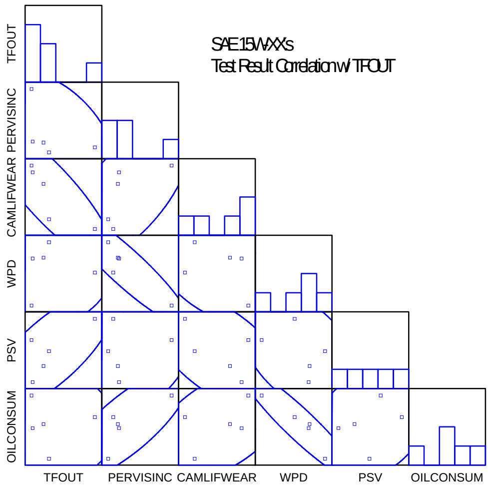


Number of observations: 5

Pearson correlation matrix

	TFOUT	PERVISINC	CAMLIFWEAR	WPD	PSV
TFOUT	1.000				
PERVISINC	-0.455	1.000			
CAMLIFWEAR	-0.849	0.665	1.000		
WPD	0.093	-0.915	-0.458	1.000	
PSV	0.746	0.174	-0.593	-0.436	1.000
OILCONSUM	-0.046	0.788	0.522	-0.932	0.302

	OILCONSUM
OILCONSUM	1.000



Number of observations: 5

```
***WARNING***
The file
     I:\IIIGSamples_15W.syd
was read for processing, and its contents have been replaced by saving
the processed data into it.

  6 cases and 21 variables processed and saved.
```

Number of observations: 13

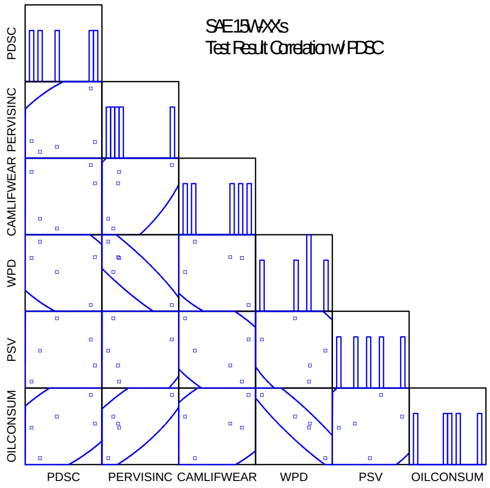
8.4 SYSTAT II analysis for all 15W-XX's data points

```
SYSTAT Rectangular file I:\IIIGSamples_15W.syd,
created Wed Aug 30, 2006 at 08:33:46, contains variables:


      VAR(1)   BOOKNUMBER$     VISGRADE$     LOCATION$          DATE    TESTLENGT


   PERVISINC    CAMLIFWEAR           WPD           PSV     HTSTCKRNG    OILCONSUM


    VISTRANS   VISINCFINAL    CAMLIFTFNL        WPDFNL    MAXCAMLIFT    PASSFAIL$


     TFOUT$           PDSC      VAR00022
```

Pearson correlation matrix

	PDSC	PERVISINC	CAMLIFWEAR	WPD	PSV
PDSC	1.000				
PERVISINC	0.573	1.000			
CAMLIFWEAR	0.371	0.665	1.000		
WPD	-0.568	-0.915	-0.458	1.000	
PSV	0.219	0.174	-0.593	-0.436	1.000
OILCONSUM	0.635	0.788	0.522	-0.932	0.302

	OILCONSUM
OILCONSUM	1.000

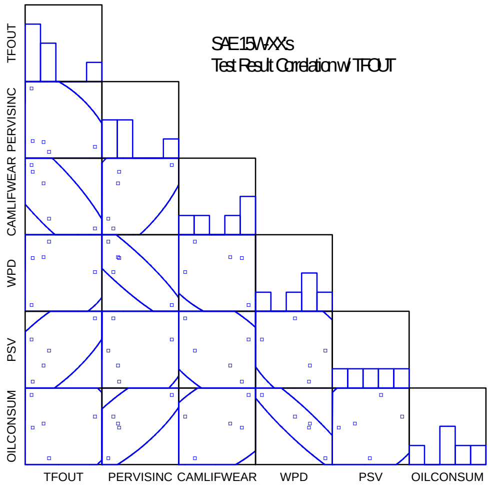


Number of observations: 5

Pearson correlation matrix

	TFOUT	PERVISINC	CAMLIFWEAR	WPD	PSV
TFOUT	1.000				
PERVISINC	-0.455	1.000			
CAMLIFWEAR	-0.849	0.665	1.000		
WPD	0.093	-0.915	-0.458	1.000	
PSV	0.746	0.174	-0.593	-0.436	1.000
OILCONSUM	-0.046	0.788	0.522	-0.932	0.302

	OILCONSUM
OILCONSUM	1.000



```
Number of observations: 5

***WARNING***
The file
    I:\IIIGSamples_15W.syd
was read for processing, and its contents have been replaced by saving
the processed data into it.

  6 cases and 21 variables processed and saved.
```

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