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The difference between 'forgiving' and 'less-forgiving' lubricants in thin film tests

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Introduction

Many users use a term 'Forgiving Oil' as a praise to the lubricant, which withstands past-due oil changes, heavy loads, contamination, overheating or many other issues without major problems to the lubricated equipment. Such abuse might lead to increased wear, some corrosion and other fixable issues. But if oil is "forgiving" it would still prevent the system from catastrophic damages, such as stalling, fractured gears or broken shafts. Although "Forgiving Oil" is not a scientific term, there are some fundamental reasons it exists as a concept. Such oil is able to retain a liquid film between moving surfaces under severe degradation. The degraded film might not assure low wear anymore, but it would still have enough fluidity to prevent metal-to-metal and other types of seizures.

These oil properties cannot be easily seen when comparing samples side-by-side using just standard tests, because the results are often similar and they only show full compliance to the specifications. Longevity and durability of formulated lubricants are often equated to the oxidative stability, which is typically measured by bubbling air through bulk oil at higher-than-average application temperatures. The increase in viscosity and acidity is considered critical with a number of other characteristics recorded as well: antioxidant activity, metal corrosion, colour change, etc. Often minor changes of these properties are viewed as decisive, disregarding the fact that many lubricants still perform quite well despite discoloration, increased viscosity or even acidity. Such temptation becomes even stronger at long testing durations, which sometimes exceed 1000 hours in degradation experiments.

One way to assess oil stability is to test its film rather than bulk volume. In almost all instances, lubricants form thin films on reservoir walls or equipment itself. This exposes oil molecules to air, moisture, hot metal surfaces, combustion gases and other aggressive factors [1], so lubricants degrade many times faster in films than in bulk volume. In engine oils and many other applications the importance of degradation in films is much more critical than that of degradation in bulk oil.

For example, degraded engine oil on piston rings or on the cylinder wall has many more negative implications than degraded oil in the crankcase. Good lubricant should be ‘forgiving’ and should not cause major failures even after severe abuse. ‘Forgiving oils’ should not vaporise off completely even after prolonged degradation. On the other hand, they should not become dry solid either, so they could dissolve in fresh lubricant, when it is finally supplied. It is nearly impossible to test these aspects in bulk oils, so the film degradation approach is used in tests such as Panel Coker, Pressurised Differential Scanning Calorimetry (PDSC), micro-oxidation and several others.

Often lubricant films continue degrading even after equipment shutdown, because it might take some time until cylinder walls, hydraulic reservoir, gears or other surfaces cool down. Film degradation is still rapid, but no new oil is supplied, which might lead to residue formation, corrosion and other major issues. In fact, degradation mechanisms in thin films are significantly different from those in bulk oils. Although oxidation, hydrolysis or saponification reactions seem the same chemically, in thin films all these mechanisms can easily combine, leading to a variety of organometallic and other unusual processes. In addition, previous experiments showed [2] that in 10 μm or thinner films, electrochemical reactions can take place, for example dissociation or oxygen reduction, despite low electrical conductivity of oils, see Figure 1.

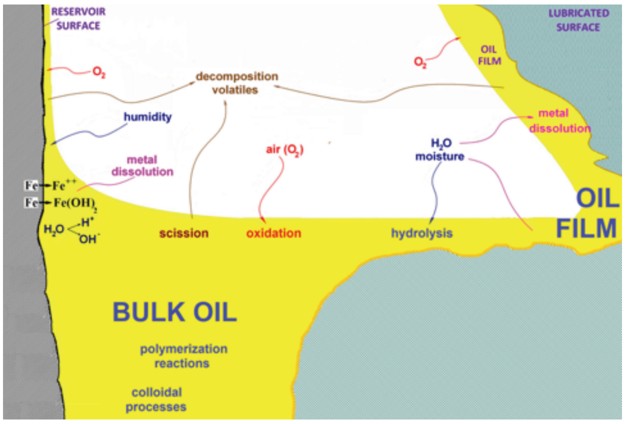

Figure 1. Diversity of chemical processes during oil degradation in thin films and bulk volume

The importance of thin film degradation in lubricants was clearly understood several decades ago, particularly in the US, but film-based tests did not become widespread worldwide. Panel Coker and micro-oxidation tests [1] never became official methods of globally accredited standards, such as ISO, DIN or ASTM, most likely due to repeatability issues. Thermo-oxidative Engine Oil Simulation Test (TEOST-MHT) using ASTM D7097, PDSC-based ASTM methods D6186 and D5483 for oils and greases along with several other standards are the only options for film degradation tests. Unfortunately, none of them achieved broad recognition in specification sheets, mostly because the results were often confusing and dependent on the skills of operators.

Thin film degradation tests for lubricants

Film uniformity is usually a predominant problem in these tests. Panel Coker and TEOST-MHT don’t directly specify its thickness. In micro-oxidation (e.g. K29200 version) or PDSC, especially its SFI version and the film thickness is specified, but the film itself does not stay uniform, see Figure 2.

Figure 2. *Comparison of typical thickness profiles of oil sample films in micro-oxidation (left), PDSC (centre) and current tests (right)*

One way of obtaining a much more uniform film thickness is to polish the sides of the holder to reduce the possibility of draining the film downwards by capillary forces. Films as thick as 500 μm were already successfully tested [3]. Temperatures between 50°C and 250°C or even higher can be used as well as various degrees of humidity, if below 100°C. Oil sample is coated on a freshly-polished coupon and exposed to selected heat and humidity. Air-flow has to be carefully controlled, but forced-draft ovens appear quite suitable. After some degradation the coupon can be carefully weighed to determine volatile losses and placed back to degrade further. Afterwards a number of methods can be employed to determine the extent of degradation: spectroscopy, titrimetry, chromatography, etc. In this report, most focus is devoted to film vaporisation trends and its solubility by soaking in fresh oils, Figure 3.

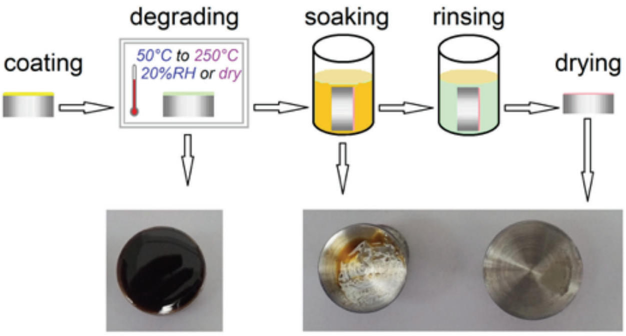

Figure 3. *Simplified scheme of the thin film degradation experiment by testing vaporisation and solubility of aged film in fresh oil. Photos of coupons with actual films at relatively low degrees of degradation are shown below.*

It must be admitted that such procedure still relies heavily on the operator skills, soaking in fresh oil in particular. However, even the vaporisation results pay back for the invested experimental effort. Counter-intuitive disagreement with widely accepted flash points was readily evident just by testing conventional basestocks, Figure 4.

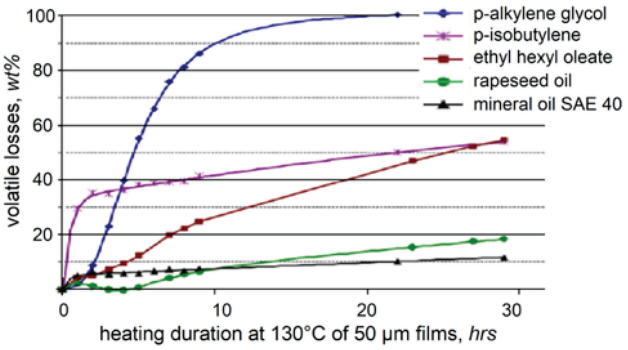

Figure 4. *Differences in oxidative decomposition intensity among several types of basestocks during thin film tests at initial 50 µm thickness*

All tested samples had flash points (ASTM D92) reported within 150°C to 250°C. Such similarity might imply that their films should evaporate at similar rates. However, after their thin films were degraded and volatile losses were measured gravimetrically [4], major differences in long-term decomposition trends were observed. During the early stages (1-2 hrs) of heating the emissions from oil films seemed to follow their flash points to some extent, but this correlation disappeared quite soon. Decomposition reactions appeared to dictate long-term volatile losses and these emission tendencies could not be forecast from either molar mass or viscosity. In-depth knowledge of sample composition (amounts of low molar mass fractions, unsaturation, aromaticity, ether linkages, etc.) could provide more avenues for predicting decomposition trends, but such exercise would not be simple. For example, it would be hard to expect that over long term mineral oils release less volatiles than synthetic or bio-based basestocks. In this particular study a possible effect of natural antioxidants in mineral oil was not addressed, but even for other basestocks the long term vaporisation trends are far from intuitive. Another notable finding shows substantial portions of high-flash basestocks being eventually vaporised from films. Tests were performed at 130°C, which is not frequent in reservoirs or other surfaces of lubricated systems. Nevertheless, if degradation duration and temperature are combined into one parameter, such as Time and Temperature Superposition (TTS) [5], decomposition trends might be extended to lower temperatures. It would become apparent that in many cases a larger volume of oil films vaporises than remains liquid over long term in additive-free basestocks.

Vaporisation from thin films of fully formulated lubricants

It is clear that lubricants lose lower molar mass components by evaporation during early stages of film degradation. However, in long-term the most emissions are generated by decomposition reactions. Testing their trends is even more important in fully formulated lubricants, than their basestocks, because various additives make it nearly impossible to predict the dominant course and cause of decomposition.

Films of similar viscosity lubricants were tested at 120°C to 140°C [4] and showed very different trends, Figure. 5.

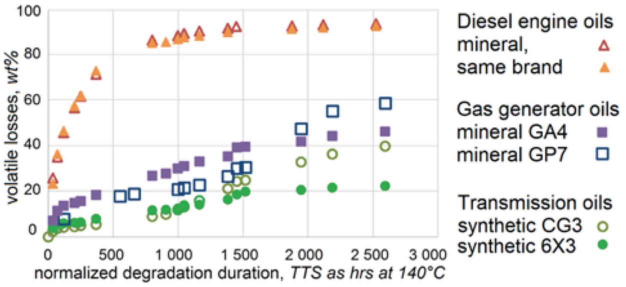

***Figure 5.** Differences in oxidative decomposition intensity of several types of commercial lubricants, using 500 µm initial film thickness and temperatures between 120 to 140 °C*

Mineral diesel engine oil of SAE 40 grade vaporised faster than gas engine oils [6] of similar viscosities at 40°C. Both samples from different batches showed very good repeatability, although initially their colour was somewhat different. Two mineral lubricants, coded GA4 and GP7 for powerful natural gas engines in electrical generators, behaved quite differently. Although GP7 was vaporising faster initially, it did not show much change in the decomposition rate. As a product from competing manufacturer, GA4 appeared less volatile during early stages. However, its vaporisation accelerated significantly afterwards and eventually exceeded the emissions of GP7. Considering similar ambient viscosities of all three brands of mineral oil lubricants (one diesel and two generator oils), the differences in long-term vaporisation are very perplexing. Not much is known about the specific basestock for each lubricant, so it would be speculative to try interpreting the underlying chemical reasons. Nevertheless, it is very likely that not just basestocks themselves, but also formulation additives had a significant effect on vaporisation trends.

When synthetic transmission oils of ISO VG100 were compared, Figure. 5, their long-term vaporisation also showed different trends. Decomposition rate for 6X3 stayed similar, while the rate accelerated for CG3. It should also be pointed out that decomposition reactions did not arrive to the complete stop even after 3000 hrs of degradation. Being more viscous, these lubricants contained higher molar mass and the vaporisation rate was lower than that of engine oils. Nevertheless, the volatile emissions continued increasing at the end of the tests.

If lubricant loses most of its volume due to decomposition, it is hard to consider it as 'forgiving,' because lower amount of liquid usually translates into lubricant starvation. Flash points or NOACK tests can only measure the rate of evaporation, caused by low molar mass components. Long-term vaporisation from thin films is a much more realistic means to describe the ability of lubricant to remain in liquid under severe degradation conditions. It must be admitted that very long testing durations are needed. However, if possible losses might be very costly, the best lubricant must be selected from several options. Often it should be reasonable to run several months-worth of thin film tests with all the candidate lubricants to find the most 'forgiving' one. In fact, per customer report, one electrical generator running GA4, experienced problems with its engine pistons and had to be stopped for maintenance, which was quite costly. Just one confirmation could not be considered as a proof, but this still gave more credibility to GP7 as more "forgiving" product than GA4.

Formation of oil-insoluble residues

Probably even more important for a "forgiving lubricant" is to ensure that it does not turn solid after prolonged degradation and it is capable of easily dissolving in freshly supplied oil. Lubricant solidification can occur through several mechanisms. Crystallisation is only important at low temperatures, which is not relevant here. The main degradation-related mechanism of solidification is oxidative polymerisation, which forms higher molar mass products with solubility problems. Another mechanism deals with colloidal processes. During degradation various oxygenated and hydrolysed compounds are formed, which organise themselves into micelles, vesicles, lamelas, etc. Resultant colloidal structures may precipitate as solids or combine into a viscous bottom phase. Usually both polymerisation and colloidal processes take place during degradation. Both of them are affected by basestock and additives. Intuitively, such solidification should be less likely if lubricant is stable oxidatively. However, this is not always the case. When standard oxidative stability tests were run on transmission oils (courtesy M. Henneberg from C.C.Jensen A/S), their induction periods were ranked quite clearly, see Figure 6.

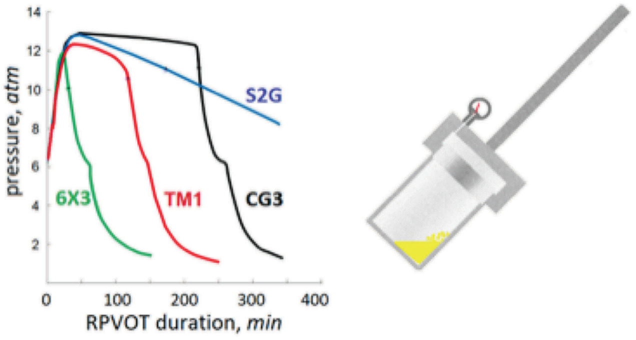

Figure 6. *Oxidation rates in RPVOT stability tests of transmission oils (left) with the illustration of RPVOT assembly (right)*

Rotary Pressurised Vessel Oxidation Test (RPVOT) is widespread in lubricant industry as a means to compare oxidative stability. In this series the vessel was loaded with 50 g of oil, 55 g copper catalyst, 5 g water and pressurised to 6.2 bar with oxygen. First it was heated to 150°C, during which the pressure went up to approximately 12 bar, and then went down due to oxygen consumption for degradation product formation. Pressure drop of 1.75 bar was assumed as a benchmark of the induction period. The sample 6X3 had a much shorter induction period than others, despite representing a well-known brand name. However, the filtration company, which was servicing transmissions on these lubricants, could not correlate RPVOT results to actual filtration issues. Thin film degradation tests were run on the lubricants, initially exposing their 500 µm films to 589 hrs of heating at 150°C. Volatile losses were significant, but did not exceed the volume of remaining films. Coupons with degraded films were placed into beakers with fresh respective oils and soaked at 90°C for 1-2 hrs. It became evident that 6X3 dissolved cleanly from the steel surface, while the rest of oils had some residues, especially CG3, see Figure. 7.

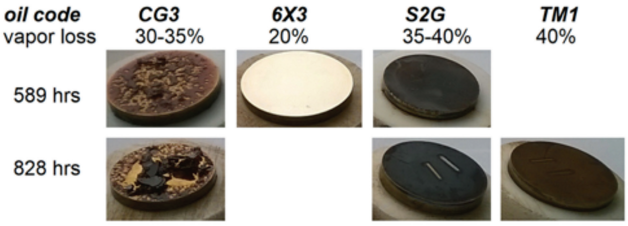

Figure 7. *Residues of degraded films after soaking in fresh hot transmission oils and rinsing. The grooves should be disregarded as attempts to run friction tests before soaking*

Since the scale of this comparative study was limited [6], only several coupons were tested. A replicate of 6X3 was run as well, unfortunately not for 828 hrs, but for 663 hrs. Its degraded film dissolved in fresh 6X3 just as easily. In this study some attempts were made to evaluate friction changes due to degradation before soaking. Consequently, some scars are visible on several coupons in Figure 7. Residue solubility of TM1 and S2G was similar, despite substantial difference in their RPVOT data. However, it can be suspected that CG3 would solidify during degradation faster than 6X3, contrary to RPVOT data in Figure 6. It is also worth referring to long-term vaporisation data, see Figure 5, where 6X3 appeared more "forgiving" than CG3.

Conclusions

Long-term degradation of thin films of fully formulated lubricants shows that basestocks and additives affect the ability of oil to remain liquid despite severe oxidation. Large differences among well-established commercial lubricants can be observed using this methodology, which might explain why only some oils are "forgiving". The thin film degradation method might be very helpful in predicting longevity of engine oils, hydraulic fluids or many other lubricants as well as various basestocks and their formulations with additives.

Low petroleum prices and rapid spread of electrical vehicles are producing major changes in lubricant industry. In long term, significant decline in engine oil demand can be anticipated, which would affect the whole lubricant industry. Petroleum companies might become less likely to commit larger resources into the development of better performing lubricants, starting with engine oils but inevitably affecting the rest of lubricant product portfolio. Switching investment priorities in large companies might reduce basestock selection, additive availability and technological intensity, which would increase the role of independent lubricant manufacturers. Until recently, when considering face-to-face competition with large companies, the smaller players would not necessarily dedicate major expenses towards engine testing, hydraulic pump stands or other costly application trials. However, with ongoing transformations in lubricant industry, the independent manufacturers often see new possibilities to develop better products. In those cases they need to demonstrate that newly developed engine oils, hydraulic fluids and many other types of lubricants have better service life and durability without running the costly trials.

Therefore, thin film degradation tests can be a useful method in giving the competitive advantage for lubricant formulators, focused on specific application as well as lubricant users, who need to screen many competing products.

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References

[1] Cvitkovic, E.E.E.F., Klaus, E.E., Lockwood, F. "A thin-film test for measurement of the oxidation and evaporation of ester-type lubricants." ASLE Trans, 22 (4), 1979, 395-401.
[2] Asadauskas, S.J., GriguceVičienė, A., Leinartas, K., Bražinskienė, D. "Application of three-electrode electrolytic cell to evaluate thin films of vegetable and mineral oils." Trib. Int. 44 (5), 2011, 557-564.
[3] Stoncius, A., Liascukiene, I., Jankauskas, S., Asadauskas S., "Volatiles from Thin Film Degradation of Bio-based, Synthetic and Mineral Basestocks" Ind. Lub. & Trib., 65 (3), 2013, 209-215.
[4] Bražinskienė, D., Liaščukienė, I., Stončius, A., Asadauskas, S.J., "Ester Basestock Vaporisation from Thin Oil Films" Lub. Sci., in print, DOI: 10.1002/ ls.1372, 2017, pp 1-17.
[5] Asadauskas, S., Erhan, S.Z., Perez, J.M., "Kinetics of Oxidative Degradation: Applicability of Time and Temperature Superposition", Trib. Trans., 42 (4), 1999, 860-866.
[6] Bražinskienė, D., Asadauskas, S., Lapinskas, D., "Thin film degradation testing of lubricants for gas generator, diesel engine and hydraulic applications", Proc. "Chemistry & Chemical Technology 2017" Int. Conf. Lithuanian Soc. Chemistry, ISBN 2538-7359, pg 21, KTU, Kaunas, 28 April 2017.
[7] Asadauskas, S. J. "From heavy duty lubricants to biobased fluids–legacy of Joseph Perez." Green Tribology, 1 (1), 2018, 1-4.

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