

Formulating Low Varnish Turbine Technology – lubricant additives with improved deposit control

Varnish and related deposits occur in a range of lubricant applications where the oil is exposed to high temperatures. It can give rise to a number of issues such as accelerated bearing wear, sticking and faulty operation of control valves, blockage of oil filters and impeded heat transfer. In an operational gas or steam turbine, under such circumstances, control systems will shut down a turbine to prevent any permanent and potentially hazardous damage, resulting in what is often termed a 'unit trip'. A non-operational turbine suffering these issues may not be able to be brought online. The unscheduled downtime arising from these unit trips and failed starts can be extremely costly for an end user. For example, an energy utility company which fails to provide electrical power on an agreed day is contractually obliged to make up the deficit by purchasing power from the market often at highly inflated rates. Costs in excess of \$1 million for a single unit trip are common. Moreover, varnish-related failures are most prevalent for peaking and cycling units, which are brought online intermittently to provide power when grid demand is at the highest. Inability to provide power when most needed therefore has consequences not only for the utility company but for the entire grid.

Several factors have been identified as contributing to varnish formation in turbines. Perhaps the prime reason is the thermal degradation and oxidation of oils by the heat emanating from the superheated steam in a steam turbine or the combustion gases in a gas turbine. Degradation can also occur by the adiabatic compression of entrained air bubbles in the oil (microdieseling), and electrostatic spark discharge leading to localised hotspots in the oil and therefore decomposition. The decomposition products are often insoluble in oil and therefore precipitate out as sludge or plate out on surfaces as varnish. The choice of base oil is also influential as solvent extracted,

hydrocracked and hydrotreated oils can have very different abilities to solubilise additives as well as additive decomposition products. Design features of the turbine itself, such as arrangement of the lubrication and hydraulic circuits, proximity of bearings to high temperature zones, and the maintenance practices applied also have a significant impact on problems due to varnish and deposit formation.

Some solutions for varnish issues have emerged. A large amount of effort has been put into developing superior condition monitoring technologies. Traditionally, the condition of an oil and propensity for forming deposits was predicted easily by tracking oxidation-related parameters such as acid number and viscosity of the in-service oil. However, with the increased availability of hydrofinished base oils, which enable oxidation lifetimes up to an order of magnitude higher than possible with solvent extracted base oils, deposit formation can occur before any noticeable changes in the viscosity and acid-number profile. Novel condition monitoring methods such as Membrane Patch Colorimetry ASTM D7843 offer the ability to predict varnish formation reliably. Improved maintenance procedures have also been advocated. Heat-tracing of pipework to minimise sharp temperature drops and therefore minimising precipitation by sudden cooling, use of advanced filtration systems with optimised filter materials, use of electrostatic precipitators and ion exchange technologies in conjunction with appropriate condition monitoring have met with success in reducing varnish-related downtime for turbine end users. As formulators of additive technology for turbine oils, Afton Chemical sought through this study to investigate the effect of the oil formulation, in other words the combination of additive chemistry comprising of antioxidants, metal deactivators, corrosion inhibitors, etc. with base oils, on the potential to form varnish and related deposits.

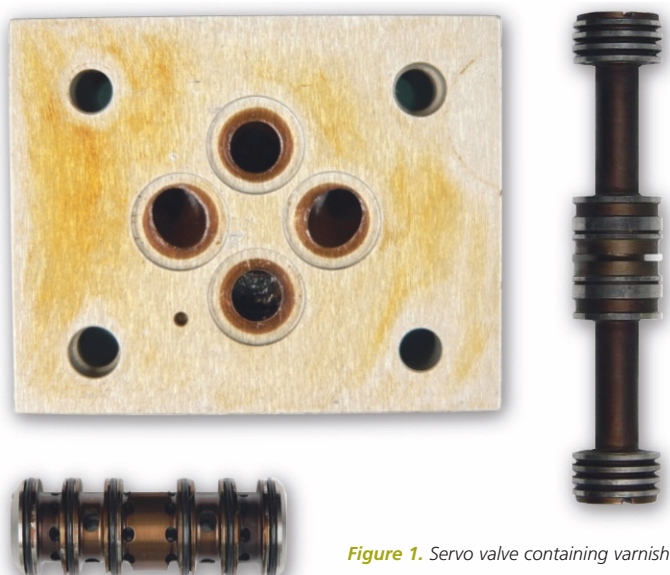


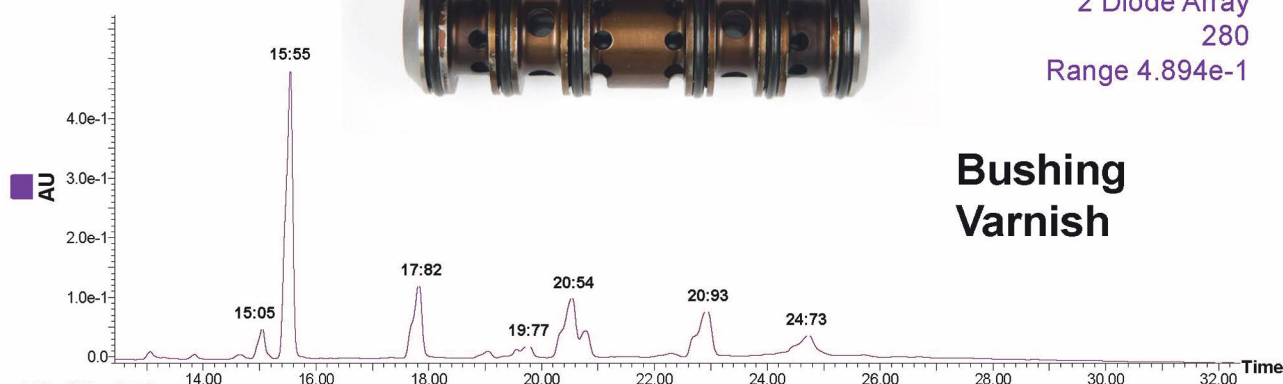
Figure 1. Servo valve containing varnish

Afton Chemical obtained samples of varnish or varnish-clogged parts from three turbines which had been experiencing varnish-related issues, namely a plugged servo valve from a gas turbine (Figure 1), the varnish from a blocked filter in the Inlet Guide Vane valve unit from a gas turbine and an electrostatic precipitator which had accumulated a large amount of varnish.

Afton Chemical also obtained samples of the new oil brands which had been used in each of the turbines, Oil A, B and C respectively. After isolating the varnish from the parts, we ran extensive chemical analysis of the varnish as well as the new oil in order to investigate any connections between new oil additive chemistry and material present in varnish. A range of techniques including ICP, FTIR, LCMS, HPLC, GCMS, UV/Vis spectroscopy, GC/NPD, phosphorus NMR, SEM and EDX were used. In some cases, virtually identical chemistry was detected in the new oil and the varnish, corresponding for example to unreacted antioxidants (Figure 2).

The varnish samples were found to contain both unreacted phenolic and aminic antioxidants, as well as their decomposition products, together with triazole metal deactivators, unreacted triarylphosphate antiwear along with base oil oxidation products. Notably, the Inlet Guide Vane varnish contained PANA, which was absent in the new oil B used in that turbine. It is possible that the PANA appears due to inadequate system flushing when this oil was first introduced into the system (Table 1) on page 24.

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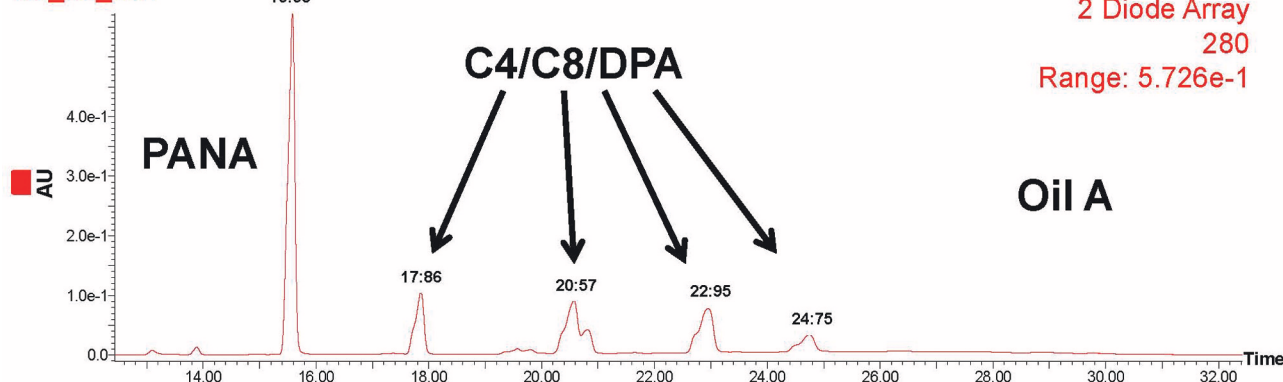


Figure 2. LCMS comparison of varnish on bushing of servo valve with antioxidants present in new oil

Varnish sample	Commercially available fresh Oil	Contents of varnish sample	Contents of fresh oil
servo valve from gas turbine	Oil A	<ul style="list-style-type: none"> PANA + degradation products Alkylated diphenylamines Base oil oxidation products 	<ul style="list-style-type: none"> PANA Alkylated diphenylamines Dialkylaminomethyltriazoles Base oil
IGV varnish	Oil B	<ul style="list-style-type: none"> Phenolic ester degradation products PANA Dialkylaminomethyltriazole Base oil oxidation products 	<ul style="list-style-type: none"> Hindered phenolic ester antioxidant Dialkylaminomethyltriazoles Base oil
Electrostatic precipitator	Oil C	<ul style="list-style-type: none"> Oxidized MBDTBP phenol Butylated triphenylphosphates Base oil oxidation products 	<ul style="list-style-type: none"> Butylated triphenylphosphates MBDTBP phenol Base oil

Table 1. Chemistry detected in varnish samples and new oils

Interestingly, all of these varnish samples were soluble in polar organic solvents such as THF, which differentiates it from the varnish deposits found, for example, on pistons in an internal combustion engine. Typically piston deposits contain large amounts of sooty carbonaceous material and insoluble polyaromatics on account of the oil being exposed to higher temperatures and coming into direct contact with combustion gases, which does not occur in a gas or steam turbine.

Around the same time as the investigation of varnish samples from the field, we set out to develop a rapid screener test in order to simulate varnish formation in the field under laboratory conditions. Approximately 50ml of oil is aged in a glass beaker in the presence of a copper and steel catalyst coil at a set temperature for a set duration. The oil is then filtered, sludge weight recorded, and viscosity, acid number and colour of the end of test oil is measured. We found that when the test is run for 7 days at 150C, on oils A, B and C, the filtered sludge was chemically very similar to the varnish from the field and

therefore showed potential for being an effective, experimentally simple, high throughput bench test to mimic varnish deposits from turbine. Moreover, along with the sludge weight, a quantitative indicator of varnish forming potential, several other data points emerge from each test that give an indication of a formulation's oxidation stability made the test a useful tool for further formulation studies.

Armed with an understanding of problematic chemistries from the field varnish study, and a varnish simulation bench test, Afton Chemical then initiated several matrix studies to identify low varnish formulations. Two Design of Experiment (DoE) matrices investigating multiple phenolic and aminic antioxidants, metal deactivators in several base oils were tested in a number of deposit formation and oxidation tests such as the ASTM D2272 RPVOT, D4310 1000h TOST, D943 life TOST as well as Afton's varnish screener test and other tests specified by turbine OEMs. Statistical analysis was carried out of the results were carried out in order to determine the main effects of each

additive component and interactions between them. Additional test matrices were put together to identify the effect of more phenolic as well as phosphorus and sulphur based antioxidants.

The combined learnings of the varnish sample analysis and the matrix studies were used to assemble further formulations which were run in further oxidation tests including the 'Dry TOST' test. Afton ran the Dry TOST essentially as a modified D943 TOST, but in the absence of water at 120°C instead of the standard 95°C with water present as in the D943. It is possible to run the test on multiple tubes of the same oil sample, with each tube running to a set duration. When each tube completes its test duration, the end of test oil is decanted, the residual RPVOT measured (relative to fresh oil) and the oil is filtered to obtain the sludge deposit weight. The residual RPVOT can be plotted on a graph against test duration to give an understanding of the oxidation stability of the oil, and the sludge can be plotted against time or residual RPVOT to show the propensity for deposit formation as the antioxidants get depleted and the oil ages. Afton Chemical has been participating in an ASTM working group to derive a formal test method for the Dry TOST.

Initially we ran the Dry TOST on the better performing formulations from the preceding matrix studies, and API Group II base oil, by using two tubes per sample, set to 500h and 700h. We had set ourselves a limit of maximum sludge of 100mg/kg and a minimum time to 25% residual RPVOT of 500h (Figure 3).

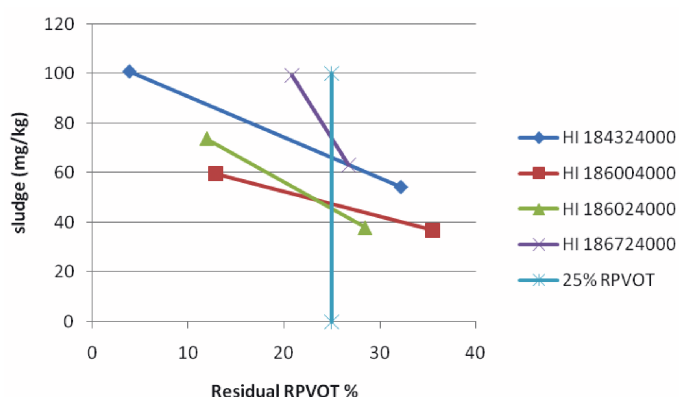


Figure 3. Dry TOST at 500h and 700h on initial candidates

Although sludge control of these early formulations was promising, we sought to improve the oxidation stability and so modified the levels of antioxidants and other components, while using a commercially available turbine oil as a reference (Figure 4). The results were encouraging, with consistently low sludge and much greater oxidation stability (higher residual RPVOT after given number of hours).

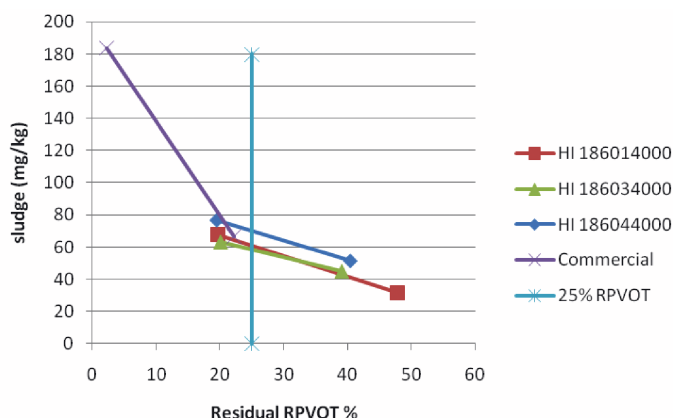


Figure 4. Improved oxidation stability

Efforts to increase the oxidation stability far beyond the limit by increasing the level of antioxidants by 50-100% of original showed that sludge formation also increased. We therefore investigated a range of solubilisers and diluents to lower the sludge while having an oxidation life beyond well beyond requirements. Dispersants, various aromatic hydrocarbons, naphthenic base oils and polyoxygenated compounds were investigated, in some cases with success but also with side-effects on other performance areas such as water separation, rust and oxidation life, for example in Figure 5.

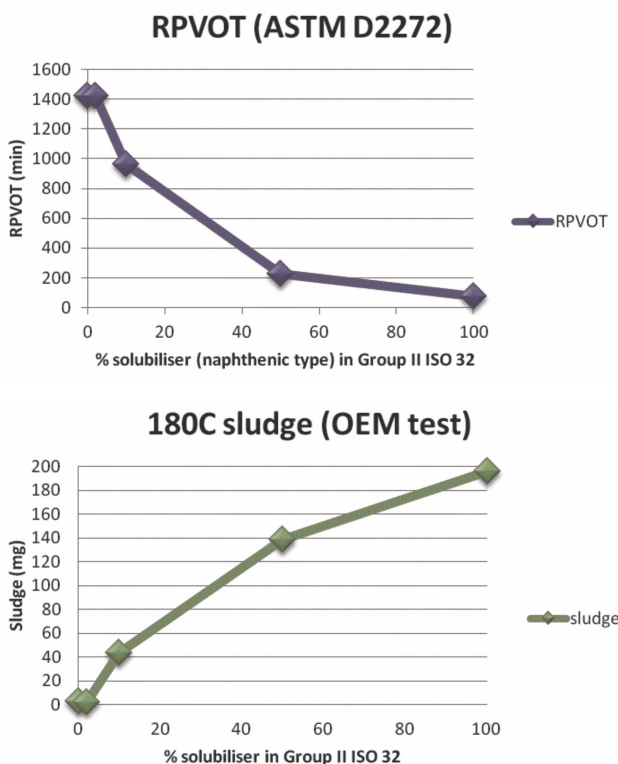


Figure 5. Example of solubilisers with negative effect on sludge and RPVOT oxidation stability

After further optimisation of antioxidant and metal deactivator levels, we evaluated a number of neutral and acidic rust inhibitors as well as combined systems in these formulations for robust performance in the ASTM D665B rust test. We then went on to optimise the water separation performance by investigation of a range of demulsifier systems in the D1401 water demulsibility and IP 19 steam demulsibility tests. In particular, we ran the testing on both fresh and thermally aged oils in order to simulate an in-service oil in a turbine. New turbine oils frequently show excellent water separation properties but after a few months in service the water separation can deteriorate rapidly as demulsifiers decompose or drop out of the oil. Effective water separation even after a thermal ageing simulation therefore displays the potential of strong performance in actual turbines (Figure 6).

With the optimised formulation defined as additive HiTEC® 2505, Afton Chemical went on to generate full datasets against key gas and steam turbine OEM specifications and industry standards. Stringent requirements on all aspects of performance, including oxidation, air release, water separation, rust prevention, foam control, filterability, compatibility with trace calcium and magnesium contaminants, yellow metal corrosion and elastomer compatibility were met consistently in Group II and Group III base oils. We then went on to test these formulations in the full Dry TOST test, running six to eight tubes. In one of the Group II base oils investigated, the test was run in duplicate and took approximately 900 hours to reach 25% residual RPVOT (Figure 7). Sludge was consistently below our limit of 100mg/kg, at 50-60mg/kg at 25% residual RPVOT (Figure 8).

Fresh Oil



Group I



Group II



Alternate Group II

Thermally Aged Oil

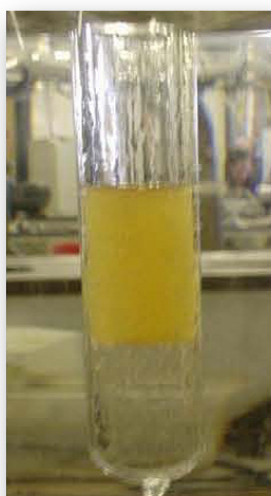


Figure 6. Strong water separation for fresh and thermally aged oils

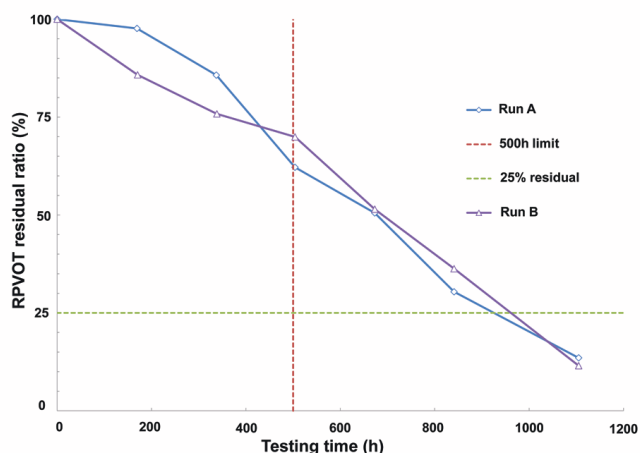


Figure 7. Duplicate dry TOST on ISO 32VG formulation using Group II base oil - oil life

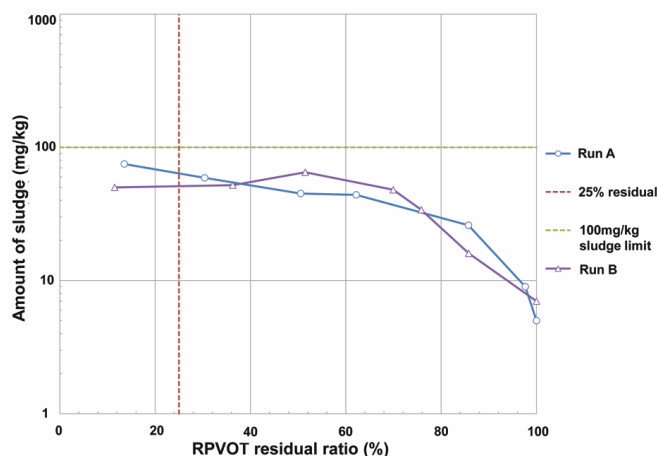


Figure 8. Duplicate dry TOST on ISO 32VG formulation using Group II base oil - sludge control

Having demonstrated strong performance in group II base oils, our attention turned to Group III base oils. We ran 6-8 tubes of our optimised HiTEC®2505 additive in two different Group III base oils to durations well over 1000h, allowing for the expected increase in oxidation stability for Group III versus Group II. Both oils took approx. 1200h to reach 25% residual RPVOT (Figure 9) and gave sludge values of approximately 40mg/kg at 25% residual RPVOT (Figure 10).

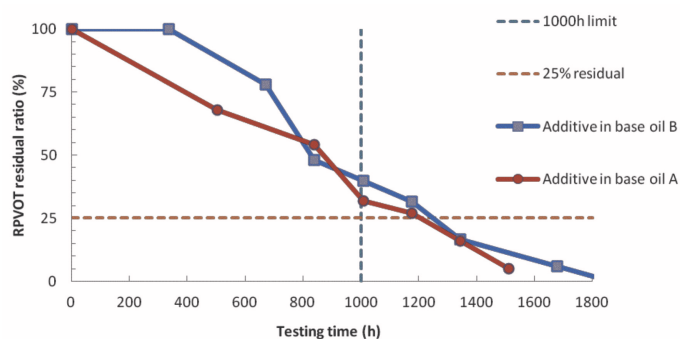


Figure 9. Dry TOST on ISO 32VG using Group III base oils - oil life

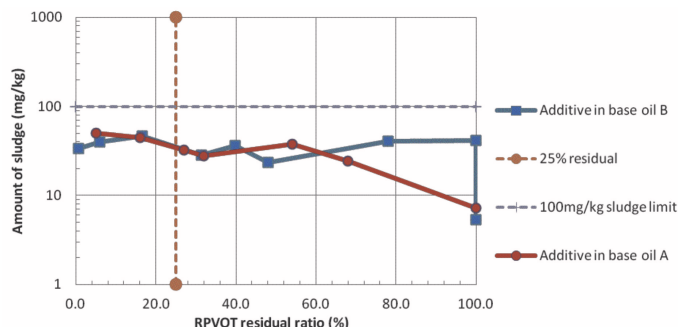


Figure 10. Dry TOST on ISO 32VG using group III base oils - sludge control

Note that the sludge is still very low even when the residual RPVOT is well below 10% residual RPVOT. In other words, even when the antioxidants are almost completely consumed, the sludge formation in the oil is still low. This has potentially beneficial ramifications in a turbine where localised extensive degradation of oil, for example in hotspots still does not lead to deposit formation.

Understanding the composition of base oils, in particular the proportions of various types of hydrocarbons (aromatics, n-paraffins, isoparaffins, polycycloparaffins) can enable us to predict performance in oxidation tests and select additive treat rates accordingly.

We are involved in on-going work to understand the application of this additive technology to a broader range of base oils, and also to investigate further the compatibility with industry solutions in the field such as electrostatic filtration, ion exchange oil purification and also new condition monitoring methods. Afton Chemical has several decades of experience in formulating turbine oil additive technology which has been highly successful in the field. Our efforts will now focus on acquiring similar field performance for our newest technologies. In conclusion, an extensive study on the chemistry of formation of varnish and related deposits in turbines has been carried out as well as development of laboratory methods to simulate deposit formation in operation. This knowledge is then applied together with an understanding of base oil chemistry to formulating oils which can perform well in challenging industry tests and exceed the more stringent turbine manufacturers' specifications whilst controlling not only sludge and varnish deposit formation but also air and water separation, foam and corrosion. A synergistic combination of suitable additive and base oil technology therefore yields turbine oil formulations which are capable of overcoming the challenges which modern turbine lubricants face.

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