Findings from a fleet test on the performance of two engine oil formulations in automotive CNG engines.

ABSTRACT

This work presents a comparative assessment of engine oil performance on field test using urban transport vehicles powered by CNG engines using two different mineral oil formulations approved by engine manufacturer. The first one is considered as a baseline reference, and the second one is a higher quality formulation in terms of base-stock refining and additive content. Higher quality oil has shown a significant enhanced lubricant performance, leading to reach the oil drain interval defined by engine manufacturer on these engines without penalties in maintenance costs.

In order to assess oil performance, an oil analysis program has been established for oil samples collected from vehicles operated under real service conditions in an urban transport fleet. Monitored parameters include: oxidation, nitration, aminic antioxidant additives depletion, anti-wear additives depletion, TAN, TBN and RUL number (as an estimation of antioxidant additive depletion including aminic and ZDDP).

Results obtained in more than 90 samples from 15 different vehicles have shown higher degradation rates for low quality lubricant oil formulation. This deviation can be explained taking into account factors related with lower antioxidant additives content and lower thermal stability that can be mainly related with the base stock quality. This lower oil performance can be finally converted into higher vehicle maintenance cost and lower engine reliability

INTRODUCTION

Automotive CNG Engine Oil Performance has been studied for many years ago. Beck [1] performed a study using standardized tests to evaluate engine performance, durability, and oil life in a "dual fuel" diesel engine, fuelled by natural gas, and using a diesel pilot ignition. Engine performance was monitored throughout the tests and oil analysis was performed at regular intervals. Results obtained shows that CNG engine life and oil life will meet or exceed typical diesel values. Later, Wilson [2] suggested that lubricant formulations need to be changed to cope with CNG engines.

Recent works revealed the requirement of CNG engine oils quality improvement as a consequence of higher thermal stress suffered by engine oil in service. This higher thermal stress results in higher oil degradation rate derived from higher oxidation. The oxidation is the most predominant and important reaction of a lubricant in service, which takes place with a combination of the lubricating oil and oxygen. Oxidation tendencies are also increased by high temperatures in the presence of oxygen, combustion products with a considerable content of nitrogen oxides, which may form acids, and metallic contaminants which act as catalysts. The minute particles of iron (scraped from cylinder walls) and copper (from worn bearings) accelerate oil oxidation at high temperatures [3]. A complete oxidation of lubricant oil happens when all carbons are completely oxidized; all hydrogens bonded to carbons are replaced by oxygens, therefore producing CO_2 and H_2O. The oxidation will lead to an increase in the oil's viscosity, deposits of varnish and sludge, and the service life of a lubricant is also reduced. The rate of oxidation depends on the quality and type of base oil as well as the used additive package [4-5].

Comparative studies between Diesel and CNG engine oils performance have shown accelerated oil oxidation and higher engine wear rate for some metals such as copper on CNG engines, as consequence of higher stress suffered by those oils related with higher thermal stress [6-9]. This situation has been observed on formulations recommended by the own engine manufacturer. As a consequence, an important oil drain interval reduction (up to 50%), is required to assure high engine reliability [10] .

The oil degradation rate by means of oxidation and the formation of undesirable compounds depends on the oil formulation, fuel type, operating temperatures, engine design and oil drain interval considered. Under adverse conditions, even a slight reduction in operating temperatures may relieve the situation, as well as the change to improved quality oils, as can be seen in the final results of this study.

The original oil drain period defined by engine manufacturers was impossible to reach without high risk of potential catastrophic failures due to high level of oxidation that have been previously identified in CNG engines [6] . This fact led to an oil drain reduction that will grow maintenance costs of both the engine and the vehicle. For this reason, the present study has been conducted to assess the real degradation rate, additives depletion and levels of oxidation and nitration in CNG engines using two different types of oil formulations. Service intervals, or oil drain periods, are usually defined by the engine manufacturers considering high engine protection level and diverse vehicle operation scenarios. The Oil Stress Factor (OSF) has been used as initial parameter for quantifying the potential stress that oil will suffer, and allows some prediction of oil degradation as a function of engine design [11-12]. This factor represents the relationship between specific volume power, oil drain period and sump capacity, as the following expression shows:

$$OSF\left(\frac{kW \cdot km}{l^2}\right) = \frac{Power\ [kW]}{Displacement\ [l]} x \frac{Oil\ drain\ period\ [km]}{Oil\ sump\ capacity\ [l]}$$

This factor has been used in previous studies in order to assess engine oil performance versus thermal and oxidative stress levels. Table 1 shows OSF value for this type of engine. Taking into account those results it will be assumed that degradation for oils coming from these engines will present worst values than other types of engine [6].

This work presents an assessment of two different engine oils performance on automotive CNG engines. Both engine oils fulfill minimum engine manufacturer requirements to be used on this type of engines. This study has been performed in a comparative way. A baseline formulation has been defined as a reference and an improved oil formulation has been compared in terms of oxidation, nitration, aminic antioxidant additives, antiwear additives, TAN, TBN and RUL number (as an estimation of antioxidant additive depletion including aminic and ZDDP). The improved formulation have higher thermal stability and higher additive package content.

EXPERIMENTAL TEST DEFINITION

Vehicle selection and sampling procedures.

One urban transport fleet has been involved on this research. The study was carried out on 15 different vehicles equipped with CNG engine, whose main characteristics are described in Table 1. These engines support severe urban engine cycles, with constant stops and starts, large periods of engine idling and a typical average speed of 13 km/h. Vehicles were operated 16 hours per day in two eight-hour shifts. During the 12-month period in which the research was conducted, all vehicles involved remained with the same service conditions.

Table 1: Main engine characteristics

Characteristics	CNG engine
Type	Indirect injection / Turbocharged
Number of cylinders	6
Bore / stroke (mm)	115 / 125
Engine displacement (cc)	7,790
Power @ 2,000 rpm (kW)	270
bmep (bar)	15.4
Oil drain period (km)	30,000
Oil sump capacity (l)	23
OSF (kW·km/l^2)	33,488
Gearbox	Automatic ZF

Tested engine oils have been selected from a list of engine oils approved by the engine manufacturer, but considering different quality levels, mainly related to oil purchasing price. All the oils approved by the engine manufacturer fulfill the minimum requirements for reaching the expected service interval (30,000 km) a priori. Five of these vehicles have used oil called oil A and the other ones have used oil called oil B. The main characteristics of each type of engine oil are presented in Table 2.

Table 2: Main Fresh oil properties

Characteristics	Oil A	Oil B	Data origin
SAE Grade	10W40	15W/40	
Basestock	API Group II	API Group I	
Density at 15ºC (kg/m^3)	865	885	
Viscosity at 40ºC (cSt)	91.8	112.0	
Viscosity at 100ºC (cSt)	14.3	14.5	Oil Manufacturer Datasheet
Viscosity index	160	125 min.	
TBN (mg KOH/g)	13.2	7.0	
Flash point, open cup (ºC)	> 220	215	
Pour point (ºC)	< -33	-27	
Aminic Antioxidant (Abs·cm^{-1}/0.1mm)	18.0	13.0	Lab Measurement
Antiwear additive (Abs·cm^{-1} /0.1mm) – ZDDP	8.0	10.9	

Oil samples were taken every 5,000 km, including the oil drain period for each type of oil. Oil B, a lower quality and cheaper oil, it has been previously used in these types of vehicles. Their oil drain interval was reduced from 30.000 km to 15.000 km by the operator, based on the results obtained from its own oil analysis program. Thus, although engine manufacturer assumes that approved oils will perform similarly, real data derived from operator oil analysis program has shown a lower performance for oil B and a reduction in oil drain interval has been made in order to assure vehicle reliability and avoid potential failures derived. Attending this consideration, oil A will be used until reach oil drain interval of 30.000 km, but oil B will be drained at 15.000 km. One of the targets of this work is to confirm operator's previous results.

All samples were extracted following a methodology in order to prevent cross-contamination and to obtain a representative sample. If sample extraction coincide with oil drain operation, a new 125ml plastic recipient was filled with the oil drained from the crankcase. Initially the crankcase screw was released and the oil was left to drain for a three seconds period. Afterwards, the recipient was filled approximately with 100 ml; so later, the sample could be well shaken previous to any measurement. If the sample was taken before the oil drain period, a different procedure had to be used. A pump, new piping and new plastic recipient are all the required materials. The capillary tube was introduced through the oil dipstick path until it arrived to the crankcase. The capillary's length can be calculated by previously measuring the oil dipstick's length. Then, the sample was automatically transferred to the plastic recipient where it was labeled and sent to be analyzed.

OIL ANALYSIS PROGRAM

Oxidation and nitration measurements were performed using a FT-IR spectroscopy apparatus from A2 Technologies Company; its main characteristics are shown in Table 3. It has been recognized for a long time that infrared spectroscopy is a powerful tool by which many individual functional groups, such as carbonyl groups, among others can be identified and quantitatively analyzed [13-15]. Measurements of oxidation and nitration levels have been reported as Peak Area Increase (PAI, units: Abs·cm^{-1} /0.1 mm), using an own internal methodology based on ASTM E 2412, ASTM D 7214 and ASTM D 7414 [16-18]. The peak area values were calculated from the measuring values obtained from a path length of 0.1 mm. Both measurements were performed using a dual baseline as detailed in Table 4.

Table 3: Main FT-IR characteristics

Characteristics	
Spectral range (cm^{-1})	4,700 to 590
Resolution (cm^{-1})	4
Number of sample scan	128
Number of background scan	128
Path length (mm)	0.1
Sampling cell material	Zinc Selenide (ZnSe)
Interface	Transmission – TumbIIR
Apodization	Triangular

In addition, FT-IR spectroscopy has been used to quantify concentrations of antiwear and aminic antioxidants additives present in lubricating oils as peak area decrease, and they were measured using an own internal methodology as presented in Table 4.

Table 4: Summary of measurement methodologies.

	Oxidation	**Nitration**	**Aminic Antioxidant (AA)**	**Antiwear**	**Antioxidant (AO)**	**TAN**	**TBN**	**Wear Metals**
Methodology	CMT-0080.11 (*)	CMT-0081.11 (*)	CMT-0124.12 (*)	CMT-0120.12 (*)	CMT-0091.11 (*)	ASTM D664	ASTM D 2896	ASTM D 5185
Analytical Technique	FT-IR	FT-IR	FT-IR	FT-IR	Voltammetry	Potentiometry	Potentiometry	Spectrometry
Units	$(Abs \cdot cm^{-1})$ / 0.1mm	$(Abs \cdot cm^{-1})$ / 0.1mm	$(Abs \cdot cm^{-1})$ / 0.1mm	$(Abs \cdot cm^{-1})$ / 0.1mm	%	mg KOH / g	mg KOH / g	ppm
Frequency Range cm^{-1}	1,725 – 1,650	1,650 – 1,600	1,550 – 1,490	1,026 - 941	-	-	-	-
Baseline 1 cm^{-1} Start – Stop	2,200 – 1,900	2,200 – 1,900	2,200 – 1,900	1,100 - 1,098	-	-	-	-
Baseline 2 cm^{-1} Start – Stop	650 - 615	650 - 615	650 - 615	911 – 909	-	-	-	-

(*) CMT procedures are own internal methodologies. CMT-0091.11 is mainly based on ASTM D 6810 Standard Test Method for Measurement of Hindered Phenolic Antioxidant Content in Non-Zinc Turbine Oils by Linear Sweep voltammetry, and ASTM D 6971 Standard Test Method for Measurement of Hindered phenolic and Aromatic Amine Antioxidant Content in Non-zinc Turbine Oils by Linear Sweep voltammetry.

TAN and TBN were measured using automatic potentiometric titration equipment (ORION 950 Ross FASTQC Titrator). All tests were performed using first derivative methodology. Titration solutions used in this study are those established on common standards methods (ASTM D 664 [19] and ASTM D 2896 [20]). These measurements can be considered as a good estimator of oil condition by reflecting oil's additive depletion, acidic contamination and oxidation level.

Remaining Useful Life or RUL number was measured using RULER® equipment (FLUITEC); based on linear sweep voltammetry technique. The RULER test quantifies the antioxidants additives (AO) in used oil, and by comparing the results obtained in fresh oil, it allows to determine the quantity of antioxidants depleted since oil has been put into service. The RUL Number (Antioxidant additives) has been measured using an internal methodology CMT-0091.11. For this application blue solutions vials have been chosen for engine oil as recommended by the equipment manufacturers [21-22].

Finally, the levels of wear metals were measured using an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The standard used was ASTM D 5185 [23] and levels of metals have been reported in ppm. These wear measurements were conducted by an external laboratory and made exclusively for the oil B samples.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of TBN and TAN from samples analyzed coming from both oil types. Following a classical approach, it can be understood the decision adopted by vehicle operator in reducing oil drain interval for vehicles using oil B in contrast with oil A performance. This has been perfectly determined since the point at which TBN and TAN meet is considered the optimal time for oil change (15,000 km); showing a lower performance, and making impossible to reach the recommended period of service defined by engine manufacturer using this oil B formulation. On the other hand, oil A shows a better performance reaching the expected 30,000 km oil drain interval as a consequence of higher basic reserve and higher amount of antioxidant additive packages as can be seen in table 2.

The different degradation rates measured for both types of oils can be observed in figures 2, 3 and 4. The same evolution has been obtained independently of the analytical technique used: FT-IR spectrometry (Figures 1 and 3) or linear sweep voltammetry (Figure 2). Lubricant oil B presents a higher anti-oxidant additives depletion rate**,** mainly as a consequence of its lower initial concentration in fresh oil, leading to a more rapid consumption. The measurements performed using FT-IR technique in fresh oil samples has yielded 1.4 times higher amounts of aminic antioxidants concentration in oil A than in oil B.

Figure 4 shows the evolution of antiwear additives. The concentration levels in both formulations are very similar with slightly differences between them, but the level of final residual amounts are different as a consequence of the different oil drain period that each formulation can be reach.

The evolution of oxidation and nitration levels can be observed on Figures 5 and 6. Although the initial behavior for both oil types is quite similar, oxidation level in lubricant oil B experienced a big increase reaching values close to 14 $Abs \cdot cm^{-1}/0.1mm$ as a consequence of antioxidant additives exhaustion as observed on Figures 2 and 3. This value represents approximately a 40% higher value that those reached in samples coming from oil A at the same running mileage. The evolution of oxidation and nitration results show the same trend although final values are quite different.

The aminic antioxidant additive package that typically acts during the first oxidation stages becomes fully depleted around 15,000 km of oil mileage for oil type B, as seen in figure 2. Exhaustion of this additive package is one of the most important factors of higher levels of oxidation and nitration obtained. These additives have also a great importance at the final oxidation stage, when other additives types such as zinc dialkyl dithio phosphate -ZDDP contribute to reduce the acidic content and metal corrosion [24-26].

Figure 7 presents the evolution of wear metals level on samples coming from oil B. Measurements for copper, iron, and lead concentrations are presented. These metals have been considered as the most problematic ones attending the concentration values reached. Copper is commonly found in bushings and bearings (turbo, camshaft, and crankshaft) in reciprocating internal combustion engines. It has been suggested that copper corrosion products are generally catalysts that accelerate the rate of oxidation as can been seen in figure 5, where higher values for oil oxidation in lubricant oil B are reached at the oil drain period (15.000 km), corresponding with the highest copper concentrations. Other metals such as: chromium, nickel, aluminum, or tin have presented more reduced values. Results have been obtained using an ICP spectrometer.

Monitoring of these metals can be considered very important attending to two different factors. As can be seen on Figure 7, copper levels can reach very high values. It has been presented that at oil drain interval for this type of oil (15,000 km), aminic antioxidant are depleted completely and acidification levels have reached quite high values; as a direct consequence corrosion wear could be a very important factor leading to these high values of some metals such as copper or lead. Furthermore, copper can act as a catalyst in the oxidative degradation process and this situation leads to a feedback process that is important to avoid [3].

As expected, oxidation level and antioxidant depletion (AA and AO) are influenced by using higher quality lubricants as can be clearly observed on Figures 8 and 9.

Excellent correlation between anti-oxidant and aminic additives depletion and oxidation were found in both formulations as can been seen on ternary diagram shown in Figure 10. The maximum values of oxidation are reached where antioxidant additives and aminic antioxidant are depleted. Monitoring just one of these variables, using methodologies defined on Table 4; allow to carry out an accurate control on lubricant oil degradation process.

CONCLUSIONS

Quick depletion of aminic antioxidant packages, which working together with ZDDP additives should cope with the lubricant oil oxidation process, could lead to important oxidation rate increase. It has been experienced that oxidation level can rise around 40% depending of the lubricant on use.

Considerable wear in engine components can occur due to the oxidation level present in lubricant oil B close to the oil drain interval (this conclusion can be extended to other low quality lubricants in use). It is assumed that the main reason is that high oxidized oils and therefore presenting higher acidic characteristics induce corrosion in some engine metal components. This inducted corrosion vary depending on the type of metal, being copper one of the most reactive elements in these kind of chemical environment, furthermore acting as catalyst of the lubricant oil oxidation process. Therefore, copper concentration level must be considered as a key parameter to control and assess engine wear.

Taking into account that oil cost can be considered a negligible aspect compared to the overall vehicle maintenance cost, it is highly recommended to use upper quality oils which will contribute to extending the oil drain interval and assuring proper engine reliability.

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NOMENCLATURE

AA	Aminic Antioxidant
AES	Atomic Emission Spectrometry
AO	Antioxidant
API	American Institute of Petroleum
bmep	Brake Mean Effective Pressure
CNG	Compressed Natural Gas
FTIR	Fourier Transform Infrared
ICP	Inductively Coupled Plasma
IC	Internal Combustion
II	Indirect Injection
mV	Millivolts
OSF	Oil Stress Factor
PAI	Peak Area Increase
PH	Peak High
ppm	particles per million
RUL	Remaining Useful Life
SAE	Society of automotive engineers
TAN	Total Acid Number
TBN	Total Basic Number
TC	Turbocharged
ZDDP	Zinc Dialkyl Dithio Phosphate

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List of Figure:

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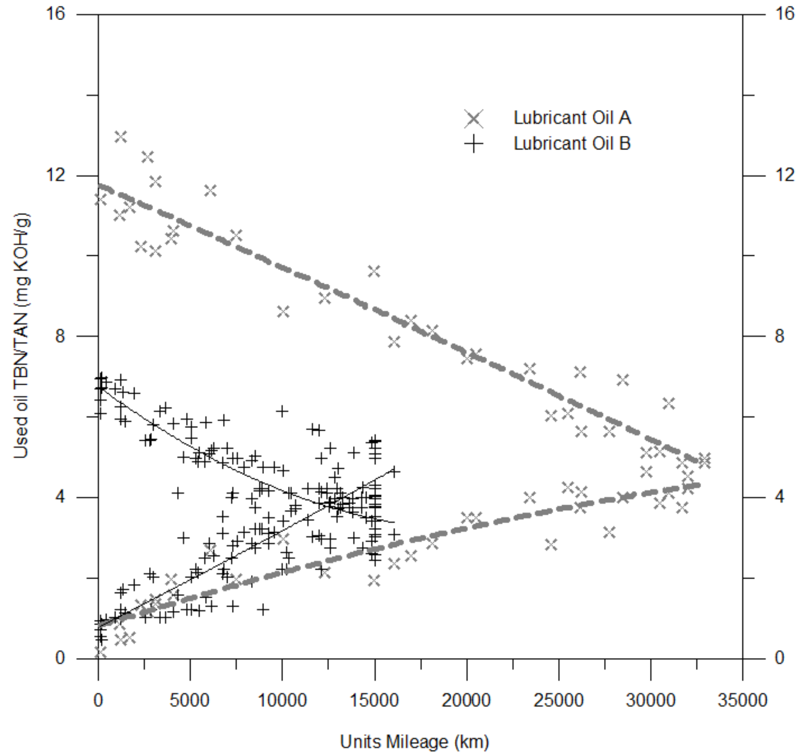

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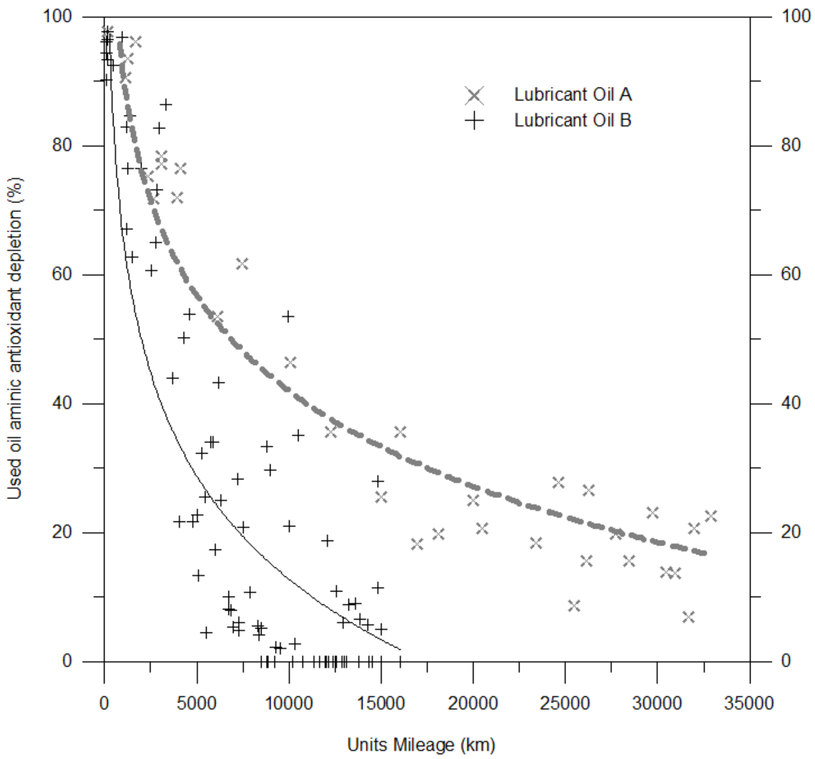

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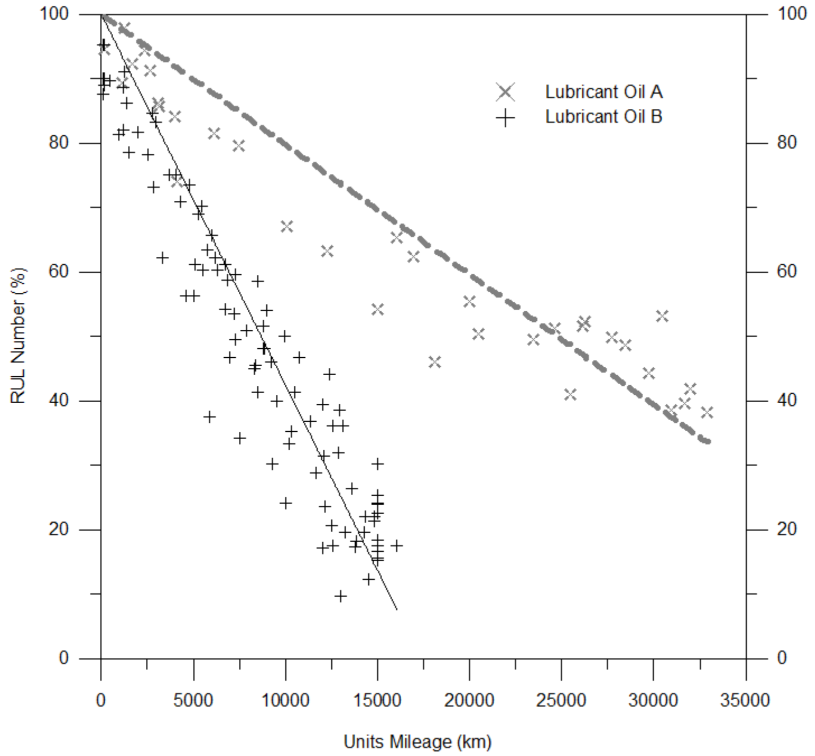

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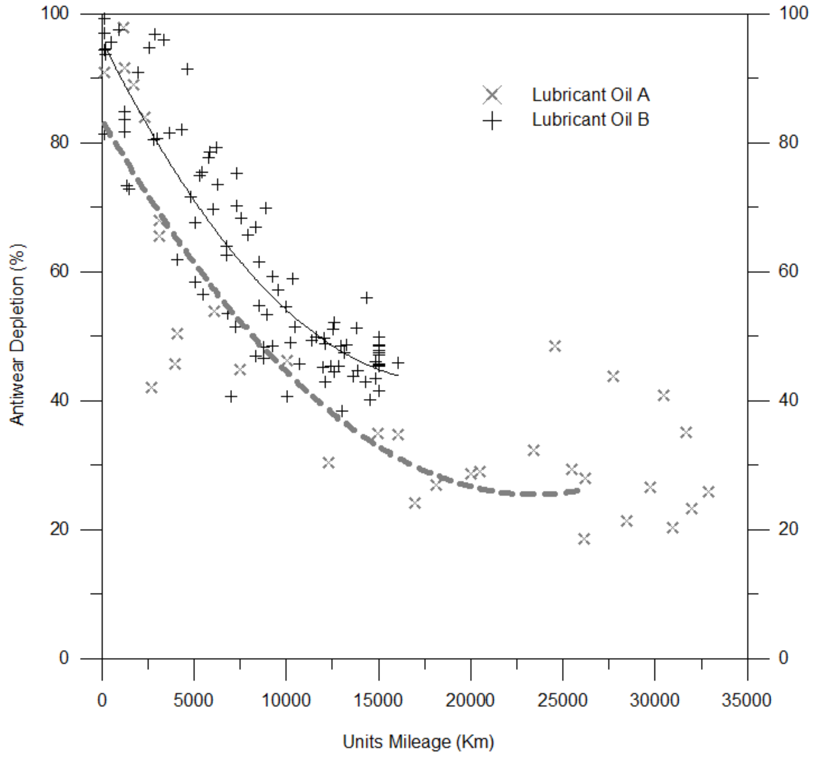

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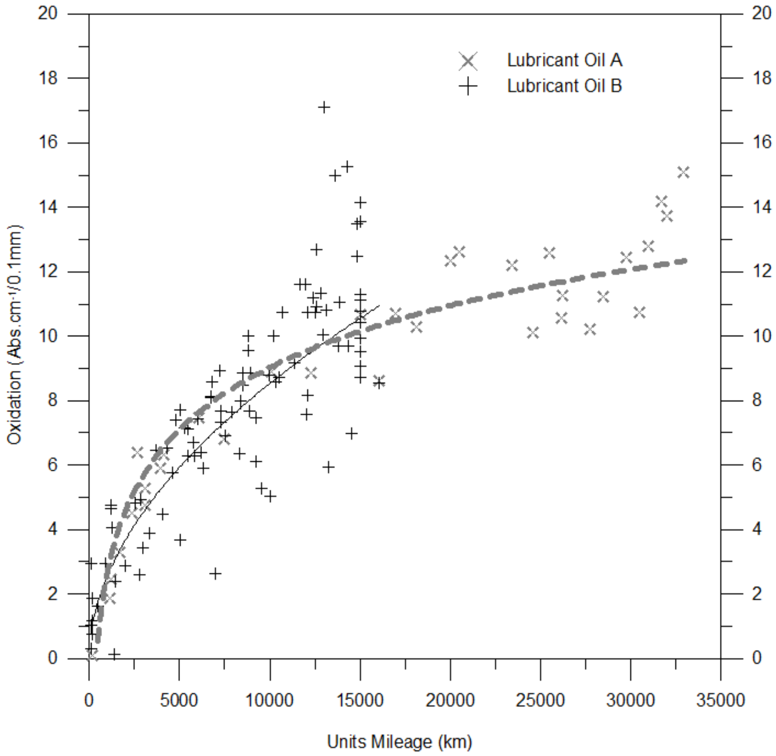

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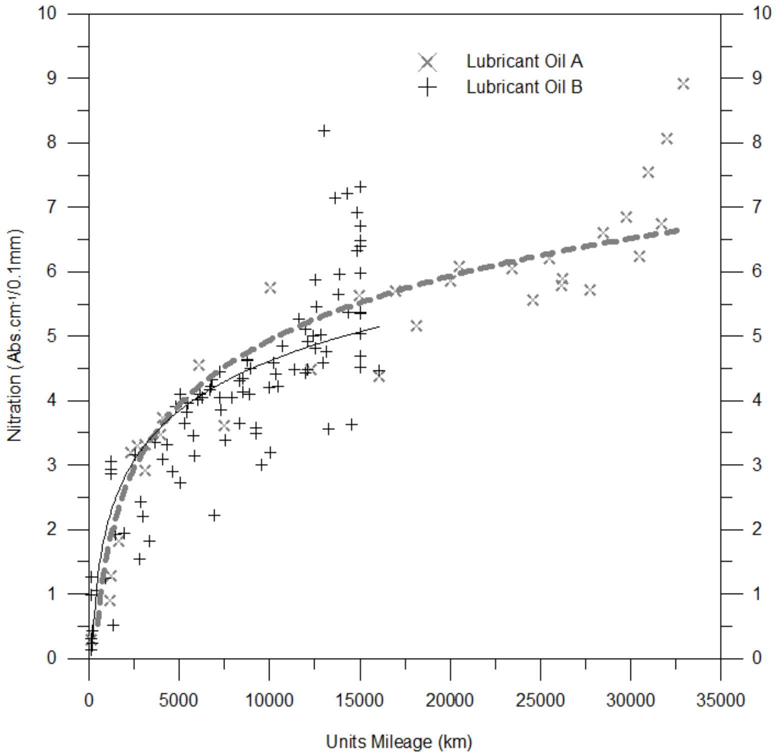

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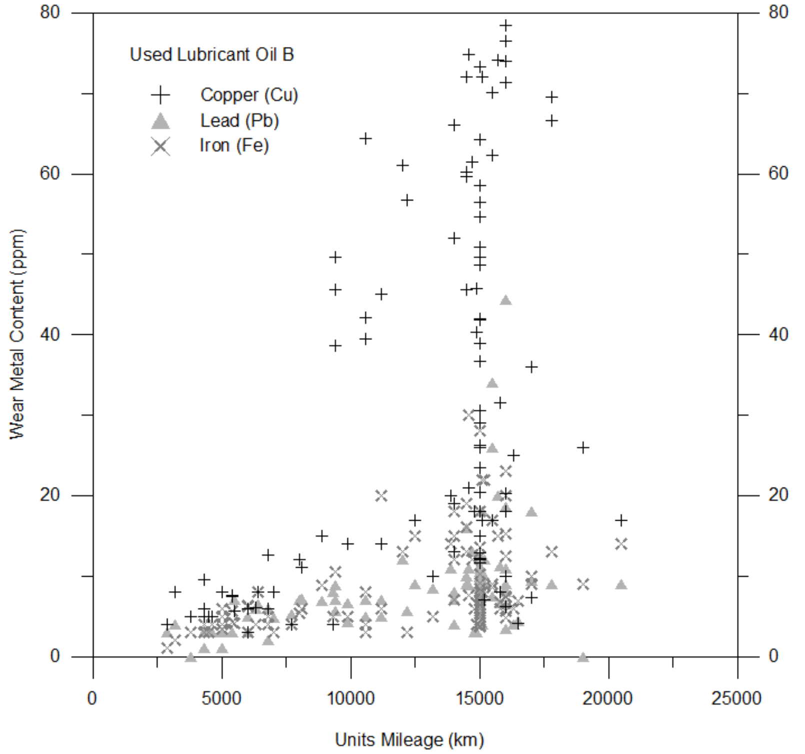

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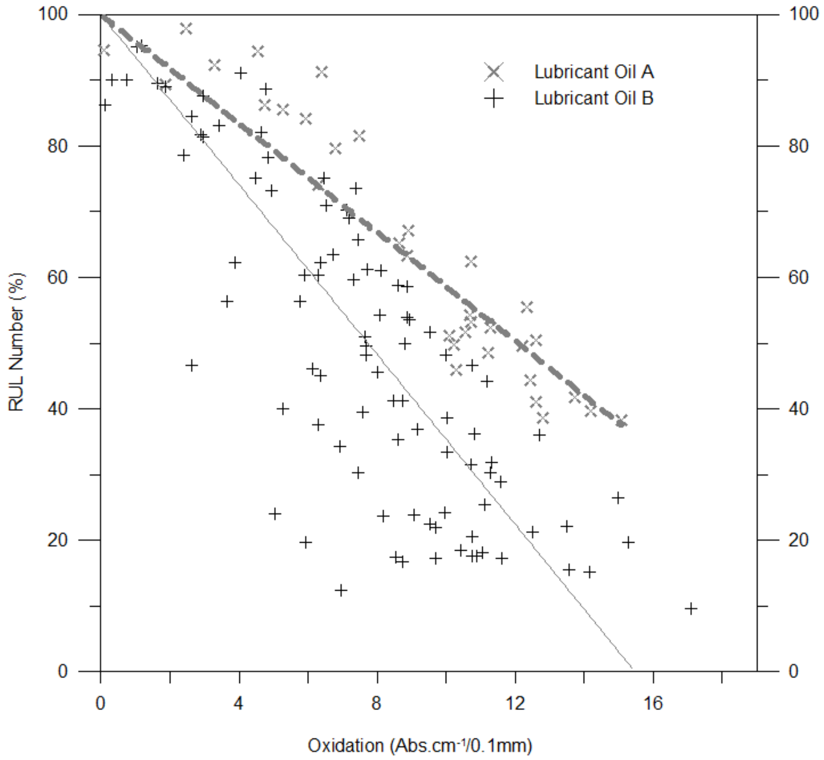

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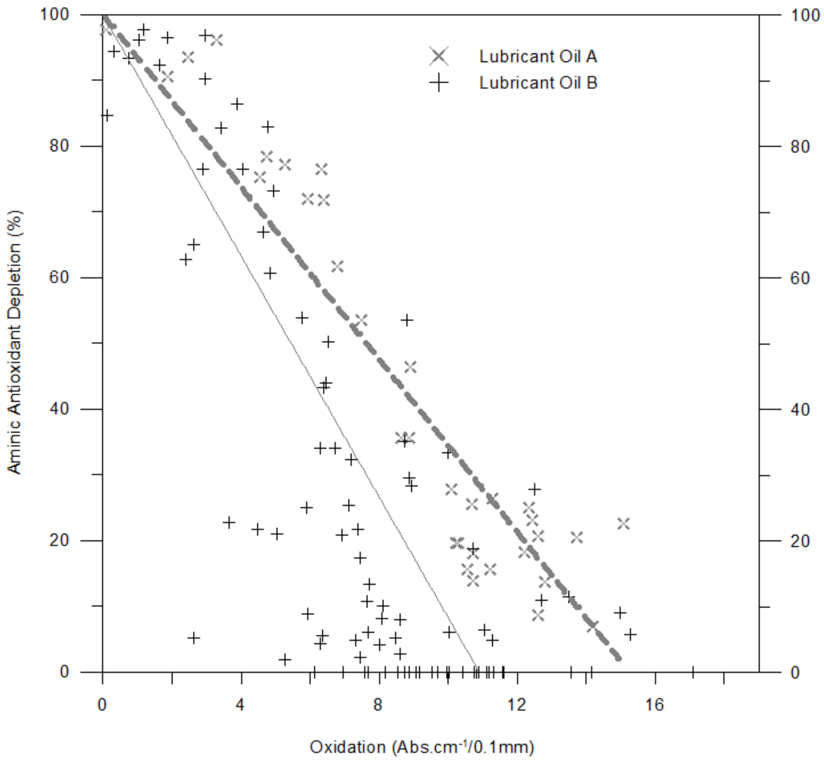

Figure 10: