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NANODIAMOND-BASED OIL LUBRICANTS ON STEEL-STEEL AND STAINLESS STEEL – HARD ALLOY HIGH LOAD CONTACT: INVESTIGATION OF FRICTION SURFACES

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In the current paper, synergistic compositions of detonation nanodiamond (DND) particles in the form of aggregates and fully deagglomerated 5nm particles were used as additives to 10W40 and 5W30 oils, correspondingly. Ring-on-disk and block-on-ring tribological tests were performed under high load conditions (300N and 980N) using friction pairs with different relative hardness. Significant reduction of wear was observed for the HRC25/25, HRC25/50 and HRC30/HRC60 steel/steel friction pairs, while for the HRC60/60 steel/steel and HRA86/HRC24 hard alloy/steel friction pairs increased wear took place. It was concluded that use of ND in lubricants under high load conditions should be approached cautiously taking into account absolute and relative hardnesses of the friction surfaces.

Keywords: Nanodiamond, Nanolubricants, Friction, Wear, Polishing.

1. Introduction

Over the last few years, interest in applications of nanoparticles as lubricant additives (nanolubricants) has steadily grown due to the demonstrated reduction of friction and wear with the use of nanoparticles-containing lubricant formulations [1]. Carbon-based ultrafine additives play a special role among nanomaterials due to their high biocompatibility [2] providing reduced environmental impact effect. Studies of lubricating compositions with detonation nanodiamond (DND) and detonation soot (a mixture of DND particles with different forms of sp^2-bonded carbon) [3–5] as additives have demonstrated their positive impact on the performance of lubricant compositions, often superior to other nanoparticle fillers.

While the positive effect of DND additives on the lubrication properties of oils has been demonstrated [3–7] and a variety of hypotheses of DND tribological action are considered, in order to optimize additive composition and expand the range of applications of DND nanolubricants, mechanisms of DND action need to be further elucidated and clearly linked to the operational conditions of tribological tests (characteristics of friction surfaces, load, rotational speed, composition of lubricant, etc.). In the current work, we have focused on understanding of the role of friction surfaces properties, particularly relative hardness of the friction pairs. In the earlier work by Zhornic et al. [5], modification of Litol-24 lubricant with detonation soot reduced wear of steel-steel friction pairs with hardness 20–25 HRC by approximately 30-fold and for the steel pairs with hardness 30–40 HRC by 5-fold, correspondingly. However, for the steel with hardness 62–65 HRC, the wear was increased ∼1.14 times. The authors attributed the increased wear of the friction pairs with an initial hardness $\geq$ 60 HRC in the presence of detonation soot to the brittle fracture of the surface layer originating from increased stress concentration due to hard nanodiamond particles embedded on the surface. The [5] concentration of the detonation soot in the lubricant, though, was relatively high, ∼1 wt.%. Since the authors used *as is* detonation soot, it can be assumed that the average agglomerate size was typical for detonation soot, a few hundred nanometers.

In the current paper, synergistic compositions of detonation nanodiamond (DND) aggregates as well as deagglomerated 5nm particles [9] were used with molybdenum dialkyldithiophosphate and zinc dialkyldithiophosphate as additives to 5W30 and 10W40 oils. The DND concentration was varied between 0.01 and 0.05 wt%. Block-on-ring tribological tests were performed using steel\steel block and ring samples with HRC30/HRC60 and HRC60/HRC60 relative hardness, correspondingly. In the disk-on-ring test steel\steel friction pairs with hardness HRC25\25, HRC25\50 and a hard alloy (WC)\steel friction pairs with hardnesses HRA86\HRC24 were used. In the comparative tests with or without DND additives, a significant reduction of wear or, on the contrary, an increase in wear took place, depending on the hardnesses of the friction pairs. It can be concluded that use of ND in lubrication of friction pairs tested under high load conditions and in the presence of hard surfaces should be approached cautiously, even when using fully deagglomerated 5 nm detonation ND particles.

2. Experimental

In the current work, agglomerates of the detonation ND particles with 100 nm average particle size (DND synthesized by NPO Altai) as well as deagglomerated DND were used. Deagglomeration of DND was done using attrition bead milling [9], resulting in particles with 4.6 nm average volumetric size in DI water as measured via a dynamic light scattering technique using a Malvern Instruments tool. The trade name of this DND produced at NanoCarbon Research Institute is NanoAmando. Stable transparent colloidal dispersions of DND in PAO oil (PAO-6) have been formulated using a special polyfluorinated surfactant [10]. Dispersion of the DND in the oil was assisted by ultrasonic treatment. An example of stable colloidal suspension of 20 nm DND in PAO oil with excellent dispersivity was illustrated earlier [8]. DND-based additives were used in combination with other synergistic additives [8], such as organic molybdenum and zinc additives, molybdenum dialkyldithiophosphate (MoDDP) and zinc dialkyldithiophosphate (ZDDP). Additive compositions were prepared with same concentration of synergistic additives, either pure MoDDP (called ND/M) or MoDDP in combination with ZDDP (called ND/M/Z).

The commercial oils for testing were the 5W30 (Semi-Synthetic) – Mobil Super API SN engine oil and Lukoil Standard 10W40 API SF/CC mineral oil. Mixing of the DND-based additives with commercial oils was done in 1:30 and 1:60 proportions. Testing of the DND-based additive performance in 5W30 Mobil Super oil was done using a block on ring test apparatus, UMT-3, produced by CETR, USA. A block from SAE 01 tool steel with hardness HRC=30 or HRC=60 and flat friction surfaces with roughness 0.2 μm rms were used. The stainless steel ring had a hardness HRC=60 and roughness 0.3 μm rms. The rotational velocity was 200 rpm and the load was 300 N. This set of experiments was done at an average temperature of 75–80 °F and 45–50% humidity. Samples were purified with IPA after the tribotests for further analysis. Scar profiles were measured using an Alpha-Step IQ stylus-based surface profiler. Roughness maps and roughness were measured using a Zygo NewView 5000

3D optical profiler. Roughness was measured at 5 points along a scar (ring surface) and averaged. At every point, the roughness was measured over a distance of 50 μm. Tribological experiments were performed using a special tribology tester (ring-on-disk module) with two carbon steels and stainless steel (austenite steel 12Kh18N10T) - hard alloy (WC, HRC= 74–76). The rotational velocity was 200 rpm and the load was 980 N, 5 hour test. Measurements of mass wear of the friction pairs were performed in this set of experiments.

3. Results and discussion

The 5 nm ND in 5W30 Mobil oil experiments were performed for 2 friction pairs of the stainless steel samples, which are designated below as H30/H60 ('soft on hard') and H60/H60 ('hard on hard') surfaces. The H30/H60 pair tests were performed for three ND-based additives (ND/M/Z at 1:30 and 1:60 dilutions in Mobil and ND/M at 1:60 dilution). The H60/H60 pair tests were performed for the composition that showed the best results in the test for the H30/H60 pair. All results were compared to the reference samples ran for pure Mobil oil without ND-based additives. For 100nm ND in 10W40 Lukoil oil, experiments were done for 1 composition of the ND-based additive, ND/M at 1:60 dilution. Details are provided below.

3.1. Tribological characteristics for the H30\H60 friction pair

Fig. 1a presents the friction coefficient as a function of time for H30 block over H60 ring for pure Mobil 5W30 oil and for the oil with DND-based additive (ND/M/Z at 1:60 dilution in Mobil). When using a ND-based additive, an improvement in the COF of 10% was observed in a 5 hour test. Modest reduction in the COF was accompanied by a significant reduction in wear. The scar area for the pure Mobil 5W30 samples was 1.777 μm^2, while for the sample tested with DND additive, it was about half that value: 980 μm^2. Scar profiles obtained with a stylus profilometer are presented in Fig. 1b. The scar profile was smoother for the sample treated with the DND additive, as compared with pure Mobil oil (Fig. 1b). Fig. 2 illustrates optical micrographs of the scars in the block samples as well as roughness maps of the scar in a block and ring surface after 5hr tests for tests run with pure Mobil oil and Mobil oil with ND-based additive. The 3-D topographical maps of the ring surfaces and the scars formed during tests using pure Mobil oil and Mobil oil with DND additive demonstrate a more pronounced topological uniformity for the surfaces of samples treated with the DND additive. Measurements averaged over 5 data points are also provided in Fig. 2, and clearly demonstrate that the presence of DND provides a significant polishing effect: the rms of the scars on the block and ring surfaces tested with the DND additive are about 28% and 37% lower, correspondingly, than the roughness of the scars and rings observed in experiments performed with pure oil.

Table 1 summarizes measurements of COF, wear and roughness for the samples tested with different type and concentration of the synergistic additives to ND. As can be seen from the table, a mixture of MoDDT and ZDDP in combination with 5 nm ND provides more pronounced resistance to wear than a combination of the ND and MoDDP. The combination of ND and ZDDP was not tested, since a residue appeared in the mixture a few days after preparation.

Combinations of ND and MoDDP and ND\MoDDP\ZDDP were transparent and colloidally stable for at least 1 month (time of observation).

3.2. Tribological characteristics for the H60\H60 friction pair

Figure 3a presents the friction coefficient as a function of time for H60 block over H60 ring for pure Mobil 5W30 oil and for the oil with DND-based additive (ND/M/Z at 1:60

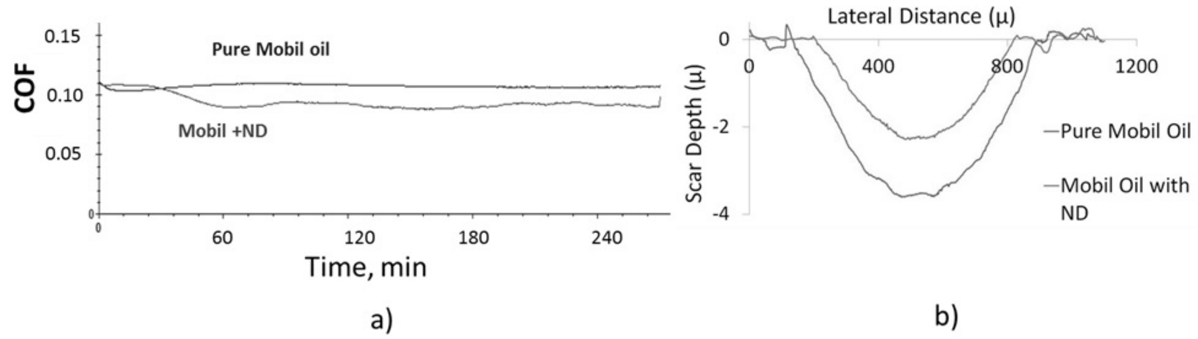


FIG. 1. Friction coefficient as a function of time (a) and scar profiles in the block (b) for H30 block obtained in the 200 rpm/30 kg 5 hrs block-on-ring tests for pure Mobil 5W30 oil and for the oil with DND additive.

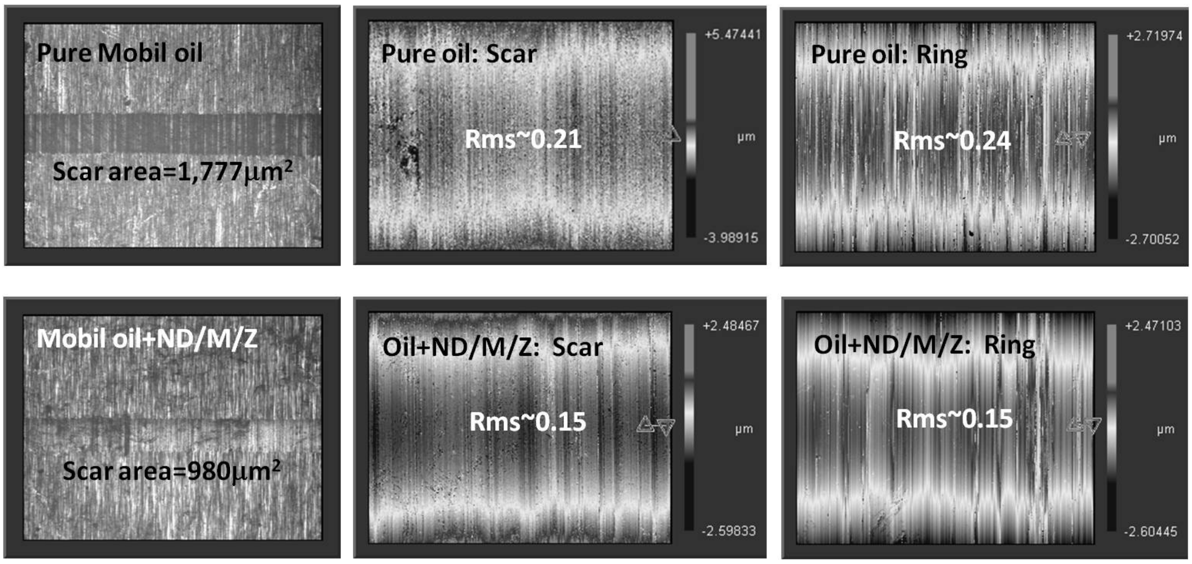
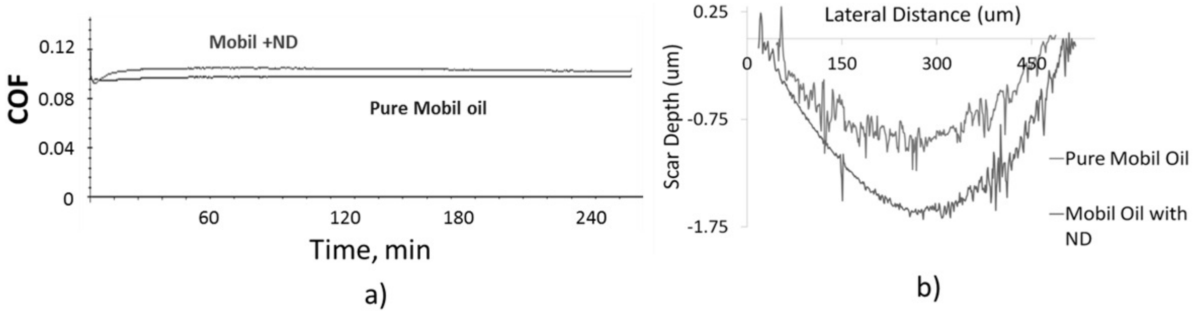


FIG. 2. Microscopy images (10× zoom) (left) and roughness maps of the scar in a block and a ring after 5hrs tests at 30 kg load and 200 rpm for pure Mobil 5W30 oil (top) and its dilution with ND/M/Z additives for the H30 block over H60 ring test (‘soft on hard’ surfaces). Dimensions of the roughness maps are 0.72 mm × 0.54 mm

dilution in Mobil). COF in a test with oil containing ND-based additive was by 4% higher in comparison with COF for pure oil. An increase in the COF was accompanied by a significant increase in wear. The scar area for the pure Mobil 5W30 samples was 525 μm^2, while the sample tested with the DND additive had a scar area about twice that level, 1190 μm^2. Scar profiles obtained with a stylus profilometer are presented in Fig. 3b; they were rough for both samples. Fig. 4 illustrates optical micrographs of the scars in the block samples as well as the roughness maps of the scar in a block and ring surface after 5 hrs for tests run with pure Mobil oil and Mobil oil with the ND-based additive. The 3-D topographical maps of the ring surfaces and the scars formed during tests using pure Mobil oil with the DND additive demonstrate that the presence of DND significantly increased the roughness when hard steel surfaces were sliding against each other at the high external load used in these experiments (300 N). This observation was also confirmed by the increased roughness values for both the ring and the scar in the block for the sample tested with a ND additive, as compared to the test using pure Mobil

TABLE 1. Samples composition, hardness of the friction pair (block/ring) and tribological characteristics of the tests (scar width and depth ($W \times D$), scar area, average COF (AvgCOF) and COF at the end of the 5 hrs test (End COF))

Sample	**Composition**	**Scar $W \times D$ (scar area, μm^2)**	**AvgCOF & (End COF)**	**RMS Scar/Ring**
H30/H60	Pure Mobil	722.78 × 3.68 (1777)	0.1086 ± 0.00266 (0.1065)	0.214 ± 0.040 / 0.240 ± 0.039
H30/H60	ND/M/Z 1:30	655.14 × 2.92 (1264)	0.1006 ± 0.01167 (0.092)	0.165 ± 0.031 / 0.141 ± 0.043
H30/H60	ND/M/Z 1:60	627.89 × 2.53 (980)	0.1005 ± 0.0117 0.090	0.152 ± 0.050 / 0.147 ± 0.031
H30/H60	ND/M 1:60	748.01 × 3.90 (1892)	0.09365 ± 0.0158 0.089	0.150 ± 0.017 / 0.222 ± 0.033
H60/H60	Pure Mobil	339.18 × 0.74 (525)	0.09674 ± 0.00205 0.0978	0.120 ± 0.030 / 0.236 ± 0.022
H60/H60	ND/M/Z 1:60	539.05 × 1.89 (1190)	0.1045 ± 0.00255 0.102	0.381 ± 0.034 / 0.272 ± 0.011



a) b)

FIG. 3. Friction coefficient as a function of time (a) and scar profiles in the block (b) for H60 block obtained in the 200 rpm/30 kg 5 hrs block-on-ring tests for pure Mobil 5W30 oil and for the oil with ND/M/Z additive

oil (Table 1, Fig. 4). Especially high roughness was observed for a scar in the block, since its surface is under constant sliding load, while for the ring, sliding contact is distributed over its periphery.

3.3. Wear characteristics for the steel\steel and hard alloy\steel friction pairs

Table 2 illustrates results of the wear tests for the friction pairs composed of materials with different composition and hardness. The following friction pairs were tested: carbon steel St45 (normalized versus normalized) HRC 25/25; carbon steel St45 (normalized versus quenched) HRC25/50; stainless steel (austenite steel 121810) HRC24 versus hard alloy (WC, 15%Co), HRA86.

A significant increase in wear can be seen from the Table 2 for the hard alloy WC in the test with oil containing ND additive.

4. Conclusion

Nanodiamond-based additive for lubricants is now available as a commercial product. Current tests indicate that application of ND-based additives need to be used with caution when

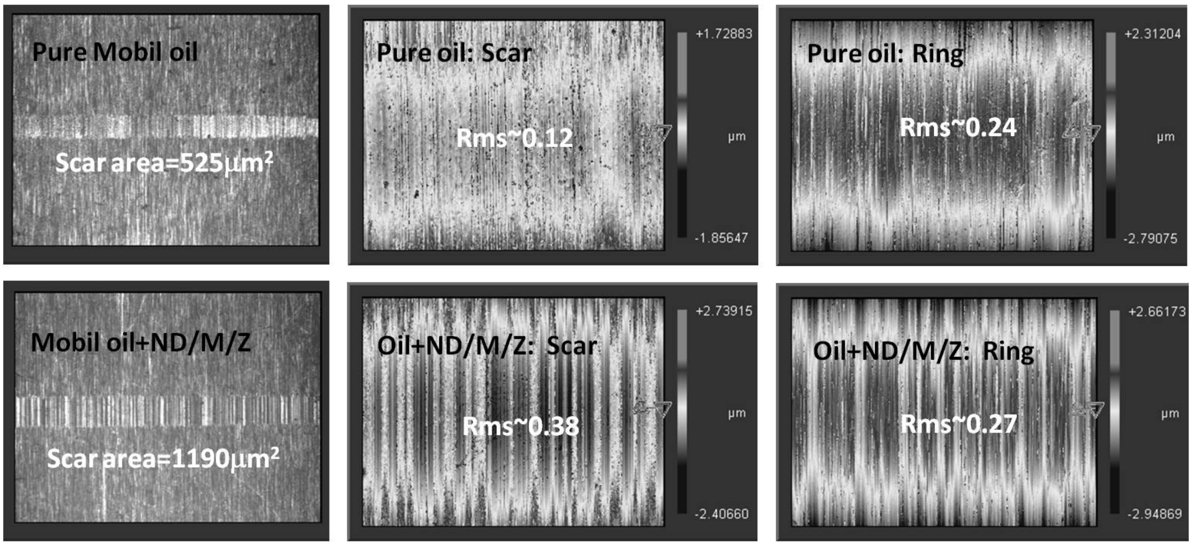


FIG. 4. Microscopy images (13× zoom) (left) and roughness maps of the scar in a block and a ring after 5 hrs tests at 30 kg load and 200 rpm for pure Mobil 5W30 oil (top) and its dilution with ND/M/Z additives for the H30 block over H60 ring test ('hard on hard' surfaces). Dimensions of the roughness maps are 0.53 mm × 0.4 mm

TABLE 2. Wear characteristics of rings and disks in the 5 hrs tests with and without ND additives in the 10W40 oil at 200 rpm and 980 N load in the disk-on-ring test.

Sample (ring/disk)	Ring pure oil, wear, mg	Ring oil+ND, wear, mg	Disk pure oil, wear, mg	Disk oil+ND, wear, mg
HRC 25/25	0.04	0.03	0.035	0.015
HRC 25/50	0.01	0.005	0.015	0.005
HRC24/HRA86	0.005	0.0	0.013	0.028

taking into consideration the hardness of the friction surfaces. While in the 'hard on soft' steel\steel friction pairs NDs provide significant reduction in wear and demonstrate a polishing effect, in the 'hard on hard' steel friction pair and in the hard WC alloy the abrasive nature of NDs plays a role and results in increased wear of the sliding surfaces. A possible mechanism can be incorporation of ND particles into the hard surface and playing a role of high stress concentrators [5]. However, a detailed mechanism for this phenomenon requires further studies.

Acknowledgments

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