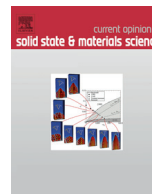




Contents lists available at ScienceDirect

## Current Opinion in Solid State and Materials Science

journal homepage: [www.elsevier.com/locate/cossm](http://www.elsevier.com/locate/cossm)

## Nanodiamond-based nanolubricants for motor oils

Michail Ivanov<sup>a,b,\*</sup>, Olga Shenderova<sup>b</sup><sup>a</sup> Ural Federal University, Yekaterinburg, Russian Federation<sup>b</sup> Adámás Nanotechnologies, Raleigh, NC, USA

## ARTICLE INFO

## Article history:

Received 3 March 2016

Revised 11 July 2016

Accepted 29 July 2016

Available online xxxxx

## Keywords:

Nanodiamond

Nanolubricant

Oil additive

Friction

Wear

## ABSTRACT

Over the last few years, interest in applications of nanoparticles as lubricant additives has steadily grown due to the demonstrated reduction in friction and wear of nanoparticle-containing lubricant formulations (so-called nanolubricants). Particularly, studies of motor oils containing a “green” all-carbon additive, detonation nanodiamond (DND) particles, revealed their positive impact on the performance of lubricant compositions and fuel economy in engine tests. In the current review we discuss critical issues toward successful implementation of DND in nanolubricants: role of DND structural characteristics, stability of colloids of DND in oils, DND compatibility and synergism with other additives in commercial oils, mechanisms of DND impact on the properties of lubricants. Owing to the abrasive nature of diamond, DND-based nanolubricants must be carefully engineered in order to avoid increased wear of the friction surfaces and get full benefit from significantly reduced friction of well-polished surfaces.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Improved fuel efficiency and service lifetime are among of the major goals in the transportation industry. Besides the obvious fact that improved operating efficiency of vehicles provides immense cost savings, there are stringent environmental regulations requiring significant reductions in greenhouse gas emissions and improved fuel economy for automobiles and trucks. According to a recent analysis of global fuel energy consumption in heavy-duty road vehicles [1], only 34% of the fuel energy is used to actually move the vehicle, while 33% is used to overcome friction in the engine, transmission, tires, auxiliary equipment, and brakes. These parasitic frictional losses, with braking friction excluded, account for 26% of the fuel energy. Particularly the viscous losses and shear in hydrodynamic fluid contacts (where a layer of fluid present between moving surfaces) give rise to significant energy losses. Therefore, if the lubricant viscosity is reduced while the anti-friction and anti-wear functions are maintained, as is the case with viscous oils, then a very large energy saving in the powertrain could be achieved [1,2]. For example, with a reduction of the engine oil viscosity by approximately 25%, the corresponding fuel savings could range from 0.6% to 5.5%. The fuel savings from lowering the viscosity of gear oil in the same fashion could range from 0.2 to 2.5% [1]. Nevertheless, there are issues related to the use of

low viscosity oils, such as weaker lubricant films, increased wear and decreased mechanism durability. These issues cannot be resolved by simply increasing the amount of traditional anti-wear additives, like zinc dialkyldithiophosphates (ZDDP) and friction modifiers like organomolybdenum compounds (e.g. molybdenum dialkyldithiophosphate (MoDDP)), due to environmental regulations of toxic elements (S, P, etc.) in oils [3]. Therefore, new approaches for advanced lubricants are being sought and new antifriction (AF) and antiwear (AW) additives are being developed [1,2].

There have been a number of recent studies that have looked at the effect of adding various classes of nanoparticles to oil-based lubricants (providing so called “nanolubricants”) [4,5]. These classes have included metals (e.g. Zn, Al, Cu, Ti, Fe) and their oxides, molybdenum disulfide and tungsten disulfide, metal borates, hexagonal boron nitride, fluorinated compounds [4–10], fullerenes, graphitic nanoparticles [4], and nanodiamond particles [11–25]. In general, these studies report significant reductions in friction (typically 10–20%) and wear, although the proposed mechanisms by which these effects are achieved vary significantly. Mechanisms include changes in lubricant viscosity and thermal transport properties, formation of protective surface films, and the creation of effectively smoother surfaces by physical removal of surface asperities or by filling in spaces between asperities. Besides the “boundary lubrication” (sliding surfaces in mechanical contact) regime, the benefits of nanolubricants were recently demonstrated in elastohydrodynamic lubrication (an intermediate stage between hydrodynamic and boundary lubrication), where reduced surface

\* Corresponding author at: Ural Federal University, Yekaterinburg, Russian Federation.

E-mail address: [m\\_g\\_ivanov@mail.ru](mailto:m_g_ivanov@mail.ru) (M. Ivanov).

roughness in rolling contact was achieved through polishing by diamond nanoparticles [11].

Ultrafine carbon-based additives play a special role amongst nanomaterials due to their high biocompatibility and resulting reduced environmental impact (“green” additives) [26]. While fullerenic structures of MoS<sub>2</sub> and WS<sub>2</sub> provide impressive results in tribological studies, they contain metals and sulfur, raising environmental concerns. At the same time, studies of lubricating compositions with detonation nanodiamond (DND) and detonation soot (a mixture of DND particles plus different forms of sp<sup>2</sup>-bonded carbon) as additives have demonstrated a positive impact on the performance of lubricant compositions, often superior to other nanoparticle fillers [19,22]. Earlier research had been focused on detonation soot [13–15], as it was assumed that the abrasive nature of NDs prevent them from being used as the sole additive (without nanographite) in lubricants. However it was discovered that pure DND particles with small sizes (<100 nm) can provide a very beneficial effect in greases and oils, when properly dispersed [19]. Another significant observation was that DND in combination with other selected friction modifying additives provide significant improvements of the lubricant’s performance (synergistic effect) [19–23]. While NDs perform nanopolishing, synergistic agents of a certain nature participate in the formation of a protective tribofilm reinforced by NDs. The use of a combination of DND with ultradispersed particles of PTFE [19,20], PTFE in combination with Cu nanoparticles [19] or Mo-containing additives [19–23] results in additives with excellent lubrication properties in oils and greases, well exceeding those when only individual additives are used. Laboratory block-on-ring tests demonstrated a reduction of the coefficient of friction of widely used motor oils more than 10x and a reduction in wear by 20–30% [19–24] following the addition of DND-based additives. Using ND-based additives prepared by our group, OEM approved fuel efficiency bench tests on engines of passenger cars demonstrated up to a 4.5% fuel efficiency improvement in gasoline engines by a top treatment of Mobil 5W30 SN with the ND-based additive and up to a 1–2% fuel efficiency improvement in diesel engines by adding the ND-based additive to Delo 400 LE SAE 15W40 diesel engine oil.

With a quest toward replacing the centuries-old oil-based lubricating technologies with more ecologically friendly lubricants, Osawa tested dispersions of 4 nm NDs in several polar liquids including water, ethylene glycol, and DMSO and observed eight- to tenfold reduction in the friction coefficients upon addition [28]. Given that the conventional additives to oil are insoluble or ineffective in aqueous and ionic liquid solvents, development of NDs as additives to polar liquids seems possible in envisioned new generations of lubricants [28].

In the current review we discuss critical issues toward successful implementation of DND in nanolubricants: role of DND structural characteristics such as surface chemistry and particle size, means to achieve stability of colloids of DND in oils, DND synergism with other additives in commercial oils and possible mechanisms of DND influence on lubricant performance.

## 2. Preparation of DND colloids in oil

It is reasonable to expect that structural and chemical characteristics of the ND particles will play an important role in their influence on performance of nanolubricants. While primary DND particles have a shape close to spherical (Fig. 1a) [27] and it is often assumed that these 4–5 nm in size hard spherical particles could play a role of rolling spacers between the contacting surfaces, this model is far from a reality. Typical commercial DNDs are available as tight aggregates (Fig. 1b) of primary particles with sizes exceeding 100–200 nm. Moreover, it is important to be aware that the

structure and chemical composition of the detonation ND particles strongly depends on their history of synthesis and processing and often is specific to a particular vendor [29]. Detonation ND is produced from molecules of explosives, which provide both a source of carbon and energy for the conversion. The detonation takes place in a closed chamber filled with an inert gas (“dry” synthesis) or water (ice) coolant (“wet synthesis”). As a rule, DND produced by a dry synthesis, has smaller size of primary particles and less tightly bond aggregates than DND produced by a wet synthesis. Electron microscopy analysis of the structure of detonation soot revealed a few tens of nanometers “primary” ND aggregates (Fig. 1b) directly within the matrix of detonation soot formed by dry synthesis using a small explosive charge [30]. Aggregation of DND is also more pronounced if larger detonation charge is used in a synthesis (for example, 10 kg vs 1–2 kg). After the process of DND purification from the sp<sup>2</sup> carbon and metallic impurities, further aggregation takes place resulting in purified DND with aggregate sizes of up to a few hundred nanometers. Non-coherent interfaces with C–C bonds and even atomically sharp grain boundaries can be formed between primary particles within aggregates. These aggregates are so strongly bonded that they cannot be broken apart by high power ultrasound, but can be disaggregated into primary particles by the bead milling technique [31]. Such aggregates possess high abrasivity and therefore increase wear of the friction surfaces when added to lubricants. A reasonable strategy toward preparation of DND suitable for nanolubricant applications is a decrease of DND size by a bead milling [31] followed by discharge of the larger abrasive aggregates by centrifugation. It is also important to keep in mind that contamination from bead milling media (zirconia, if zirconia balls had been used for milling) typically is present in the disaggregated ND material and can be partially removed by centrifugation. From a practical standpoint, there must be a balance between DND size and their cost, since the cost of NDs strongly depends on their size (there is more than a 10x difference in the cost of 5 nm and 100 nm DND). Therefore, in order to avoid increased wear by adding DND particles to lubricants, our recommendations extend to DND aggregates below 100 nm and preferable below 50 nm.

To be effective as lubricant additives, nanoparticulates must also exhibit long-term colloidal stability. Stability of dispersions in polar solvents is known to be determined by the surface charge density that is typically characterized by the electrokinetic potential, or “zeta-potential”. It is the electrostatic repulsive force that prevents the dispersed nanoparticulates from coagulation and consequent precipitation (Fig. 2). DNDs can be produced and are available from vendors with both positive and negative zeta potentials, depending on the method of oxidation of sp<sup>2</sup> carbon in the detonation soot during purification [29]. Treatments resulting in NDs with negative zeta potential seem to provide more complete oxidation with predominant carboxylic acid and acid anhydride groups on the surface, which are responsible for the negative zeta potential in water suspensions over a wide range of pH. Functional groups on the surface of NDs with positive zeta potential are much more diverse. In a recent thorough analysis of fully deagglomerated 4 nm ND with positive zeta potential [32], it was concluded that the groups are amphoteric, with high concentrations of phenols, pyrones, and sulfonic acid groups. The presence of phenols and pyrones is consistent with the presence of graphitic surfaces formed during bead milling of DND. It was concluded that the positive surface potential of these NDs originates from the presence of pyrones. DND surfaces can be also on purpose functionalized with a number of chemical groups to vary the zeta potential without compromising the diamond core properties [29]. Sign and value of ND’s zeta potentials are important because they influence electrostatic interactions with dispersants and surfactants used for NDs dispersion in non-polar solvents.

Download English Version:

<https://daneshyari.com/en/article/5451487>

Download Persian Version:

<https://daneshyari.com/article/5451487>

[Daneshyari.com](https://daneshyari.com)