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Boris ZHMUD,
Bogdan PASALSKIY,
Nadiia CHYKUN

NANOMATERIALS IN LUBRICANTS

The present communication overviews the use of various classes of nanomaterials in lubricant formulations. The following classes of nanomaterials are considered: fullerenes, nanodiamonds, fumed silica, clays, ultradispersed boric acid and PTFE. Current advances in using nanomaterials in engine oils, industrial lubricants and greases are discussed. Results of numerous studies combined with formulation experience of the authors conclusively suggest that nanomaterials, indeed, have potential for enhancing certain lubricant properties, yet there is a long way to go before balanced formulations are developed.

Key words: nanomaterials, lubricants, fullerenes, nanodiamonds, fumed silica, clays, ultradispersed boric acid, ultradispersed PTFE.

Жмудь Б., Пасальський Б., Чікун Н. Наноматеріали в мастилах. *Представлено використання різних класів наноприсадок в мастильних матеріалах. Розглянуто такі типи наноматеріалів: фулерени, наноалмази, аеросили, глини, високодисперсні борна кислота та тефлон. Результати численних досліджень, а також практичний досвід авторів у виробництві мастильних матеріалів, дають змогу зробити висновок, що хоча наноматеріали безсумнівно уможливлюють покращання окремих властивостей мастильних матеріалів, проте ще належить пройти тривалий шлях до розробки збалансованих продуктів.*

Ключові слова: наноматеріали, мастильні матеріали, фулерени, наноалмази, аеросили, глини, високодисперсна борна кислота, високодисперсний тефлон.

Жмудь Б., Пасальский Б., Чикун Н. Наноматериалы в смазках. *Представлено использование различных классов наноприсадок в смазочных материалах. Рассмотрены следующие типы наноматериалов: фуллерены, наноалмазы, аэросилы, глины, высокодисперсные борная кислота и тефлон. Результаты многочисленных исследований, а также практический опыт авторов в производстве смазочных материалов, дают возможность прийти к заключению, что хотя наноматериалы несомненно позволяют улучшать отдельные свойства смазочных материалов, однако еще предстоит пройти длительный путь к разработке сбалансированных продуктов.*

Ключевые слова: наноматериалы, смазочные материалы, фуллерены, наноалмазы, аэросилы, глины, высокодисперсная борная кислота, высокодисперсный тефлон.

Introduction. The continuing pursuit for better fuel efficiency stands behind many recent advancements in engine technology. "Downsize and charge" has become the major development trend alongside broad acceptance of fuel stratified injection [1]. The introduction of higher power densities (around 65 kW/L and 150 Nm/L in modern diesel engines) raises performance requirements for engine oil. "We understand that fleets are under constant costs pressures. Any product that can help reduce fuel consumption is important for fleets to consider," says Jim Gambill, Commercial and industrial brand manager, Chevron Products Company.

Nanoadditives open new ways to maxing out lubricant performance [2; 3]. Even though nanomaterials have been around for quite a while, large-scale market introduction of nano-fortified lubricants is still facing serious technical and legislative obstacles. The present communication overviews current advances in using nanomaterials in engine oils, industrial lubricants and greases. Examples are presented to demonstrate the general marketing trend of abusing the word "nano" while overlooking specific technical challenges and failing to develop balanced formulations meeting stringent performance and safety requirements.

Applications of nanomaterials in lubricants. *Fullerenes*. Fullerenes are cage molecules which are claimed to enable "rolling" lubrication mechanism, which has never been actually proven. Most studied is C_{60} carbon material [4]. Inorganic fullerenes comprise another class of nanomaterials with "fullerene" tag. Most studied are inorganic fullerene-like WS_2 nanoparticles synthesized by reacting sulfur with WO_3 nanoparticles in a hydrogen atmosphere at 500–650°C [5]. The IF-WS_2 nanoparticles have a closed hollow cage structure with an average size of about 50 nm, which is much larger than the size of C_{60} molecule. Studies suggest that addition of C_{60} fullerene soot in a lubricant significantly increases the weld load and seizure resistance [6]. Due to their smaller particle size *(Fig. 1)*, C_{60} fullerene soot and IF-WS_2 nanoparticles form much more stable dispersions in hydrocarbons as compared to regular graphite and WS_2 powders.

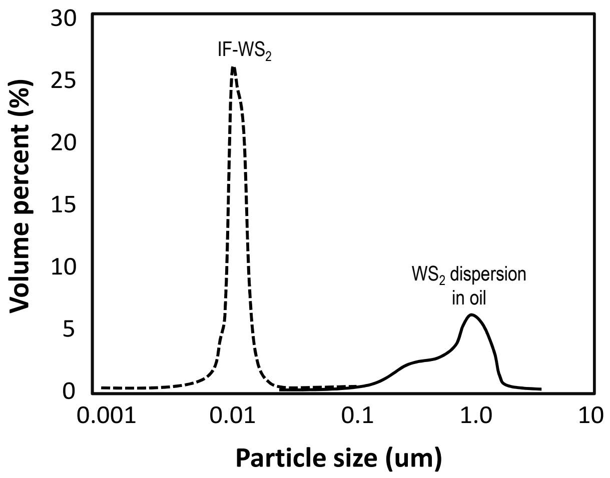

Figure 1. Particle size distributions for IF-WS_2 and a regular WS_2 dispersion in oil

Apart from improved dispersion stability, IF-WS_2 does not appear to offer any obvious performance benefits over regular WS_2 powder. For instance, when used in grease, IF-WS_2 scores below regular WS_2 in a number of tribological properties *(Table).*

Effect of WS_2 and IF-WS_2 on the tribological properties of lubricating grease

Tribological performance characteristics	NLGI 2 food safe grease	Same + 5% WS_2	Same + 5% IF-WS_2
Four ball wear, mm (ASTM D 2266, 75°C, 40 kg)	0.59	0.39	0.45
Four ball weld, kg (ASTM D 2596)	315	670	540
Timken OK load, kg (ASTM D 2509)	18	30	24

The grease used in this study was a food-grade aluminum-complex grease which did not contain any traditional EP/AW additives such as moly and sulfur.

IF-WS_2 is marketed as the EP/AW additive for engine oils, gear lubricants and greases, yet its applications so far are very limited. Among the chief limiting factors is the uncertainty about the HSE profile of fullerenes. IF-WS_2 also has issues with copper corrosion and poor oxidation stability. As a result, IF-WS_2 fortified engine oils are likely to fail ILSAC GF-2 Sequence L38 and GF-3 Sequence VIII tests. Changes in various oil properties due to deployment of IF-WS2 in formulation are shown in *Fig. 2*.

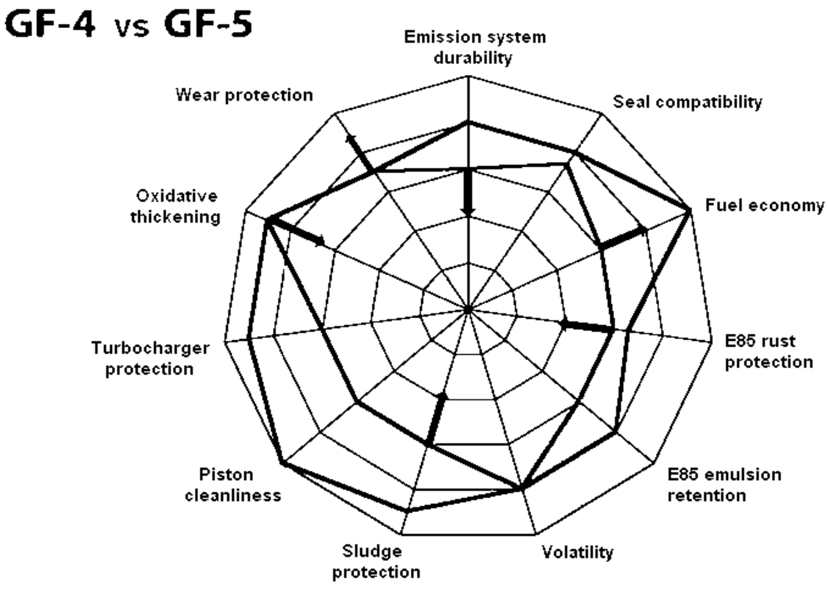

Figure 2. Changes in the performance spectrum of ILSAC GF-4 oil top-treated with IF-WS2 emulsion

Modest improvement (outward arrows) in valve train protection and fuel economy are outweighed by degradation (inward arrows) in such pivotal properties as corrosion protection, with a specific risk for main bearing corrosion, oxidative thickening, and emission system durability. IF-WS2 doped oils may cause severe damage to engines such as BMW M52 and M60 with Nikasil cylinder bore coatings. For comparison, the upgraded ILSAC GF-5 specifications are shown as well.

Nanodiamonds. The term is usually used to describe ultradispersed diamonds produced by detonation of hexagen or trinitrotoluene in a closed camber [7]. The average particle size is 4 to 6 nm. As a lubricant additive, nanodiamonds are claimed to embed into the sliding surfaces rendering them more resistant to wear, or alternatively, enable "rolling lubrication" between the surfaces, thus reducing friction and wear [8; 9]. For instance, Chou and Lee have observed reduction in pin-on-disk tests for lubricants doped with 50 to 150 ppm nanodiamonds *(Fig. 3)* [8].

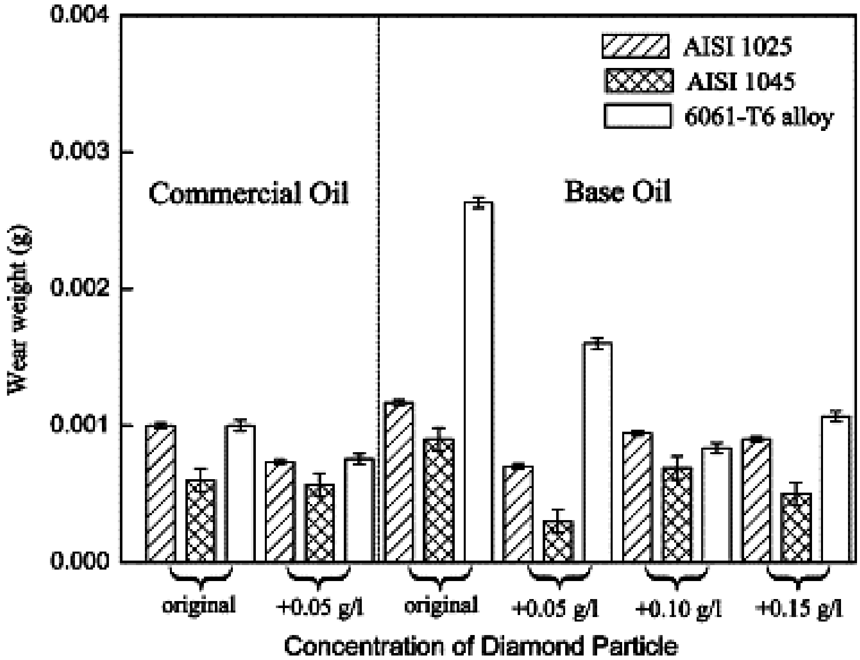

Figure 3. Wear of rotating disk in pin-on-disk tests carried out by Chou and Lee [8]

The pin was made of carbon chromium steel. The rotating disks were made of AISI 1045 steel, AISI 1025 steel and 6061-T6 aluminum alloy. Note that pin wear was not quantified by the authors.

However, our studies and formulation experience have led us to a different conclusion regarding the EP/AW efficiency of nanodiamonds: the fact that a reduction in friction is observed when nanodiamonds are added to lubricant formulations is consistent with their micropolishing effect resulting in faster running-in and smoother mating surfaces. As a result, the transition from full-film to boundary lubrication occurs at a lower velocity-to-pressure ratio, and the Stribeck diagram is shifted to the left *(Fig. 4)*.

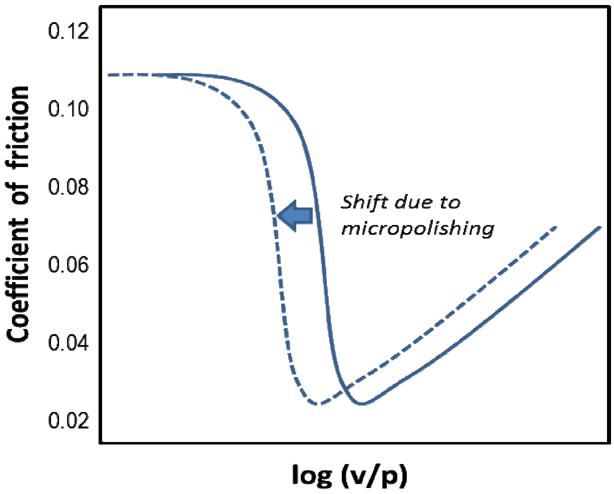

Figure 4. Shift in the Stribeck diagram due to the micropolishing effect of nanodiamonds. Here, v is the sliding velocity and p is the contact pressure

However, this micropolishing effect becomes insignificant in the case of aged oil, where wear rate and steady-state surface roughness are dominated by other factors. Furthermore, since the abrasiveness of nanodiamonds does not go away after the initial running-in period, there is a risk for excessive wear over a longer period of time *(Fig. 5).* Analysis of oils from engines run with engine oils doped by nanodiamonds (available as aftermarket oil treatment packages) reveals unusually high levels of wear metals such as aluminum, copper and chromium, indicative of accelerated wear of bearings and piston rings. Nanodiamonds may also alter the tribology of finger roller follower valvetrain, increasing risk for roller skidding. On the other hand, the micropolishing effect of nanodiamonds in engine oil seems to improve surface finish of certain components after the running-in. Therefore, nanodiamonds may prove useful in running-in oil formulations, yet more studies are needed to discern possible unintended consequences.

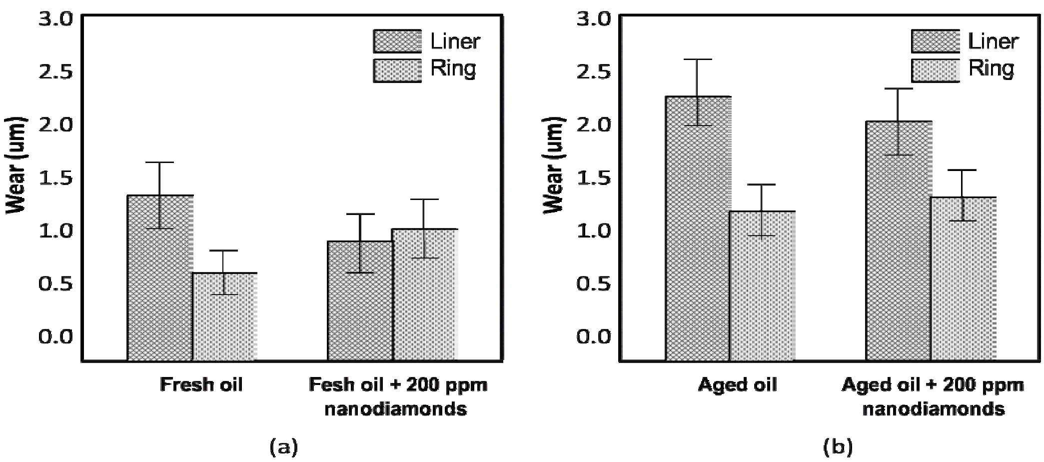

Figure 5. Wear of piston ring and cylinder liner lubricated by SAE 30 engine oil with and without nanodiamonds

A reciprocating ring-on-liner tester was used under the following conditions: test duration 1 hour, frequency 20 Hz, load 360 N, lubrication: (a) fresh SAE 30 engine oil; (b) pre-oxidized SAE 30 engine oil diluted with 10 wt.% diesel fuel and "contaminated" by 0.2 wt.% particulate matter containing a mix of soot, quartz, alumina and kaolinite 800 mesh; oil temperature 90^{o}C. Note the increased ring wear with nanodiamond-doped fresh oil (a).

Fumed silica and clays. Based on their structural characteristics, fumed silica and clays can well be classified as nanomaterials, but they usually are not since they have been around long before the nanotech era began. Fumed silica and clays such as montmorillonate are used as thickeners in specialty grease formulations, such as silicone greases, where traditional lithium, calcium or aluminium soap thickeners are not applicable.

Boric acid. In not too distant past, boric acid used to be a common additive in metal-working fluid (MWF) formulations thanks to its excellent EP/AW properties and bacteriostatic and bactericidal actions. Nowadays, it has been largely phased out from MWFs because of HSE concerns. However, some recent studies mention "boron-based nanoparticulate lubrication additives that can drastically lower friction and wear in a wide range of industrial and transportation applications", indicating renewed interest in boric acid. By replacing sulfur and phosphorous, boron additives are hoped to eliminate the main sources of environmentally hazardous emissions and wastes [10]. Recently, it has been proposed to combine electrochemical boriding with the use of nano-colloidal boron nitride additives for improving tribological performance of drivetrain components in advanced wind turbines [11].

Unfortunately, there are quite a few technical hurdles to mar that optimism. First of all, boric acid has no antioxidant effect, so it cannot replace ZDDP. Second, boric acid is not compatible with some essential lubricant additives, specifically with the TBN buffer in the engine oil, which may lead to corrosion and sludge problems. For instance, engine oils containing boric acid are likely to fail ASTM D 6557 and D 6593 (aka ILSAC GF-3 Sequence VG) tests.

PTFE. Polytetrafluoroethylene has a well-defined footstep in the lubrication engineering with impressive performance profile in greases, chain oils, dry-film lubricants, etc. [12; 13]. Recognition of potential to reduce friction and wear has led to use of PTFE as a dry-film lubricant and friction modifier long before the buzzword "nano" has come into daily use. PTFE-fortified oils and greases are known to exhibit higher welding loads, higher load wear indexes, and reduced stick-slip. Though PTFE nano-dispersions are used in a number of aftermarket engine treatment products, the use of PTFE in engine oils is rather limited because of inherent instability of PTFE dispersions in oil, the risk of oil filter clogging, as well as difficulties with recycling. As a matter of fact, the application of PTFE in engine oils is discouraged even by the major PTFE producer, DuPont Company [13].

Conclusion. Nanomaterials have potential for enhancing certain lubricant properties, yet there is a long way to go before balanced formulations are developed.

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