PENNZANE^{TM} LUBRICANT COMPOSITIONS: THE PROS AND CONS OF "HERITAGE" TECHNOLOGY

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ABSTRACT

One of the often-overlooked requirements of lubricant performance for space mechanisms is the time spent in a storage room or on the launch pad. Pennzane^{TM} lubricants are fortified with antioxidants, enabling them to withstand long periods on Earth. Lubricants designed for flight must meet additional demands, the most critical of which are stability in vacuum and low propensity to outgas and condense on critical equipment. Heritage Pennzane^{TM} formulations have satisfied these requirements; however, their solution stability is poor and is a significant drawback. In this paper we will explore different antioxidant technologies suitable for use in Pennzane^{TM} lubricants. Three different viable alternatives were identified and benchmarked against the heritage technology, offering solutions for the future.

1 INTRODUCTION

Since 1991, Space mechanism engineers have had access to lubricants formulated with Pennzane^{TM} base oils. Pennzane^{TM} based lubricants offer advantages over traditional lubricants in multiple critical areas for Space applications, including excellent vacuum stability as well as superior wear protection and life performance.[1]–[5] Examples of these lubricants that are available today, such as Synthetic Oil 2001 and Rheolube® 2000, offer the reassurance of thousands of flight hours and proven reliability for critical Space applications. This heritage is challenging to match and is indisputable, but there are some negative aspects to using this technology.

Notably, these lubricants employ a robust antioxidant package composed of a blend of phenolic and aminic components, herein referred to as the "heritage antioxidant." This heritage antioxidant offers protection and stability to the formulation during the lubricant's time on Earth; whether it be in a storage room or on a launch pad, oxidation resistance ensures that the lubricant will perform as intended once the mechanism is launched into Space. This heritage antioxidant serves its purpose, but there is a drawback – its solubility in Pennzane^{TM} is limited, resulting in occasional crystallization (Fig. 1) or cloudiness in oil formulations.

This crystallization or cloudiness occurs because the heritage antioxidant is used at a treat rate that is approaching the limit of the maximum amount that can be stably dissolved in Pennzane^{TM}. As a result, the slightest changes in environment or conditions can sometimes cause the antioxidant to "crash out" of solution and return to its solid, undissolved form. This is problematic particularly in oil formulations since unanticipated solids can catastrophically impact lubricant performance.

Figure 1. *Example of crystals in Synthetic Oil 2001*

Fortunately, over the last thirty years, additive technology has advanced and formulators have access to many alternative antioxidant technologies. In this work, alternative antioxidants were screened in Pennzane^{TM} lubricants and benchmarked against the heritage antioxidant. Critical performance parameters were defined to include solubility, outgassing, and oxidation resistance (Tab. 1).

Table 1. *Critical Performance Parameters for Alternative Antioxidants in Pennzane^{TM} Formulations*

Performance Parameter	Test Method	Requirement
Solubility	Visual Inspection	Stable for 24 months
Oxidation Resistance	ASTM D6186 (150 °C)	> 500 min
Outgassing	ASTM E595	TML < 1% CVCM < 0.1%

Ultimately, any viable alternative would ideally be a "drop-in" replacement for the heritage formulation, demonstrating comparable behaviour across all lubricant properties. Prototype Synthetic Oil 2001 formulations containing promising alternative antioxidant technologies were prepared and underwent thorough testing beginning with the critical properties listed above, followed by an expanded test regimen including evaluation of pour point, kinematic viscosity (KV) measurements across multiple temperatures, as well as wear protection evaluation, indicated by performance on the Spiral Orbit Tribometer (SOT) ASTM F2661 and Vacuum 4 Ball Wear Tribometer.

2 EXPERIMENTAL METHODS

2.1 Sample Preparation

Experimental lubricant samples were prepared using commercially available raw materials as received. Ingredients were combined in the appropriate ratios and mixed with heat (if necessary) to form a uniform solution. Once prepared, samples were stored in amber vials.

2.2 Oxidative Stability

Oxidative stability was assessed following ASTM D6186, Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)[6]. In this technique, thermal transitions of a material can be detected by a sensitive calorimeter. The sample is placed in a pan and held at a constant temperature (150 °C or 175 °C, as indicated) under a 100 mL/min flow of 99.99% purity Oxygen held at a pressure of 3500 kPa. An exotherm, indicating oxidation of a sample, is characterized by needing less heat applied to maintain temperature. The test was run for 24 hours or until an exotherm was observed.

2.3 Solution Stability

Samples for solubility observations were stored in amber vials, kept in a dark drawer. At periodic intervals, the sample bottles were taken out for examination and a sample of oil removed for observation. The sample would be drawn into a glass Pasteur pipette and examined visually for evidence of solids.

2.4 Pour Point

Pour point data was collected per ASTM D97, Standard Test Method for Pour Point of Petroleum Products[7]. In this test, a sample is warmed to 45 °C, then gradually cooled. As the sample is cooled, it is examined periodically and tested for motion when the jar is tilted. The temperature prior to the point at which the sample becomes motionless when the jar is moved is considered the “pour point”. Once the sample is motionless, 3 degrees Celsius are added to give the reported Pour Point.

2.5 Outgassing

Outgassing performance was evaluated following ASTM E595, Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment[8]. In this test method, a sample of known mass is heated to 125 °C and subjected to vacuum, with a chilled (25 °C) plate of known mass suspended above it. After exposure to these conditions for 24 hours, the sample is weighed again to determine total mass loss (TML), and the plate is weighed again to determine the collected volatile condensable materials (CVCM). Historically, a TML maximum of 1.00 % and CVCM maximum of 0.10 % have been the accepted thresholds for Space flight materials.

2.6 Kinematic Viscosity

KV data is obtained when a fixed volume of liquid is allowed to flow under gravity through a calibrated glass capillary viscometer a specified temperature. Data collected at -40 °C was obtained following ASTM D445, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids[9]. Data collected over the range of -20 °C to +100 °C was obtained following ASTM D7042, Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)[10], using a Stabinger automated viscometer.

2.7 Spiral Orbit Tribometer

Lubricant life was evaluated per ASTM F-2661, Determining the Tribological Behaviour and the Relative Lifetime of a Fluid Lubricants using the Spiral Orbit Tribometer (SOT) [11] (Fig. 2). This method is a tribological test comprised of a lubricated ball clamped between two parallel plates operating in the boundary lubrication regime. As one plate rotates (typically 100 RPM), it causes the ball to roll in a near-circular orbit, which is actually an opening spiral (Fig. 3). A typical contact pressure of 1.5GPa is achieved by the stationary disc loading the system. Upon every rotation, the ball, which is lubricated with ~ 50µg of lubricant, makes contact with the scrub, or guide plate. This stationary plate forces the ball back into its original orbit radius. The scrub plate is mounted on a force transducer which records the reactionary force required to “scrub” the ball back into its starting orbit radius. Using the applied force, and the reactionary scrub force, the coefficient of friction (CoF) is calculated for each rotation. The test concludes when 3 consecutive rotations have a CoF of 0.28 or greater. It is at this point that it can be concluded that the initial charge of lubricant has been depleted by tribodegradation and the system is essentially running unlubricated. The resultant data point is calculated by dividing the total number of orbits before failure by the total number of µg of lubricant applied at the beginning of the test, giving units of orbits/µg.

Figure 2. *Spiral Orbit Tribometer*

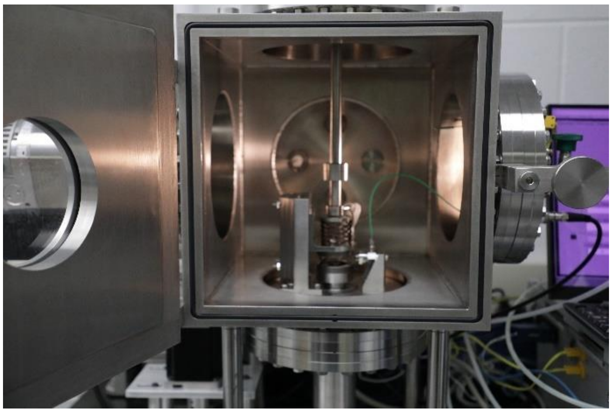
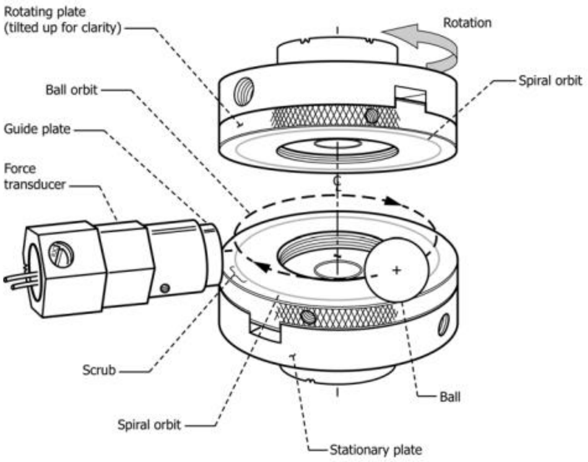


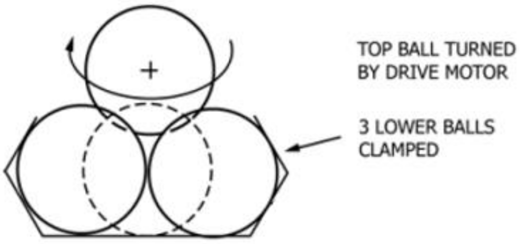
Figure 3. *Detail of the Spiral Orbit Tribometer*[11]



2.8 Vacuum 4 Ball Wear

Wear testing on the Vacuum 4 Ball Tribometer (a custom built rig controlled with a LabView DAQ system) was used to evaluate lubricants' performance under conditions more closely resembling the environment in space. In the test method used for this work, a vacuum level of $6.7x10^{-4}$ Pa was achieved before initiating the test, typically by the end of the test the vacuum level had further dropped to $1.3x10^{-4}$ Pa. Selection of other parameters was based off of ASTM D4172, Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method)[12], with some modifications, largely made to reduce the amount of sample needed to a volume of 4 mL. The contact geometry from ASTM D4172 was maintained, with 3 stationary balls clamped in the bottom of the sample cup while a fourth ball is centred on top of them with axial load applied as it is rotated (Fig. 4). For specimens, 7.9375 mm (5/16 inches) 52100 Alloy Steel balls were used with a hardness of Rockwell C60. An applied load of 290 N was used for testing, resulting in an initial contact pressure of 4.2 GPa. The test was run for three hours at room temperature and a speed of 600 rpm. After completion of the test, wear scar diameters on the lower three balls were measured using a microscope and the average reported. Each sample was run in duplicate.

Figure 4. *Vacuum 4 Ball Test Specimen Geometry* [12]



3 RESULTS AND DISCUSSION

A total of 14 different alternative chemistries were first evaluated in Pennzane™ X2000 oil and were screened for solubility, outgassing and PDSC performance. Of the fourteen (14) alternatives screened, eight (8) were eliminated immediately due to not meeting the level of oxidation protection offered by the heritage antioxidant package. One (1) alternative offered comparable oxidation performance and acceptable solubility, but its outgassing performance was inferior when compared to that of the heritage antioxidant package. Two (2) alternatives offered comparable oxidation resistance, but failed solubility testing. It is worth noting that these solubility-failing alternatives were solids prior to being incorporated into the oil, like the heritage antioxidant package. The majority of the alternative antioxidants screened were in the liquid form; it is anticipated that this property may contribute to better solution stability in Pennzane™.

Three (3) of the alternatives screened offered far superior oxidation protection and excellent solubility, but their outgassing performance not as good as that of the heritage antioxidant package. For these alternatives, their treat rates were further optimized to balance oxidation resistance and outgassing performance, ultimately resulting in three options offering superior performance over the heritage antioxidant package in all three critical properties (Tab. 2). It is worth noting that the baseline sample with heritage antioxidant had good solution stability for the first 12 months of monitoring, but over the course of the second year crystal formation was observed.

Table 2. *Performance of alternative antioxidant packages in Pennzane™ X2000 Oil*

Sample Name	**Solution stability 24+ months (Visual)**	**Exotherm Time (ASTM D6186, 150 °C)**	**Outgassing (ASTM E595, TML, CVCM)**
Heritage Antioxidant	Fail	520 min	0.457%, 0.121%
Antioxidant A	Pass	586 min	0.299%, 0.021%
Antioxidant B	Pass	637 min	0.370%, 0.149%
Antioxidant C	Pass	869 min	0.354%, 0.147%

Once optimal treat rates were determined and top alternative antioxidant packages were identified, fully formulated Synthetic Oil 2001 Prototype samples were generated, incorporating the heritage antiwear additive that is typically included in Pennzane^{TM} formulations for space applications. These samples (Synthetic Oil 2001 Prototype A, B, and C) were subjected to a full testing regimen, covering solution stability, PDSC and outgassing (Tab. 3), vacuum 4 ball wear (Fig. 5), and Spiral Orbit Tribometer (Fig. 6). In all respects, all three Prototypes offered comparable, if not superior performance over the heritage formulation. In the SOT performance, the data may appear to suggest some differences in lubricant life among the four samples, but these variations are within normal limits for this test, especially when evaluating Pennzane^{TM}-based samples with exceptionally long life. Additional replicates of this test are underway to improve robustness of the results.

Table 3. *Performance of Synthetic Oil 2001 Prototype Formulations*

Sample Name	**Solution stability 24+ months (visual)**	**Exotherm Time (ASTM D6186, 150 °C)**	**Outgassing (ASTM E595, TML, CVCM)**
Synthetic Oil 2001 Heritage Formulation	Pass	565 min	1.748%, 0.817%
Synthetic Oil 2001 Prototype A	Pass	581 min	1.311%, 0.604%
Synthetic Oil 2001 Prototype B	Pass	732 min	1.564%, 0.764%
Synthetic Oil 2001 Prototype C	Pass	704 min	1.500%, 0.752%

Figure 5. *Vacuum 4 Ball Wear Performance*

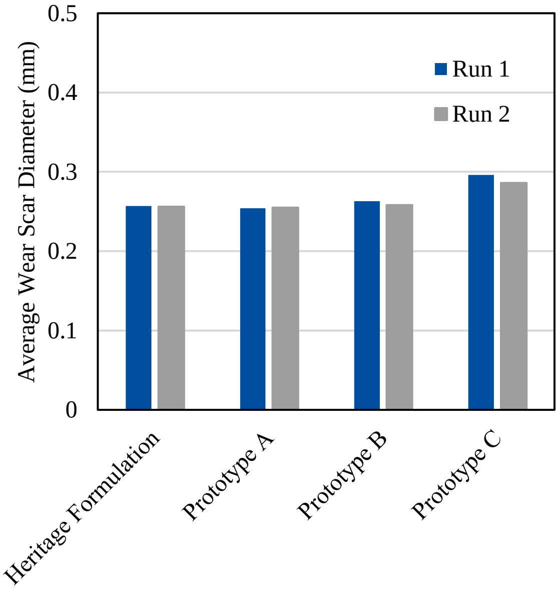
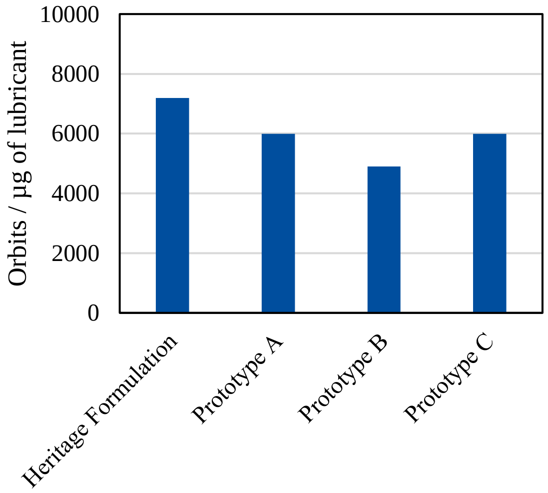


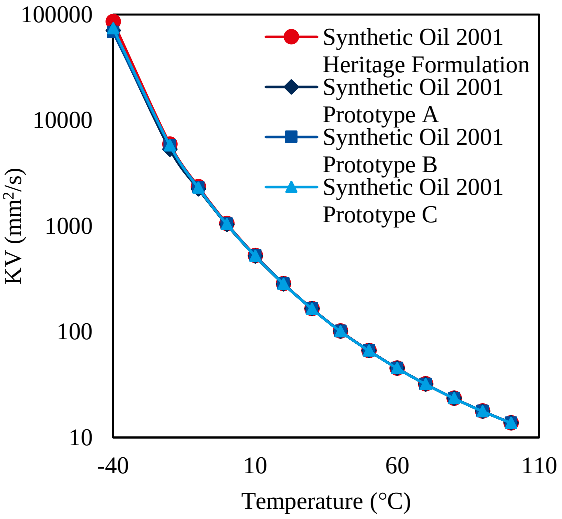
Figure 6. *SOT (ASTM F2661) Performance*



Since solution stability was one of the properties that motivated this study, it was investigated two-fold. Initial work involved monitoring prototype formulations long term; at the time of this paper's submission, monitoring had been completed for 24 months and was ongoing. At 24 months, no samples, including the heritage formulation, showed signs of instability such as cloudiness or formation of crystals. To more aggressively test solubility of alternative antioxidants in Pennzane™, a secondary set of prototype samples were prepared, in which the antioxidant treat rate was quadrupled. Since it is known that the heritage antioxidant is on the borderline of becoming a saturated solution at heritage treat rates, increasing the concentration of antioxidant should generate conditions where solution instability will become more evident. Indeed, when the antioxidant treat rate was quadrupled in the heritage formulation (Synthetic Oil 2001-4xAO), heat was used to prepare the sample and dissolve the antioxidant, resulting in a clear solution. However, immediately upon cooling to room temperature, the antioxidant “crashed out” and the mixture turned cloudy. In contrast, all three prototype samples with quadrupled antioxidant treat rates, Synthetic Oil 2001 Prototype A-4xAO, B-4xAO, and C-4xAO, remained clear solutions upon cooling to room temperature. These prototype samples with elevated antioxidant concentrations were monitored weekly for an additional three weeks with no change to their appearances; monitoring was continued.

With confidence in critical performance properties established, the prototype formulations (without quadrupled antioxidant treat rates) then underwent further viscosity and low temperature performance evaluation. The heritage Synthetic Oil 2001 and all three Synthetic Oil 2001 Prototypes (A, B, C) had the same pour point (ASTM D97) of -54 °C; indicating that the change in antioxidant additive package had no impact on the lower limit of the lubricant usable temperature range. Temperature vs. KV curves for heritage Synthetic Oil 2001 and all three Synthetic Oil 2001 Prototypes (A, B, C) overlay nearly perfectly (Fig. 7). The only exception being at the coldest part of the curve, where all three prototype formulations offer a slightly lower KV when compared to Heritage Synthetic Oil 2001. This data suggests that all three Synthetic Oil 2001 Prototypes (A, B, C) are promising candidates for replacement of heritage Synthetic Oil 2001 in Space applications.

Figure 7. *Kinematic Viscosity vs. Temperature Properties*



4 CONCLUSIONS

While the same heritage antioxidant has been used in Pennzane^{TM} formulations for decades, this work has demonstrated that there are multiple viable alternative technologies available. Of the alternative antioxidant additive packages evaluated, three (3) different options were identified as contenders for replacement of the heritage antioxidant package, offering comparable or superior performance in all aspects evaluated; most importantly, all demonstrated significantly improved solution stability over that of the heritage formulation. Additionally, all alternatives offer comparable or improved oxidation resistance and outgassing performance without compromising wear protection, pour point, or KV properties. These alternative technologies should be strongly considered by Space mechanisms engineers, particularly for missions that may be on a longer timeline or at risk for experiencing longer delays, causing lubricants to spend more time in storage on Earth.

5 ACKNOWLEDGEMENT

The work reported in this paper was a highly collaborative effort that was supported by multiple members of the Nye Lubricants (Member of the FUCHS Group) R&D team. All experiments were designed in collaboration with Jayna DeMedeiros. Sample preparation, solution stability, oxidative stability, pour point, and kinematic viscosity testing was supported by Paul Moses. Outgassing testing was supported by Jayna DeMedeiros. The SOT test rig used in this study was built by Gus Flaherty and the testing was supported by Richard Raithel. The Vacuum 4 Ball Wear Tribometer used in this study was designed, built, and validated by Mason Wood, who also advised on the test conditions used and performed all of the testing on this rig.

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