

## MINIATURIZATION OF LUBRICANT DEGRADATION TESTING FOR NATURAL GAS ENGINES

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**Abstract:** Lubricant evaluation in natural gas engines is expensive due to large sump volumes and high equipment costs. A new laboratory protocol was developed to miniaturize oil degradation conditions in order to provide a rapid screening method for lubricants. Steel coupons were coated with 200 µm films of three commercial lubricants for natural gas engines. The films were oxidized for up to 90 hrs at 150 °C, 180 °C or 200 °C, then their tribological properties were compared using ball-on-plate tests. No deterioration in tribological performance could be noticed after film oxidation. Sump drains of the three lubricants were also obtained from actual engines with service life in excess 5000 hrs. Only slight reduction in tribological properties was observed, despite dropping alkalinity. This testing protocol can be further refined and possibly applied in lubricant industry, where it would reduce development time of natural gas engine lubricants and further improve their effectiveness.

**Keywords:** Oxidation; Wear; Friction; Engine oil; Oil Maintenance

### 1. INTRODUCTION

Growing usage of engines and generators, fueled by natural gas, puts more demand on lubricant manufacturers for higher quality products. Many electrical generators, fueled by natural gas, operate on industrial and commercial equipment as a part of large, continuously functioning installations. Truck and bus fleets represent another growth area for such engines, with spreading usage of compressed natural gas and liquefied natural gas for fuel. Lubricant applications in these generators or engines often face the need for high product quality in order to assure excellent operation of expensive equipment. Since any shut-downs and stoppage times might be costly, demands for long-term durability represent another challenge. Lubricants play a key role in protecting the mating parts from wear and friction fatigue. Conversely, low viscosity lubricants for natural gas engines often provide improvements in fuel efficiency, translating into significant savings on continuously operated equipment. These reasons ignite customer motivation to obtain side-by-side comparisons of different lubricants, especially when more suppliers focus on natural gas engines.

Lubricant comparison in actual engines, fuelled by natural gas, is complicated due to many issues. Usually the number of natural gas engines in one site is small and they cannot be considered identical, so side-by-side runs of different lubricants is not meaningful. Running lubricants one after another is often not possible in electrical generators due to long term durability, such as 40 000 hrs service life of high quality lubricants, which translates into nearly 5 years of continuous operation. Engine cost is also a major issue, because any risk of mechanical damage cannot be tolerated. Therefore, a thorough laboratory evaluation is highly welcome among manufacturers and users of oils for natural gas engines.

As reported by numerous research groups, thin film oxidation represents a rapid method of lubricant degradation, especially when the film is exposed to metal surface [1-3]. Obviously, lubricants degrade not only via oxidation, but due to many other factors, such as fuel contamination, mechanical shear, NO<sub>x</sub> reactions, moisture entrainment, etc. However, oxidation is often considered a primary cause, so merging of thin film oxidation and friction into one testing protocol is the main objective of this study.

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## **2. EXPERIMENTAL**

Lubricant testing in this study involved four main methodologies: 1) lubricant film oxidation 2) lubricant film friction 3) wear measurements 4) investigation of acid build up in lubricants. The respective tests are presented accordingly below.

### **2.1 Lubricant oxidation**

The main principles of the lubricant film oxidation test were described previously [4-5]. Briefly, low carbon steel coupons were polished with the 2000 grit SiC abrasive cloth before coating a sample, cleaned with acetone, dried and weighed on analytical balance ALJ-160-4NM (Kern An. Instr. GmbH) with  $\pm 0.1$  mg accuracy. Sample lubricants films were uniformly applied at pre-calculated amounts with a pipette and weighed to confirm the 200  $\mu\text{m}$  film thickness accuracy within  $\pm 3\%$ . Then the coupons were placed into a forced-draft oven HCP-108 (Mettler GmbH) for the specified temperature and duration. Afterwards, they were taken out, cooled, weighed and used for further tests.

### **2.2 Friction measurements**

Friction was measured on CSM Tribometer (Anton Paar Switzerland AG) in ball-on-plate linearly reciprocal configuration. Load of 50N was applied onto 6 mm OD steel ball in contact with the moving steel coupon from the lubricant oxidation test. The coupon was mounted on a pre-installed tribometer module with a self-made stabilizing holder. As shown in Fig. 1, one reciprocal friction cycle of 4 mm interval produced 8 mm cycle length, with 12 500 amounting to 100 m total friction distance. At 2 cm/s velocity nearly 100 data points of 'instantaneous' friction coefficient  $\mu$  in one friction cycle were calculated automatically by dividing torque  $F_T$  by load  $F_N$ . The average  $\mu$  was extracted as an arithmetical average from the central 80% segment of the path. The results were presented as  $\mu$  variation with progressing friction in terms of number of friction cycles.

### **2.3 Wear measurements**

After 12 500 friction cycles on the tribometer, the wear scars were measured on Surtronic S25 contact profilometer. A needle of 2  $\mu\text{m}$  tip radius scanned the scar in several selected cross-sections, selected from the central 6 mm segment of the wear track length. The data was transferred into a spreadsheet and the wear loss was calculated as an average area beneath the assumed surface plane. Wear rate was calculated as the volume loss (in  $\text{mm}^3$ ) per one centimetre of imaginary average wear track.

### **2.4 Acidity measurements**

The extent of lubricant degradation was studied by adapting the ASTM standard D4739 "Base number determination by potentiometric titration". Lubricants or oxidized samples were diluted with xylene, isopropanol and chloroform (at 1:1:1) to 10% or until fully dissolved and placed into a flask with a glass electrode, which was filled with saturated LiCl solution in isopropanol. The stirred blend was titrated with 0.1 molar HCl solution in isopropanol. Response from the electrode was recorded on a voltmeter with each change of 10 mV or more followed by equilibration of 1.5 min or longer. Solution of collidine at 2.42% wt. was used to calibrate the electrode at 370 mV. The electrode response was recorded in arbitrary units from 0 to 8 as "relative alkalinity", somewhat reminiscent of the pH scale. The relation of reported units to the actual proton concentration was not studied.

## **3. RESULTS AND DISCUSSION**

The study progressed through three main stages: 1) development of a miniaturized test protocol; 2) evaluation of tribological properties and 3) monitoring of alkalinity.

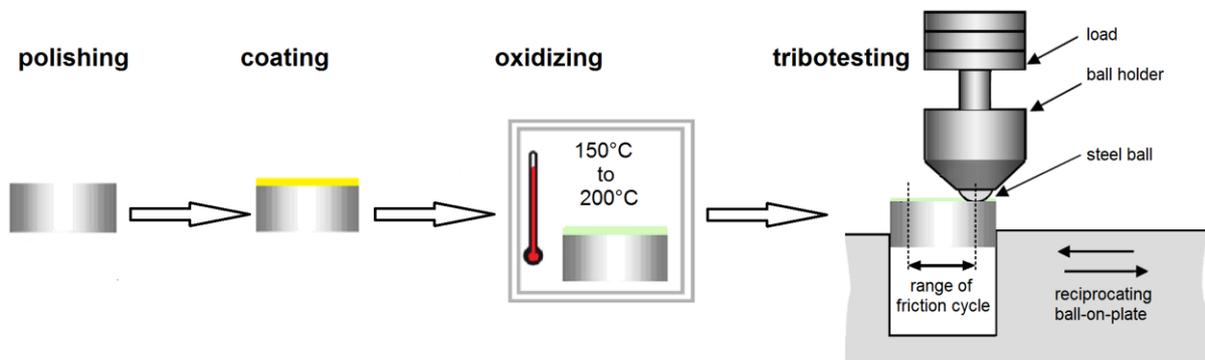
### **3.1 Development of testing protocol**

During the gas engine operation, lubricant oil degrades mainly through oxidation. Other degradation mechanisms might be possible, in particular water and dust contamination. However, in a properly operating engine with well-functioning air filters these two factors should not be significant. In other engine oils, fuel-derived issues might be important, such as the entrainment of unburnt or partially combusted fuel, contamination with fuel tank residues or injector deposit buildup etc. Since methane, ethane, propane, butane and nitrogen comprise more than 99.9 % wt. of natural gas contents, the

engines operate on relatively clean fuel, whose combustion products are nearly always gaseous. Natural gas engines are usually installed on industrial and commercial equipment, which typically runs for long durations with very limited start-up and shut-down regimes. So it is extremely unlikely that any liquid or solid contaminants might form during partial combustion of natural gas. This makes a laboratory simulation of oil degradation in natural gas engines easier than that in liquid fuel engines.

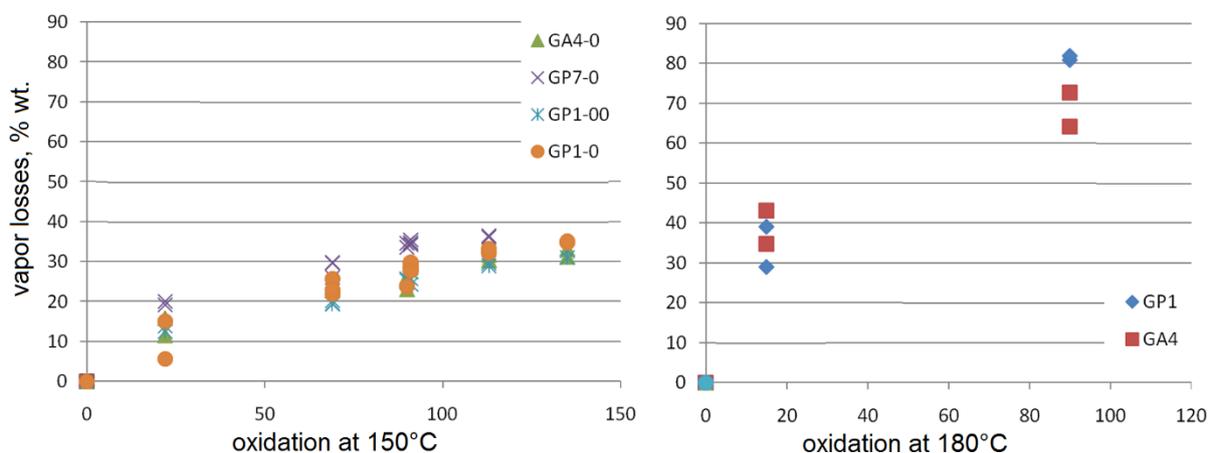
In addition to oxidation, a probability exists that oils for natural gas engines might degrade due to exposure to metal surfaces, humidity and nitrogen oxides. While the latter two could not be addressed in this study due to limitations of the test equipment, effects of metal surface were taken into account by exposing a thin oil film on a steel coupon. Degradation in oil films is much faster than in bulk oils due to such exposure to the metal surface as well as much more abundant air oxygen [1-3].

Therefore, in this study the test protocol is based on oxidation of thin oil films, which are coated on low carbon steel surface. The coated coupons were placed into an oven and oxidized at specified duration and temperature before measuring oil degradation. Two main characteristics were considered for the measurement: 1) tribological properties and 2) alkalinity. In this report the oil film oxidation was employed only for evaluation of changes in friction and wear, see Fig 1. Alkalinity measurements were performed just for field samples.



**Figure 1.** Thin film testing protocol for evaluation of oil oxidation effects on tribological properties.

As the most likely regime of oxidation temperatures between 150 and 200 °C have been selected. These are higher than oil temperatures in sumps of natural gas engines, which typically are less than 120 °C. However, degradation takes place not just in a sump, but also on cylinder walls and piston rings. Temperatures are much higher in those regions, often exceeding 250 °C and resulting in rapid oil vaporization. Therefore, test regime was selected to avoid major volatile emissions from oil films.



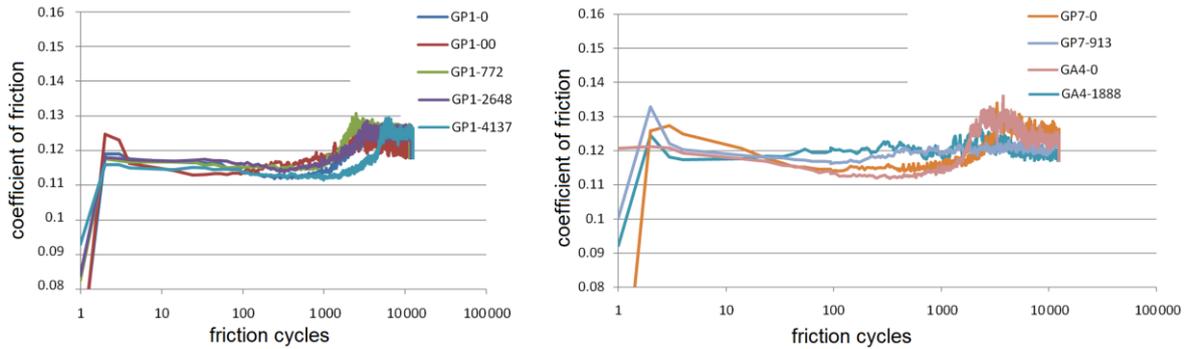
**Figure 2.** Influence of temperature and duration on volatile emissions from oil films with initial 200 μm thickness.

Investigated oils were screened in the oxidation tests to compare their vaporization tendencies, Fig 2. The results show that volatile emissions of studied oils are quite significant at 150 °C or higher temperatures. At 180 °C more than half of oil is lost due to vaporization in less than 4 days and just 7

hrs at 200 °C with 50 %, 53.5 % and 50 % wt. volatile losses by GP1, GP7 and GA4 resp. Nevertheless, at 150 °C most oil remains liquid for longer than a week. Mostly low mol.wt. fractions are vaporized from oil films, most likely producing a significant increase in viscosity. Obviously, viscosity changes can result in different friction and wear. However, in this study such viscosity variations have not been investigated because of resource availability.

### 3.2 Evaluation of tribological properties of fresh and degraded oils

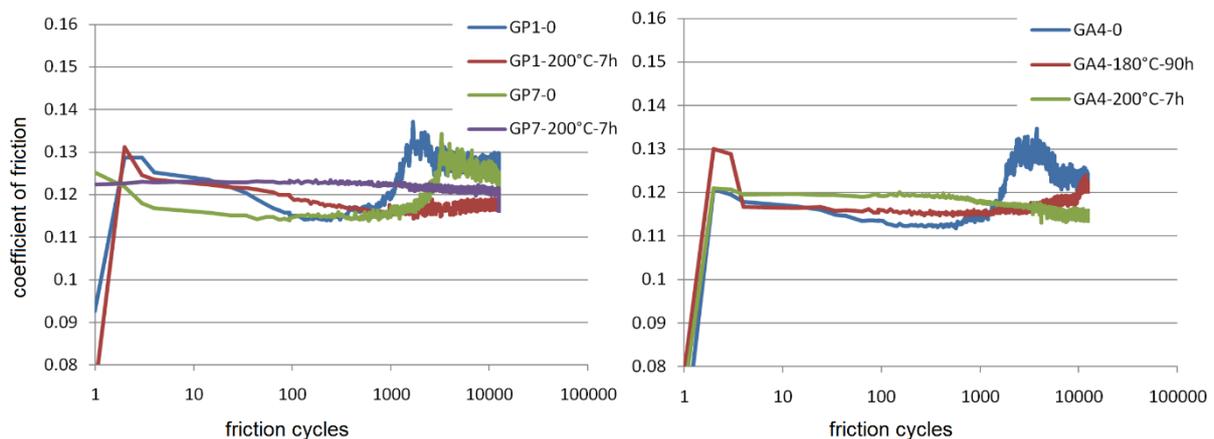
Specimens of fresh and used oils were collected from field and their friction tendencies were compared by recording friction coefficients for 12 500 cycles, Fig 3.



**Figure 3.** Friction characteristics of GP1 (left chart) GP7 and GA4 (right chart), both fresh (denoted “-0”) and used in natural gas engines. Service hours are shown after hyphen in the sample code.

No significant deterioration of frictional characteristics could be observed in the field drains, despite quite long service life of approx. 6 months. In fact, compared to fresh oils, some drains showed slightly better capability of sustaining low friction coefficient. Lower friction of drain samples might imply a highly unexpected conclusion that oil lubricity could actually improve with its ageing in natural gas engines. More detailed study would be needed to confirm such counter-intuitive findings, however. Nevertheless, it is quite safe to state that oil frictional properties do not deteriorate after 6 months service in natural gas engines.

Ball-on-plate performance was also compared between fresh oils and their films, which were oxidized in the laboratory, Fig 4.



**Figure 4.** Friction tendencies in lubricant films before and after oxidation in laboratory.

All three oxidized oils sustain stable friction for longer periods than fresh oils. This again implies that ageing might improve oil lubricity. However, a major difference between film oxidation in the laboratory and ageing in natural gas engines must be considered. In the latter only little increase in viscosity was observed per outsourced testing, while in film oxidation major volatile losses are incurred, which significantly increase oil viscosity. Film viscosities were not measured in this study, but undoubtedly their effects could be prominent in ball-on-plate performance. Nevertheless, it is clear that even severely oxidized oil films demonstrate good frictional characteristics, as an evidence of high quality lubricant package.

Another lubricity aspect, which is very critical for long service life, is protection against wear. In this study, the ball-on-plate tribotest was run for 12 500 cycles and then wear track depth was measured using a profilometer, Table 1.

**Table 1.** Wear of fresh oils, field drains and lubricants, oxidized in the thin film test, as determined by the profile measurements after 12 500 ball-on-plate cycles at 50N load, 4mm and 2 cm/s with 6 mm OD steel ball. Wear volume in mm<sup>3</sup>/cm, including some replicates, is presented for 0.6 cm central segment of the 0.8 cm long track.

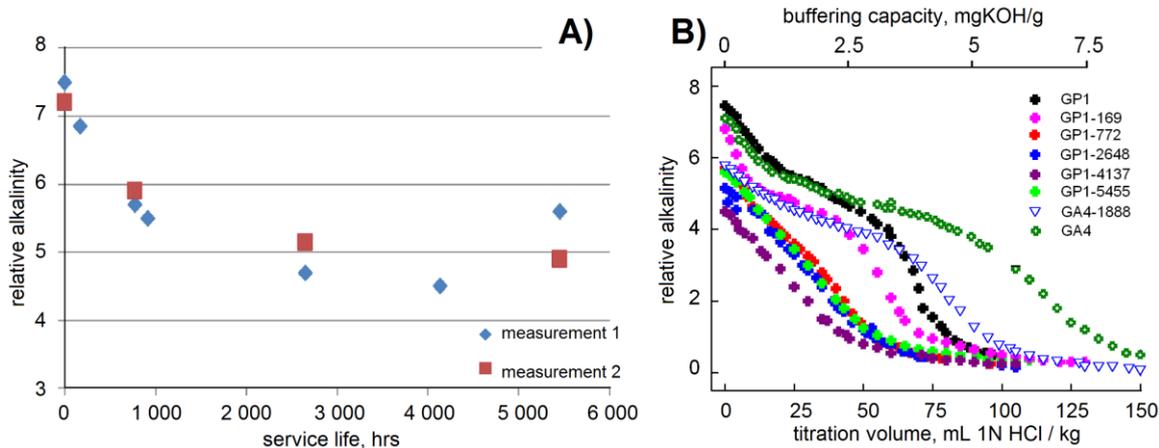
Oil	Drains of used oils		Fresh oil	Thin film protocol <sup>1</sup>
	Service life hrs	Wear volume mm <sup>3</sup> /cm	Wear volume mm <sup>3</sup> /cm	Wear volume mm <sup>3</sup> /cm
GA4-0	1888	0.02296	0.02267	0.00512
GP1-0	169	0.02116; 0.01900	0.02012	0.00269
GP1-00	5455	0.01777	0.01056; 0.00962	n. d.
GP7-0	913	0.02396	0.02071; 0.01942; 0.02569	0.0022

<sup>1</sup> laboratory oxidation of 200 μm films for 7 hrs at 200°C

Under these conditions wear of oil drains was somewhat higher than that of fresh oils, except GP7. It must be noted that field sample consistency fluctuated quite significantly, which is evident by comparing GP1-0 and GP1-00. Both samples represent the same brand of lubricant, just different supply lots, but wear rate of GP1-0 is twice as high. Nevertheless, it is apparent that a certain extent of oxidation or usage in engines does not jeopardize wear resistance of tested lubricants. On the other hand, the thin film protocol shows a major reduction of wear, which agrees with the supposition that film viscosity increased significantly after more than half of lubricant was vaporized in 7 hrs at 200°C.

### 3.3 Reduction of lubricant alkalinity

Problems of wear and corrosion in lubricants are often associated with acidity buildup. Therefore, most oils, including the studied lubricants, contain alkaline additives to combat acids. In this study, oil samples were diluted in chloroform, xylene and isopropanol and their alkalinity was measured potentiometrically with or without titration with HCl. The volume of thin film specimens was too small for sufficiently accurate alkalinity determination. Therefore, only fresh oils and field drains were evaluated, Fig 5.



**Figure 5.** Influence of service duration on alkalinity of GP1 (chart A) and capability to neutralize acid buildup of GP1 and GA4 oils (chart B).

Alkalinity units in Fig. 5 should be considered arbitrary, because they are dependent on the utilized electrode. It must be noted that the magnitude of measurement values does not affect observed tendencies or titration breakpoints. Caution should be exercised in correlating the buffering capacity to conventional TBN values, because it is not certain that electrodes in this study are equivalent to those

specified by ASTM D4739. Repeatability of the measurements in this study is not excellent, but sufficiently accurate for qualitative comparisons.

It is evident from Fig. 5 that lubricants are exposed to acids during their service in natural gas engines. Reduction of GP1 alkalinity is evident in Fig. 5A, retaining a rather linear character in the interval from 100 to 5000 hrs. Higher alkalinity at 5455 hrs can be explained by the fact that all drains were collected from various natural gas engines, which operated at different conditions. Initial drop in alkalinity can also be attributed to dilution with residual lubricants.

Titration with HCl reveals in Fig. 5B that acid-neutralization capability of GA4 is somewhat better than that of GP1. Even after 1888 hrs service GA4 retains more than half of its original buffering capacity. Meanwhile, GP1 seems to use up more than half of its alkalinity after just 772 hrs in service. Nevertheless, it would be premature to claim that their ability to neutralize acids directly correlates to combating wear. Thin film oxidation and ball-on-plate tests showed that tribological properties remain very good even after severe degradation, which is very likely to completely eliminate all alkaline additives and turn the degraded lubricant into acidic media. Survival of AW properties in acidic media again witnesses of the outstanding capability of studied lubricants to assure excellent protection of mating surfaces.

#### 4. CONCLUSIONS

- The main principles of a thin film testing protocol to rapidly screen lubricants for natural gas engines have been established and confirmed experimentally.
- Test temperatures, which assure low volatile losses, are the most appropriate for the thin film protocol.
- Even after severe thin film oxidation or long service in engines, friction remained low in lubricants.
- Protection against wear was retained in tested oils despite thin film oxidation or service in engines.
- Despite decreasing alkalinity, many lubricants are still able to assure protection against wear.

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