

Varnish Mitigation: Relative Effectiveness of Non-Deposit-Forming Next Generation Lubricants vs. the Use of Varnish-Removal Filters with their Conventional Counterparts

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Abstract

Turbine lubricants employ a variety of base fluids. Mineral oil-derived base stocks remain the most prevalent, however, synthetics are becoming increasingly common. These fluids are exposed to severe oxidative stress during service, leading to breakdown and varnishing (the primary cause of downtime in gas turbine applications). Recently, PAGs have been positioned as varnish-free alternatives to more conventional mineral turbine oils. Our findings suggest that this claim is overstated. PAGs possess several advantages relative to conventional oils, however, well-formulated mineral oils proved almost as resistant to varnishing. Moreover, the risks associated with mineral oil varnishing can be effectively mitigated using established varnish-removal technologies.

Keywords:

Gas Turbine Oil; Polyalkylene Glycol; Soluble Varnish Removal.

1 INTRODUCTION

Modern lubricants are formulated using a variety of base fluids and additives [1]. Many different base stocks are available. Those derived from crude oil (Groups I, II and III) are the most common as a result of their favorable lubrication properties and relatively low cost. Group IV and V fluids are made up of synthetic hydrocarbons and non-hydrocarbon synthetics, respectively. These synthetics generally feature improved performance and resistance to breakdown relative to their naturally-derived Group I – III analogs. These improved characteristics, however, typically come at a higher cost.

In gas turbine applications, the trend towards smaller, more powerful units and peaking in place of base load service has resulted in increased lubricant stress. Indeed, modern gas turbine peak temperatures may reach 150 - 280°C [2]. During service, thermo-oxidative lubricant breakdown yields polar degradation products (acids and other varnish precursors) from non-polar base fluid hydrocarbons. With regards to polarity, “like dissolves like”, therefore, polar degradation products often precipitate from non-polar hydrocarbon oils. As these

breakdown products fall out of solution, organic varnish deposits form, leading to numerous problems including: filter plugging, restricted oil flow, poor heat transfer, valve sticking, fail-to-start conditions and costly unit trips [3]. Varnish is now the leading cause of unplanned downtime in the power generation industry.

Polyalkylene glycols (PAGs) are specialized Group V synthetics that have been positioned as more oxidatively stable, non-varnishing substitutes to conventional turbine lubricants [4]. PAGs are polyethers which feature oxygen amongst the carbon and hydrogen in their base oil molecular structure (Figure 1). As a result, they are more polar than hydrocarbon mineral oils. Like mineral oils, thermo-oxidative PAG stress yields polar breakdown products. PAG lubricants are, however, better able to dissolve these polar varnish precursors as a consequence of their own polarity. As a result, PAGs are often referred to as “non-varnishing” lubricants. While PAGs may indeed offer technical advantages over conventional turbine lubricants (lower coefficient of friction, greater viscosity index, faster air release), relatively inexpensive varnish removal technologies have been shown to effectively mitigate the risks associated with varnishing [5].

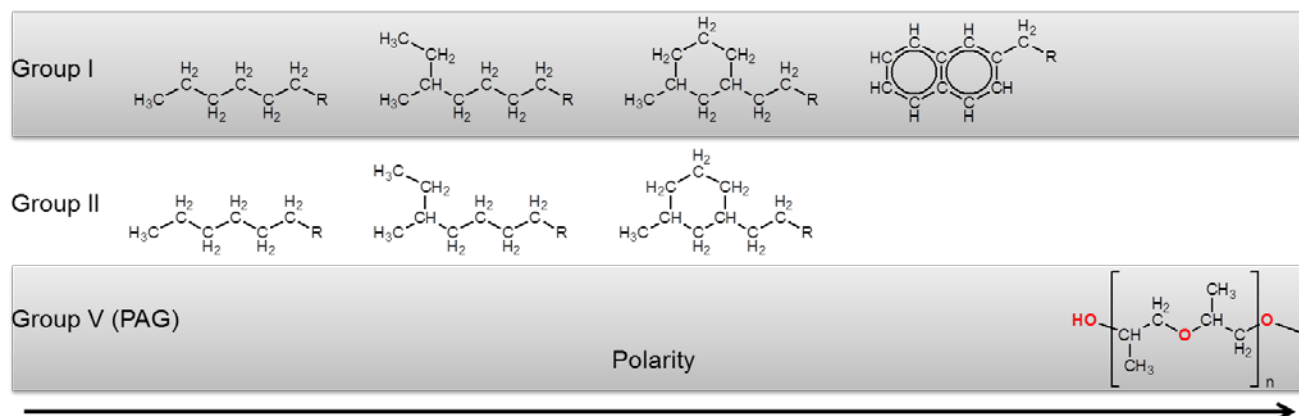


Figure 1 : Molecular Structure of Mineral Oils vs. PAGs (Where R is an Arbitrary Organic Fragment).

To date, head-to-head comparisons of established hydrocarbon turbine lubricants and newer PAGs are lacking. PAGs undoubtedly represent an advancement in lubrication technology, however, their increased cost relative to the use of varnish-removal filters and well-formulated mineral oils has not yet been justified. Moreover, claims that PAG lubricants are non-deposit-forming require empirical confirmation.

2 THERMO-OXIDATIVE LUBRICANT BREAKDOWN: VARNISH FORMATION IN MINERAL OILS VS. PAGS

PAGs are often described as being more oxidatively stable than mineral oils. In an effort to evaluate the oxidative stability of PAGs relative to more conventional oils, EPT subjected 3 commercially available virgin gas turbine lubricants to severe thermo-oxidative stress. The 3 turbine oils evaluated included a Group I oil (A), a Group II oil (B) and a Group V PAG (C). Dry air was passed through the stirred turbine oils while they were heated to 150°C in the presence of an ASTM-standard copper strip [6]. The test temperature of 150°C was selected to be representative of the peak temperatures experienced by gas turbine lubricants during service. Aliquots of the degrading lubricants were collected regularly to monitor their properties. The following tests were used to evaluate the condition of the lubricants:

- Varnish potential analysis by membrane patch colorimetry (MPC) [7];
- Potentiometric acid number analysis [8];
- RULER antioxidant additive analysis [9].

2.1 Group I Turbine Oil

As anticipated, the Group I turbine oil A was the least stable of the 3 commercial turbine oils examined (Figure 2). Indeed, critical levels of organic varnish were detected in this fluid by MPC analysis after only 2 hours at 150°C. While the varnish potential of this oil increased rapidly, its acid levels were quite stable initially. Once the oil's amine antioxidant additive depleted, however, its acid number increased dramatically. This acid number increase occurred despite the continuing presence of phenol antioxidants. These results suggest that the amine additive plays a key role in mitigating acid build-up in this lubricant. The phenol additive appeared to be ineffective with regards to acid management and synergistic regeneration of the more vital amine additive. Clearly both additives were poorly suited to manage the build-up of the organic breakdown products which produce varnish as the fluid's MPC varnish potential became critical before any additive loss occurred.

2.2 Group II Turbine Oil

Unlike the Group I fluid examined earlier, the Group II turbine oil (B) proved to be quite robust (Figure 3). While the varnish potential of A reached critical levels in only 2 hours, 384 hours were required to breakdown B to a similar degree. Even after 1,224 hours at 150°C, no significant change in the acid number of the Group II oil was noted. This is in stark contrast to the Group I lubricant whose acid number increased by more than 60 times following 97 hours of thermo-oxidative stress. The antioxidants present in B also appeared to function as intended with phenols depleting prior to amine additives. An inverse correlation between the oil's antioxidant amine

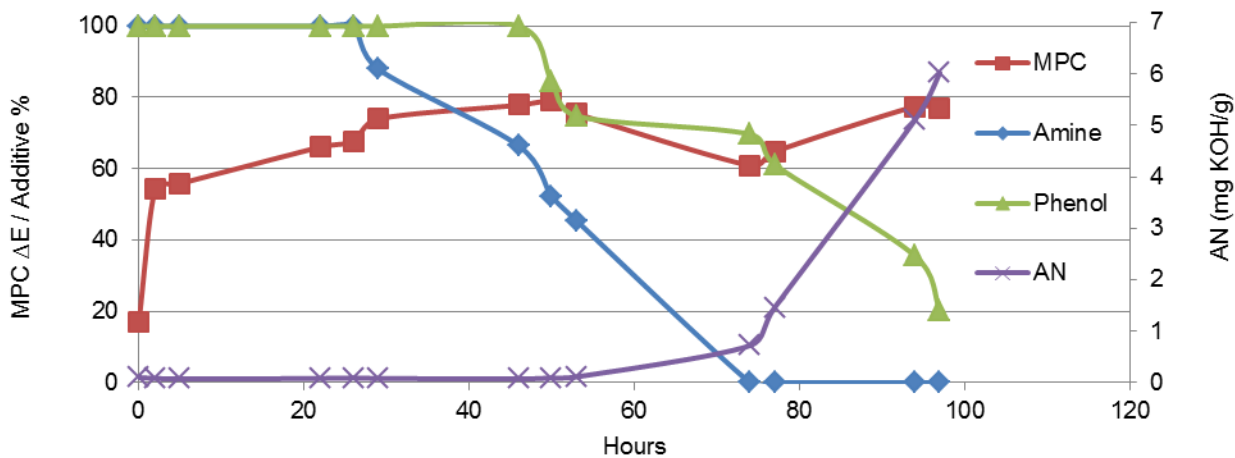


Figure 2 : Properties of the Group I Commercial Turbine Oil (A) During Thermo-Oxidative Degradation.

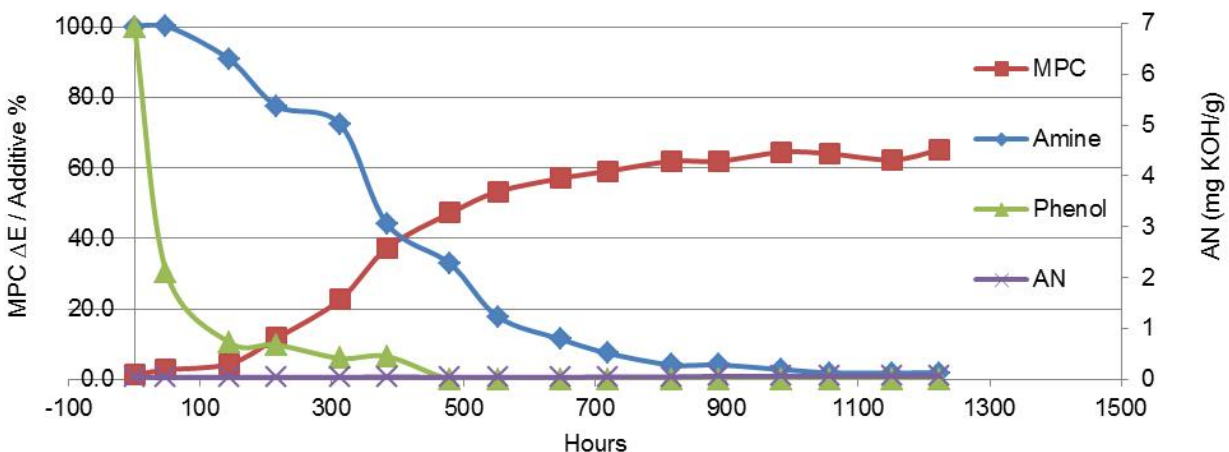


Figure 3 : Properties of the Group II Commercial Turbine Oil (B) During Thermo-Oxidative Degradation.

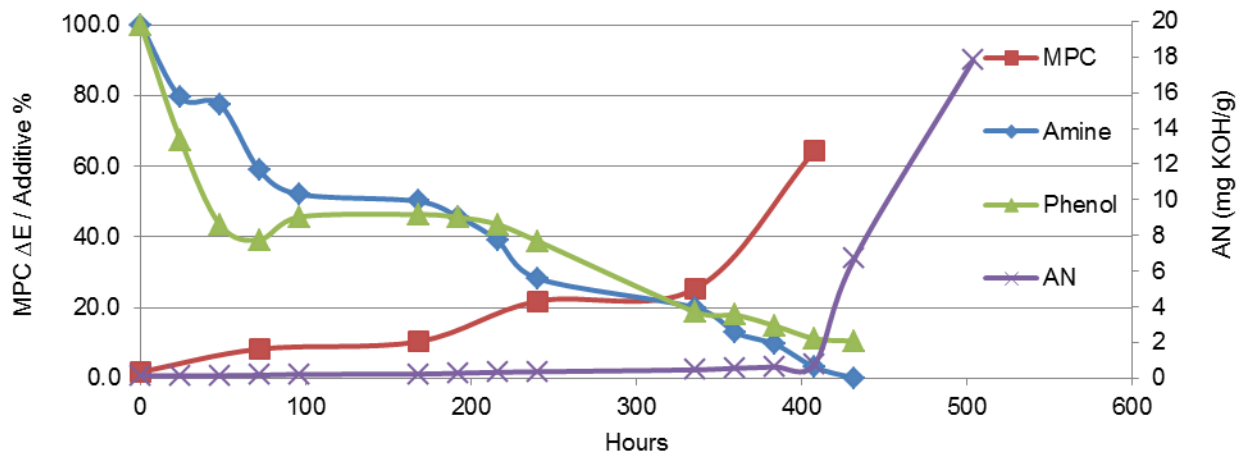


Figure 4 : Properties of the Group V Commercial PAG Turbine Oil (C) During Thermo-Oxidative Degradation.

levels and its MPC varnish potential was observed; as amine depletion proceeded, the fluid's MPC values increased accordingly. All-together, these results suggest that lubricant **B** is comprised of an oxidatively stable base stock which benefits from effective antioxidant protection.

2.3 Group V PAG Turbine Oil

Of the 3 turbine oils tested, PAG **C** was, as expected, the most resistant to the formation of varnish (Figure 4). Be that as it may, the PAG lubricant did not outperform mineral oil **B** by a significant margin in this regard; while 384 hours at 150°C were required for **B** to reach a critical MPC varnish potential, 408 hours under identical conditions were required for **C** to reach analogous varnish levels (Table 1). The observation of organic deposits on an MPC filter patch suggests that PAG lubricant breakdown can, indeed, lead to the formation of varnish on turbine surfaces; this is in contrast to the claims espoused by proponents of PAG use in gas turbine applications.

While PAG oil **C** and Group II lubricant **B** produced similar levels of varnish over a similar timeframe, the PAG fluid produced significantly more acid than **B**. Whereas critical acid levels never accumulated in **B**, critical acid levels were observed following 192 hours of PAG breakdown. Alarming, PAG breakdown accelerated exponentially beyond a certain point; within a 24 hour period, the acid number of **C** jumped from 0.79 mg KOH/g to 6.7 mg KOH/g. This jump appears to correspond with the exhaustion of the lubricant's amine antioxidant. Once the amine was exhausted, the PAG's acid number rapidly became extreme (17.83 mg KOH/g) and the lubricant became highly viscous. This level of acidic breakdown products was far beyond the highest observed for either

the Group I or Group II mineral oils (6.02 and 0.06 mg KOH/g, respectively). Steady increases in the varnish potential of **C** accompanied the fluid's acid number increases, suggesting that the deposits produced by PAGs are the result of breakdown mechanisms similar to those established for mineral oils. Despite the presence of critical acid levels after 192 hours, critical varnish potentials were not observed until 408 hours. This is a testament to the superior polarity/solvency of PAG lubricants. Indeed, **C** darkened significantly within 2 hours of heating, suggesting that breakdown products were already dissolved in the fluid at this time. By contrast, the Group II oil remained "clear and bright" after more than 1,000 hours at 150°C.

3 VARNISH REMOVAL

The prevalence and potential economic impact of varnishing in gas turbine applications is so significant that original equipment manufacturers (OEMs) recommend the use of varnish removal systems to mitigate risk [10]. These removal systems can be categorized as either particulate removal systems or soluble varnish removal (SVR) systems. Particle removal systems function on the basis of mechanical filtration, removing insoluble varnish but leaving its soluble precursors (breakdown products) behind. Since varnish can be dissolved in fluids at higher operating temperatures, these systems are most effective during shutdowns and are ill-suited to continuous use during operation. These systems cannot remove dissolved varnish feedstocks; they eliminate the effect (insoluble varnish) but not the cause (soluble varnish/breakdown products) of varnishing problems.

Turbine Oil	Property	Most Degraded Measurement	Degradation Hours to Critical
Group I A	MPC ΔE	79.0	2
	AN (mg KOH/g)	6.02	74
	Antioxidant %	0 (Amine); 20 (Phenol)	74
Group II B	MPC ΔE	65.2	384
	AN (mg KOH/g)	0.06	> 1,224
	Antioxidant %	2 (Amine); 0 (Phenol)	552
Group V PAG C	MPC ΔE	64.5	408
	AN (mg KOH/g)	17.83	192
	Antioxidant %	0 (Amine); 11 (Phenol)	336

Table 1: Degradation Time Required for Turbine Oil Properties to Reach Critical Values.

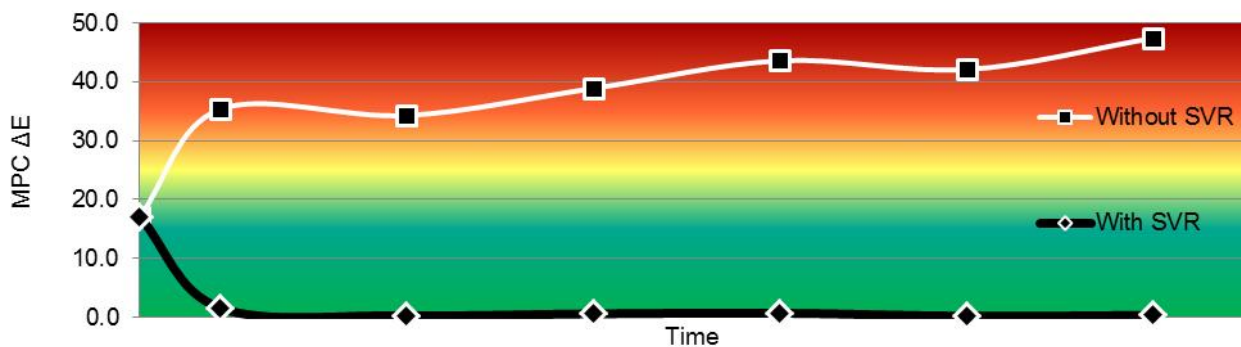


Figure 5 : MPC Varnish Potential of Group I Oil A Samples Degraded With and Without SVR Treatment.

SVR systems are engineered to remove soluble contaminants and degradation products (including varnish and acids) from lubricants. Unlike particulate removal systems, SVR systems are effective at turbine operating temperatures, meaning that they can be employed continuously. This makes these systems ideally suited for lubricant restoration or maintenance. By removing soluble breakdown products, SVR systems effectively mitigate the risks associated with lubricant varnishing.

In an effort to demonstrate the potential benefit of SVR treatment, duplicate samples of the Group I mineral oil A were degraded at 90°C. The duplicate samples were subjected to identical conditions with and without laboratory-scale SVR treatment. A was selected as its poor oxidative stability was expected to lead to observable varnish formation within a reasonable experimental timeframe. The MPC varnish potential of the duplicate samples was monitored regularly as thermo-oxidative degradation proceeded (Figure 5).

This side-by-side breakdown experiment yielded dramatic results. As anticipated, the varnish potential of the untreated fluid increased rapidly, reaching critical levels within 72 hours. Beyond this initially rapid MPC increase, breakdown products continued to accumulate at a relatively steady rate.

By contrast, the varnish potential of the SVR-treated oil actually decreased following the application of thermo-oxidative stress. By the time that the untreated sample's varnish potential had become critical, the SVR-treated oil featured a near-zero MPC ΔE. The initial MPC decrease noted occurred as a result of SVR removing the relatively low levels of breakdown products that were already present in the initial new oil sample. Impressively, as the degradation continued, SVR treatment maintained the lubricant's near-zero varnish potential for the duration of the experiment (1,272 hours). These results clearly demonstrate the advantages of continuous SVR filtration, which allows varnish and its precursors to be effectively removed as they form, preventing varnish problems altogether.

Fluid	AN (mg KOH/g)	Amine (%)	Phenol (%)
PAG C	0.14	100	100
SVR-Treated C	0.13	100	100
Change	- 7%	- 0%	- 0%

Table 2: Properties of Virgin PAG Turbine Oil C Prior to and Following Laboratory-Scale SVR Treatment.

Although the more oxidatively robust PAG oil C could not be broken down/treated by SVR within a reasonable experimental timeframe, lab-scale SVR treatment of the virgin PAG lubricant confirmed that it is compatible with SVR filtration media (Table 2). These results suggest that, in addition to being beneficial with mineral oils, SVR treatment can be used to maintain PAG lubricants as well.

4 SUMMARY

Modern turbine lubricants are formulated using a variety of base fluids and additives. Mineral oil-derived base stocks (Groups I, II and III) remain the most prevalent, however, hydrocarbon and non-hydrocarbon synthetics (Groups IV and V, respectively) are becoming increasingly common in gas turbine applications. These fluids are exposed to high levels of thermo-oxidative stress during service, leading to lubricant breakdown and varnishing which has been identified as the primary cause of downtime in the power generation industry. Among the Group V oils employed, PAGs have been positioned as varnish-free alternatives due to their inherent oxidative stability and superior base stock solvency.

In an effort to better understand the manner in which different turbine oils breakdown under thermo-oxidative stress, 3 commercially available virgin turbine lubricants were subjected to conditions representative of those present in an operating gas turbine. As anticipated, the Group I mineral oil A exhibited the poorest oxidative stability. Indeed, this fluid broke down rapidly (< 2hours) under the test conditions. The more highly refined Group II mineral oil B, on the other hand, proved quite robust requiring nearly 200 times longer (384 hours) than its Group I analog to degrade. Lastly, the PAG alternative C proved to be the most resistant to varnishing, requiring 408 hours to reach a critical varnish potential. Despite this finding, we must note that PAG C did not outperform mineral oil B by a significant margin in this regard. Indeed, while C slightly outperformed B from an MPC perspective, B dramatically outperformed C from an acid number standpoint. The ability of PAG C to hold such high acid levels is, no doubt, evidence of its superior base fluid solvency. The eventual observation of organic deposits on an MPC filter patch, however, suggests that PAG C is not non-varnishing as claimed.

While the production of varnish from mineral oil breakdown is well-established, OEM-recommended technologies provide a convenient means of managing the risk of varnish-related failures in gas turbine applications. Varnish-removal technologies can be divided into particulate-removal systems and soluble varnish removal (SVR) systems. The latter are more effective under turbine operating conditions since varnish tends to be dissolved in turbine oils at operating temperatures. In an

effort to demonstrate the effectiveness of SVR treatment, duplicate samples of turbine oil **A** were degraded under identical conditions; one sample was continuously treated with SVR while the other was not. As before, the untreated sample broke down rapidly, reaching a critical varnish potential. The varnish potential of the SVR-treated sample, however, fell to near-zero levels and remained there over the duration of the experiment (1,272 hours). Lab-scale tests also suggest that SVR filtration is compatible with PAG turbine oils and that these fluids would benefit from SVR treatment in the same manner that mineral oils do.

While PAG turbine oils undoubtedly offer advantages relative to their more-established mineral oil analogs, their performance in these trials was not notably superior to well-formulated mineral oils with highly refined base stocks. Moreover, the evidence presented herein suggests that the description of PAG turbine oils as non-varnishing fluids is overstated. Like other lubricants, severe thermo-oxidative stress leads to the formation of organic deposits (varnish) in PAGs. The solvency of PAGs is, undoubtedly, superior to that of mineral turbine oils, however, soluble varnish removal provides an effective means of overcoming this limitation in the latter.

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