LUBRICATION BY SELF-ASSEMBLED MULTILAYER _ NEW AVENUE FOR LOW COST LUBRICATION ALTERNATIVE TO MoS2

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ABSTRACT

Lubricating space mechanisms is a real challenge due to the stringent requirement imposed by such application. Indeed, lubrication must be sustained in dry and humid air, in vacuum, and it must remain stable over long period of time, etc. Miniaturization and cost effectiveness impose the development of new lubricants.

In this study, lubrication based on self-assembled molecular layer made of alkylphosphonic acid (APA) deposited by spray has been evaluated as a new avenue to lubricate contact in air and vacuum. Easy to use, fully environmentally friendly, and known to lubricate highly loaded contact in metal blanking when dispersed in solutions, APA self-assembled agglomerates formed during evaporation of the solvent were shown to resist exposure to vacuum through their imaging under SEM. It was hence decided to evaluate their friction performances under space related conditions. Macroscale tribological tests in both humid air and in vacuum have been conducted under pure sliding and under rolling+sliding. Two contact pressure have been used 860MPa and 1100 MPa.

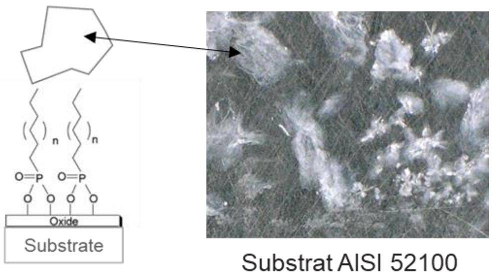
The results from the friction tests and post-test morphological analysis shows that the material demonstrates low friction in both environments, equivalent to MoS_2 in most cases. The study paves the way towards further tests at component level, with a targeted application related the NewSpace where on-shelf solutions can be appropriate for short to medium service life.

1 INTRODUCTION

The development of lubricants for the space industry is a highly specific challenge, given the mechanical and physicochemical environments in which the mechanisms operate. Whether on the ground in air, in a vacuum, in a thermal vacuum, or in space, systems evolve in a succession of extreme environments. A range of lubricants already exist, each with different specificities and fields of application: fluid lubrication (oils) for systems with relatively high operating speeds within a restricted temperature range, greases for lower speeds or where oil migration may be a problematic, solid materials (burnished deposits, PVD deposits, self-lubricating composites) for low speeds and wide temperature ranges, etc. All these solutions give rise to recurring constraints, such as: (i) maintaining performances in different environments, notably air and vacuum, (ii) ease of application and associated cost, (ii) thickness management in preload calculations.

In order to address these constraints, we propose to test a lubricant operating at the molecular scale, and which can be by simple spray application. It was initially developed to lubricate contacts subjected to high mechanical stress, particularly in stamping and blanking operations [1]. This patented lubricant (Unil Opal, CIPELIA, France) [2] is composed of Alkyl-phosphonic acid (APA) molecules dispersed in a solvent. This synthesis of the molecule and its dispersion within the solvent is an eco-friendly process, as well as its use, and discard. That makes it meet the REACH requirements.

As shown in Figure 1, when the solvent evaporates, the molecules self-organize themselves to create a self-organized layer on top of which, remaining molecules self-assemble to form agglomerates. Under friction it has been demonstrated that the higher the load, the lower the friction coefficient is [3]. The explored range of loading (700 MPa to 1.7 GPa) makes it a perfect fit for tribological application such as gear boxes or bearing applications. However, the existing literature concern short wear life applications (few cycles of friction), and none has explored longer test, except our study in 2019, published in 2023 [4,5]. In this study, we faced fretting wear anomaly on the dispenser of the satellite ANGELS, during the ejection tests on ground. APA were selected alongside grease as potential lubricant to solve the issue. Contact pressure was low (around 13 MPa). Nonetheless, APA offered low friction coefficient (<0.1) equivalent to the one obtained by grease, over 3000 cycles. The objective was 6000 to pass the test, but 3000 cycles demonstrate very promising performances from a molecular lubricant. Finally, as shown in Figure 1, it is possible to image the clusters, which means that the self-organized structure can sustain high vacuum (10^{-6} mbar), without undergoing morphological modification. Moreover, during friction tests, no fragment of molecules has been detected with the mass spectrometer. That can be in line with a potential absence of vacuum induced outgassing. Outgassing tests are nonetheless currently being conducted following ECSS-Q-ST-70-02C. For all those reasons, APA are attractive to be use as lubricants in space mechanisms.



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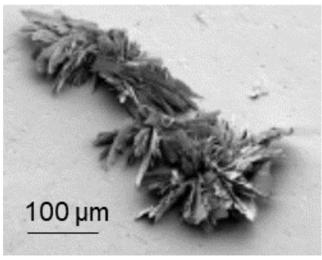

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Figure 1 - (a) schematic of the self-organisation of the molecules after evaporation of the solvent, with an associated optical image of large clusters ; (b) SEM image of a very large cluster, demonstrating the creation of platelets.

The objective of the present study is to evaluate the tribological performances (friction and wear) of APA molecules spray-deposited on stainless steel samples. Pure sliding and rolling+sliding experiments are conducted in two environments (humid air, and vacuum) under two different contact pressures.

2 EXPERIMENTAL METHODS

Friction tests have been performed on an in-house designed tribometer (Figure 2) which allows performing tests in pure sliding and rolling+sliding configurations. Table 1 summarizes the friction tests conditions. Three tests per conditions have been done to better assess the reproducibility of the tribological performances.

Prior to the tests, samples (disc, roller, and balls) were cleaned following a procedure developed by CNES [6]. Only the disc has been coated with APA molecules. They were sprayed with the APA solution in different steps. The nozzle was positioned 5 cm above the disc and for brief spray separated by 30s were done. After that, the sample were left in open air for 5 min to let the solvent evaporate. Only then they were ready to be tested. Figure 2 shows an optical image of the coated disc. It can be observed that the white agglomerates are evenly distributed over the surface of the disc.

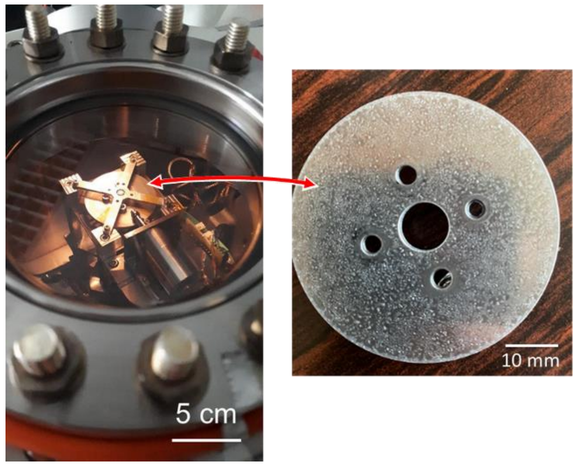


Figure 2 - Tribometer used for the study and optical image of the disc coated with APA molecules

Note that comparisons with grafting techniques using immersion of the disc in the solution for few hours, and followed by drying in open air have been done. Tribological performances of our sprayed samples are equivalent to immersed samples that underwent 2h30 of immersion. Longer immersion did not improve significantly the tribological performances.

Table 1 - Sample specification and conditions used for tribological tests

Substrates	disc	AISI 440C, 58HRC, Ra < 0.09 Ø 50 mm, track radius = 20 mm
	ball	AISI 440C, 58HRC, grade 10 Ø 5 mm
	Roller	AISI 440C, 58HRC, Ra < 0.1 Ø 5 mm, curvature r = 1.3 mm
Environments		Vacuum (4.10^{-7} mbar)
		Air 50%HR
Contact pressure		0.86 GPa
		1.1 GPA
Sliding speed		67 mm/s (32 rpm)
Sliding to Roll ratio		13%

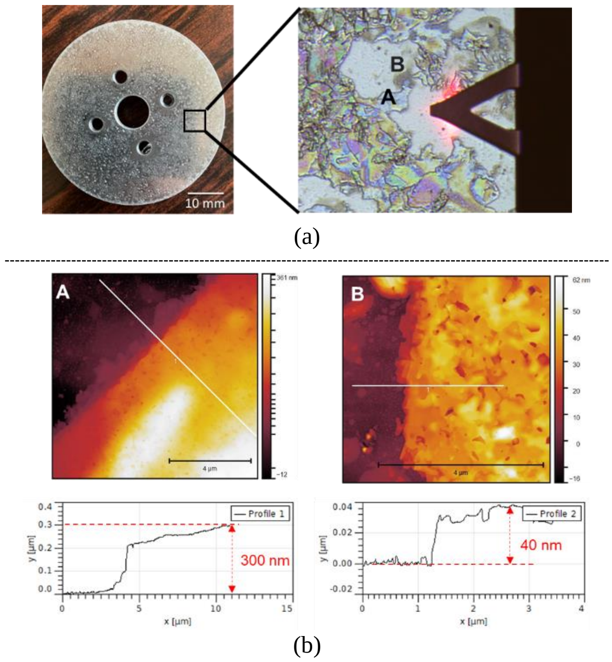


Figure 4 – (a) zoomed in optical image of the coated surface; (b) AFM image of the surface topography with a line profile of two different regions

In order to better understand the morphology of the APA agglomerates, they have been imaged using atomic force microscopy (AFM). As can be seen on Figure 4 all the surface is covered with APA molecules. Even the regions where the substrate can be seen, there thin agglomerates of 30 nm thickness. They are surrounded with even smaller clusters of only few nanometres in thickness. Large agglomerates exhibit thicknesses of 300 nm in average. Stacking and agglomeration of thick agglomerates can also be observed.

Thin and thick clusters nonetheless exhibit the same morphology. They are indeed comprised of stacking of individual perforated layers. Consequently, whatever the thickness, agglomerates exhibit the same elementary “constitutive brick”.

3 RESULTS

Figure 3 shows the mean friction coefficient obtained from the tribological test. All friction curves are presented, and only one standard deviation is presented so the reader can have an idea of the dispersion of the values of friction coefficient over one cycle. The standard deviation presented is representative of what is observed for all 3 three tests of the related test conditions. On the legend, “PS” means pure sliding, and “RG” stands for rolling+sliding.

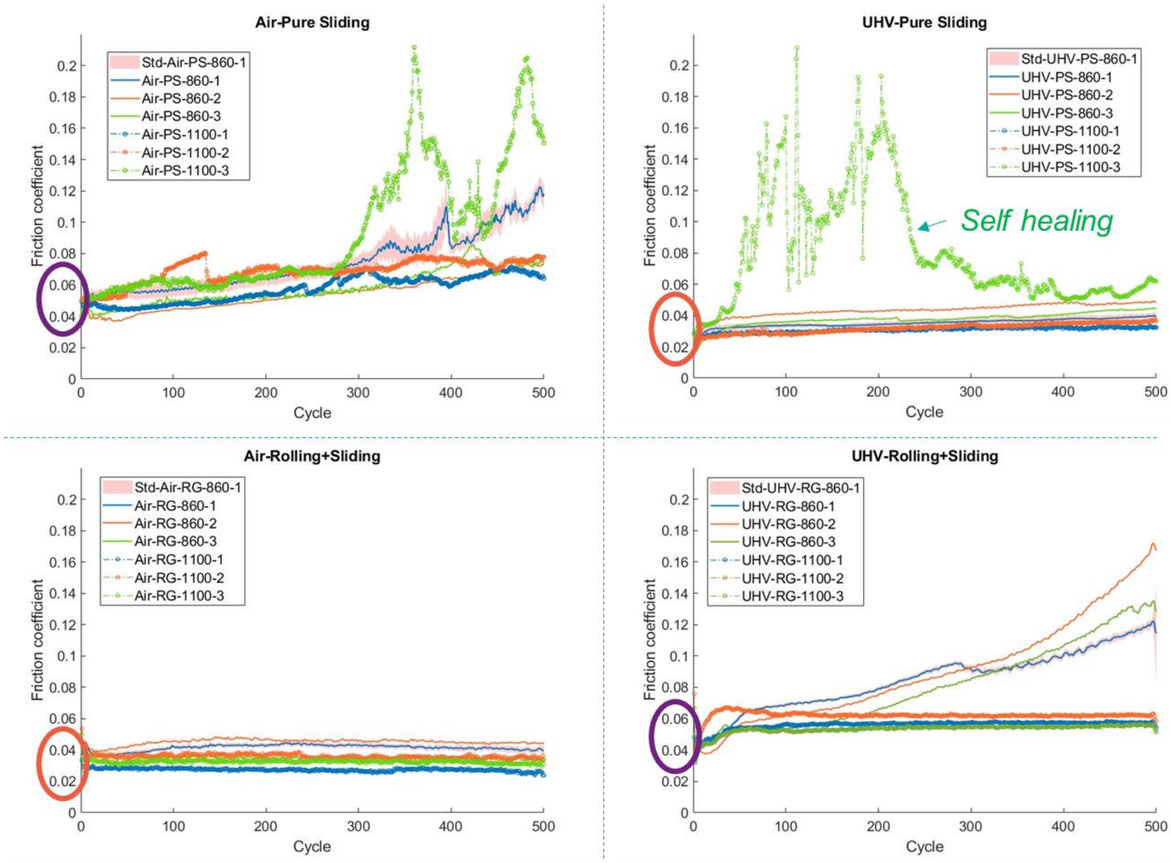


Figure 3 - friction coefficient obtained from tribological tests

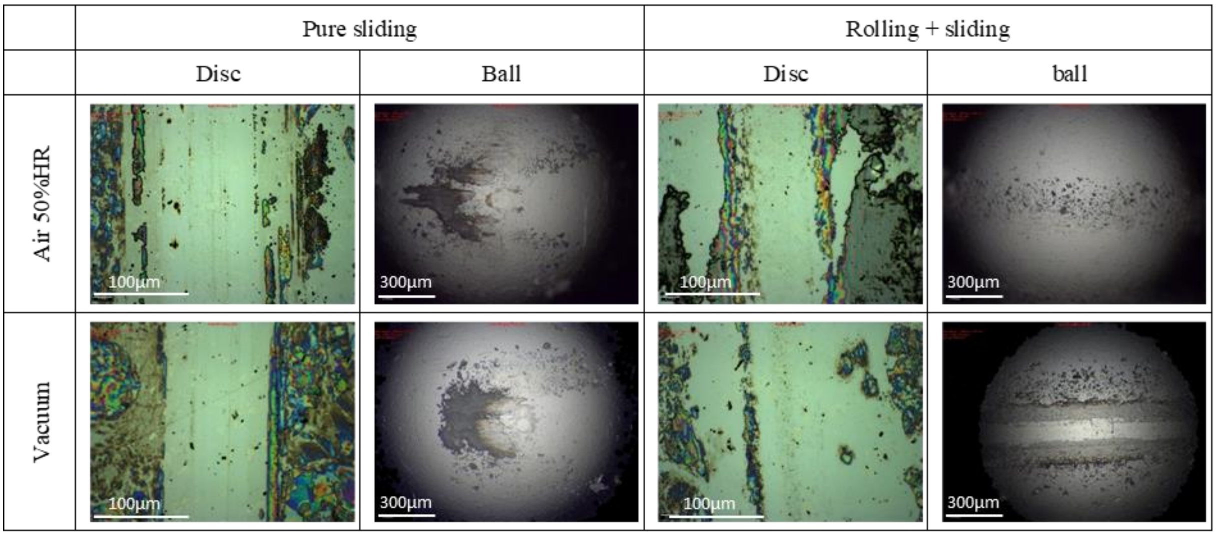


Figure 5 - Optical images of the friction tracks, after test under 860 MPa

Overall, friction coefficient values are very small in lubricious regime, they are in the range of 0.03 to 0.08, which is equivalent to friction coefficient obtained with regular dry lubricants, such as MoS_2. Except for the pure sliding friction in humid air, the friction coefficient under 1.1 GPa contact pressure is slightly lower than the friction coefficient obtained at 0.86 GPa. There is a clear difference between the contact pressures in the rolling+sliding experiments in vacuum. The dispersion of behaviour from one test to another is low. The pure sliding tests in humid air displays the highest dispersion. Such dispersion is also observed in the standard deviation of the friction coefficient value over one cycles of friction. In all other environments and contact conditions, standard deviation are very low, barely visible on the graphs.

The friction coefficient variations in pure sliding in air is similar to those observed in Rolling+sliding in vacuum. And the friction coefficient variations in pure sliding in vacuum is similar to those observed in Rolling+sliding in air. Such counter intuitive observation is not explained yet.

Finally, tests are demonstrating a “self-healing” capability of the material. The 3rd test in pure sliding condition, under 1.1 GPa, in vacuum, appeared to fail early. However, the live data during the test showed that the friction force regularly drops over 1 rotation of the disc, so we decided to pursue the test. The overall friction per cycle eventually decreased to reach a mean value below 0.06.

Looking at the optical images of the friction tracks from the low contact pressure tests (Figure 5), it appears that the best behaviour (rolling + sliding in air, and pure sliding in vacuum) are obtained because the material stays within the close vicinity of the contact. In pure sliding condition, it indeed appears that, in air, debris and accumulated materials are farther away from the track (particularly on the ball). That means that would hardly re-enter inside the contact. In rolling+sliding conditions, the material accumulates significantly on the ball and on the side of the main rolling track, while in air the material mostly stays on the disc and in close vicinity of the contact. On the ball, 3rd body particles are seen inside the main rolling track. Optically, the 3rd bodies and debris exhibit similar morphologies.

Figure 6 shows the optical images of the friction tracks from the test demonstrating lowest and most stable friction coefficient under 1.1 GPa of contact pressure. Although the surface of the roller is clearly rougher than the surface of the ball used for low contact pressure tests, the agglomeration and distribution of the 3rd body is similar to what is observed in the best-case scenario at low contact pressure. It can thus be assumed that the driving mechanisms of successful lubrication are similar.

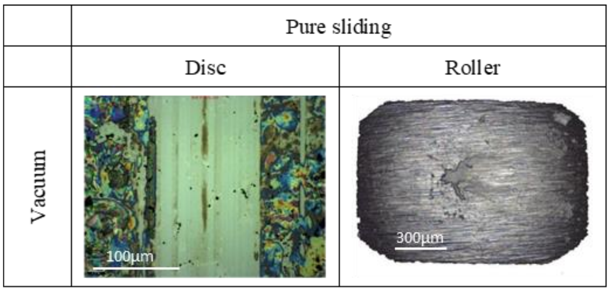


Figure 6 - Optical image of the friction tracks on the disc and the roller after friction test under 1.1 GPa contact pressure. Thoses conditions are the ones providing the best friction behaviour in vaccum.

SEM images and AFM measurements inside the friction track of the pure sliding test in vacuum shows that the 3rd body material is indeed detected everywhere within the friction track (Figure 7). It can be seen as thin ribbons with thick patches on the side of it. But it is seen as very thin layer of material covering large areas of substrate. Due to the thinness, it is barely visible under SEM. The AFM analysis conducted on such areas demonstrate that this thin 3rd body is comprised of flat nanoparticles whose thickness lies between 4 to 6 nm. They agglomerate to form a thin layer whose thickness lies between 10 nm and 20 nm. The layer is spread and “extruded” colinearly to sliding direction.

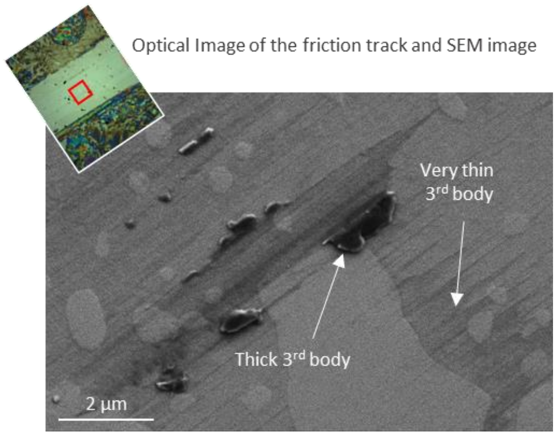
Regarding the composition of the 3rd body, it is important to note the change in colour the molecules underwent due to friction. The 3rd body becomes very dark, with varying colour from dark grey to black. The colour is similar to the one observed during the test performed to solve the anomaly related to the on ground ejection tests of satellite ANGELS [4,5]. In that study Fourier Transform InfraRed Spectroscopy (FT-IR) had been performed, it showed that the material transformed into a graphene oxide like material. That would be in-line with the flat nanoparticles detected in the friction track after friction.

In order to confirm that the 3rd body observed in the present study is of similar nature, different analysis were performed: Raman, XPS, and REELS. The set of data is significant, and not shown here. It will be part of a dedicated scientific article. What can be said is that C-C bonds are detected, and that the overall analysis demonstrates the presence of either turbostratic carbon (disordered graphitic structure), or H-reduced graphene oxide, or functionalized graphite or turbostratic material. Further analysis is currently being done to identify the nature of the functional groups. However, the current data is in line with what is known regarding DLC and H-DLC lubrication in air, in inert environment, and in vacuum [7].

4 CONCLUSION

In this study, lubrication based on the self- assembly of Alkylphosphonic acid (APA) molecules has been evaluated in two environnements (humid air, ultrahigh vacuum), under two kinematics (pure sliding, rolling+sliding), and under two contact pressure (0.86 GPa and 1.1 GPa). The APA solution is patented and commercially available, it is eco-friendly from manufacturing process to use and discard. Applied by spray in the study, it offers a low-cost solution for lubrication.

The tribological tests showed that the friction coefficient obtained is equivalent to MoS_2 and lies between 0.03 and 0.08. The higher the load, the lowest and the most stable the friction. The thickness of the lubricant is very low (30 to 300nm for the multi-layered agglomerates), which may help facilitating the design of components, such as ball bearing for which preload are calculated considering the lubricant thickness. Another targeted application would gear boxes, harmonic drives, etc.



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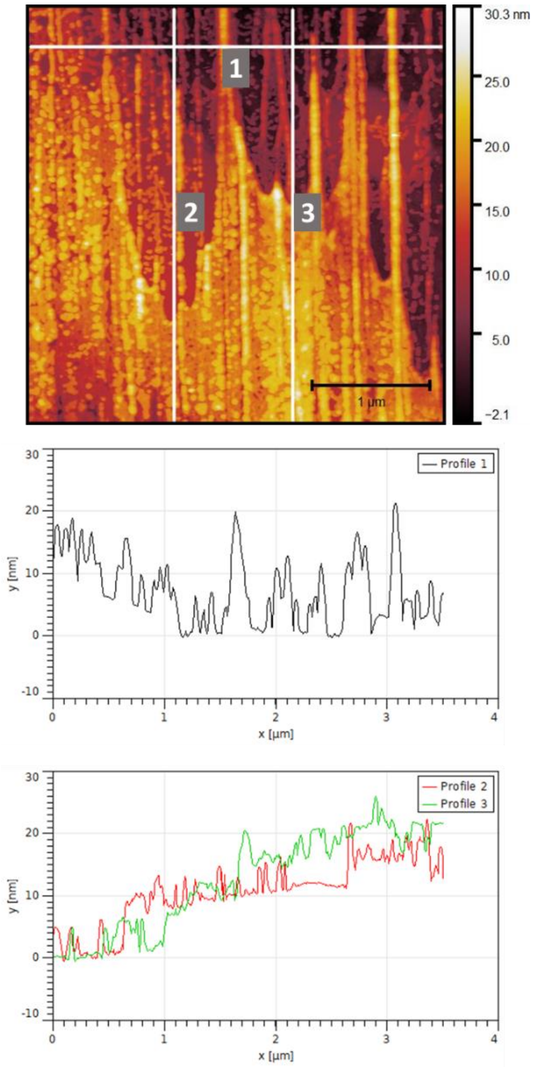

(b)

Figure 7 - SEM Image and AFM analysis of the friction track obtained from the friction test conducted pure sliding, under vacuum and 860 MPa of contact pressure

However, work remains to be done to fully homogenize the coating to increase the anchorage of the agglomerates, and homogenize the thickness. No ejection of agglomerates is detected, some are pushed forward and remained adherent to the sliding/rolling part in close vicinity of the friction track. Enhancing the bonding of the agglomerate may help increasing keeping larger volume of APA inside the contact. The sensitivity to humidity and temperature variation also remains to be verified, and wear life needs to be estimated.

Overall, the study shows that the use of self-assembled multilayer for lubrication represents an interesting new avenue for low cost, low to medium life, application.

5 ACKNOWLEDGEMENTS

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