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Environmentally friendly material: Hexagonal boron nitride

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ABSTRACT

Importance of environmental issues has increased every year and several global summits were held on this subject. As a result, research efforts are focused on environmentally friendly materials, reducing energy usage and emissions. Hexagonal boron nitride (hBN) with superior lubrication is an environmentally friendly material. It's structure of strong bonds between atoms in layers with weak Van Der Walls bonds between layers gives low friction. Also, hBN is an inorganic artificial material with high heat shock resistance, heat conduction, electrical insulation and chemical stability. These properties makes hBN suitable for various applications. In this study, friction and wear behaviors of products containing hBN were reviewed, in order to see effects for sustainable environment.

1. Introduction

As of this writing population of world is 6.976 billion, it is expected to be between 7.5 and 10 billion at 2050. The increase in population, causes an increase in energy usage that is expected to increase 1.7% every year until 2025 [1]. Related to these, it is expected that total number of vehicles in the world to reach 1.116 billion in 2020 and number of vehicles in developing countries will be equal to the developed countries (Fig. 1) [2]. Although hybrid and electrical vehicles can be used, it is seen that petrol based fuel consumption in vehicles will continue. Thus it is predicted that, research on energy and environment will increase [3, 4].

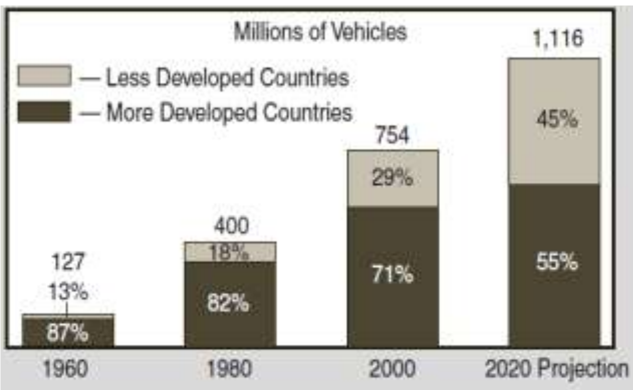

Figure 1. World vehicle amount: 1960 to 2020 [2]

Most of the energy produced is lost due to friction. Friction is a mechanical force that resists against movement or prevents movement on sliding or rolling surfaces and causes energy loss [5]. Internal combustion engines that are used in most land and sea vehicles, because of their safety and performance are greatly affected by friction. In these engines, maximum theoretical energy can not be used due to friction and heat loss, thus productivity decreases. It is estimated that decrease in friction in engines and transmission parts might generate a 120 billion USD gain in USA alone [6]. The decrease of friction and wear on moving parts in vehicles and efficient use of energy is a topic of many studies [7]. In highly industrialized nations, the total annual cost of friction-and wear-related energy and material losses is estimated to be 5–7% of national gross domestic product [8].

The part of the energy from fuel devoted to mechanical power to overcome friction in passenger car can be shown in Fig.2. Only 21.5% of the total energy is used to move the vehicle [9].

Studies to decrease the friction have been an important research topic since first moving parts. In history; lubrication was applied to wheels, chariots, mills and in construction between stone blocks. It is known that lubrication was applied since Sumer and Egypt

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civilizations (5000 to 3500 years ago) [10]. According to an investigation conducted in 2007, if western developed countries can adapt all the lubrication techniques known today, a gain of 0.4% GDP can be achieved [11].

Friction can be decreased by using a thin film of low shear strength gas, liquid or solid material to achieve better movement of surfaces. Relation between lubricant film thickness and friction coefficient is given in Fig. 3. [12]. It is assumed that different engine parts have different lubrication regimes to reach expected performance. Usually bearings work in hydrodynamic lubrication side in which surfaces are separated by a lubricant film. At low speeds or start and stop conditions, lubricant film is sheared and metal surfaces contact each other. On piston rings and gearboxes usually boundary and mixed lubrication conditions are applicable. The aim of lubrication is to decrease friction between contact surfaces. In order to achieve this, engine and transmission oils are used. When these oils are used alone, lubricant film between moving engine parts gets thinner and sometimes is sheared, thus surface contact is observed. To prevent this phenomena some additives are added to oils. It is expected that, these additives; will not react with engine oil, has no residue, endure at working temperatures, do not cause corrosion on metal parts, do not cause environment harming emissions in exhaust and they will increase engine performance.

Effects of lubrication is researched not only in engines but also on micro mechanical systems [13-19] and biomechanical systems [20]. Developments in machinery, high work speeds, increased temperatures and a high pressure system creates an increased demand for lubrication [21]. Research on lubricants used in internal combustion engines still continues [22]. In 1916, oil in Maxwell automobiles had to be changed every 100 miles or every day [23], today cars can be used for 30.000 km or more without an oil change.

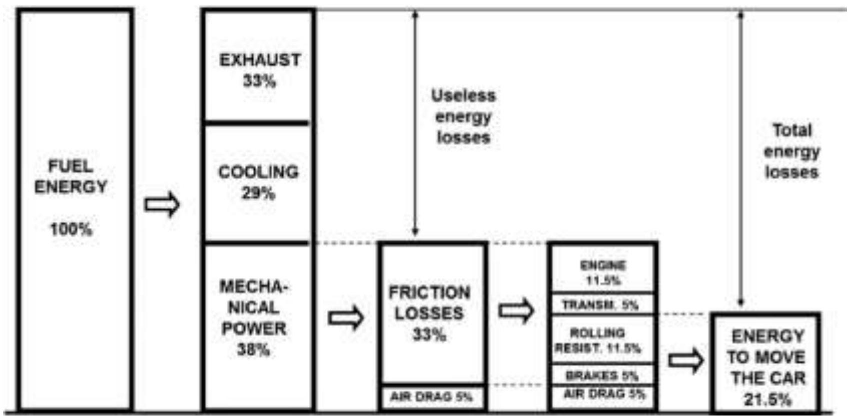

Figure 2. Breakdown of energy consumption of passenger car [9]

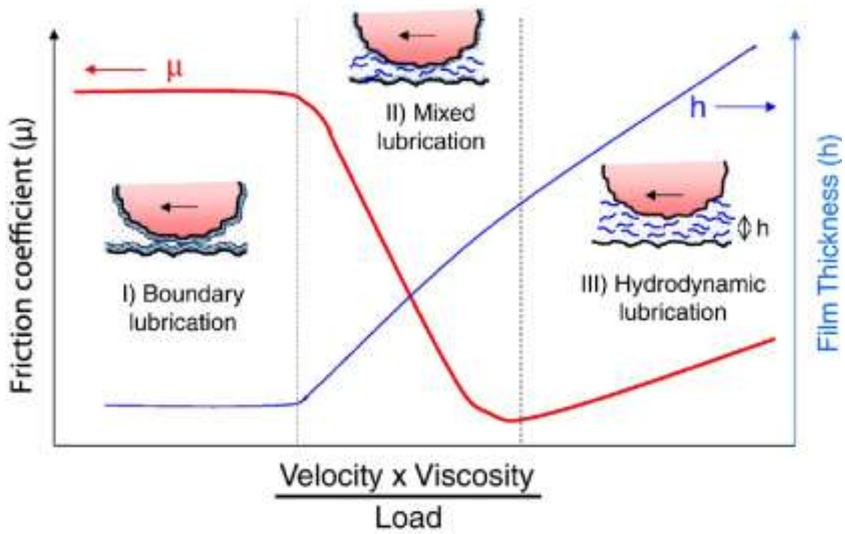

Figure 3. Effect of lubricant film thickness on friction [12]

2. Lubricants

Lubricants can be classified as liquid (petroleum based or synthetic), solid or gaseous lubricants. Solid lubricants are used at conditions where liquid lubricants are technologically or economically not feasible or when lubrication properties of liquid lubricant requires improvement. Many materials and coatings are considered as solid lubricant. The most used solid lubricants are given in Table 1. In order to meet aerospace industry's requirements, research on solid lubricants has increased since 1950's. Although various materials are found to have solid lubricant properties, most used materials are graphite and molybdenum disulphide. The lubrication properties of MoS_2, graphite and boron nitride are originated by their crystal structure [10, 24]. Prabhu et.al. [25] investigated the tribological behavior of Cu/silica composites using different solid lubricants. This study showed that MoS_2, graphite, and hBN improve the wear resistance of the Cu/silica composites, respectively. The researches with boron nitride nano sheets (BNNSs) have shown that a small amounts of hBN nanosheets could enhance the wear resistance and reduce friction coefficient [26-28].

Table 1. Solid lubricants [11]

Graphite	Graphite Fluoride
Molybdenum disulphide	Molybdenum diselenide
Tungsten disulphide	Tungsten diselenide
Niobium disulphide	Niobium diselenide
Tantalum disulphide	Tantalum diselenide
Titanium disulphide	Titanium diselenide
Titanium telluride	Cerium fluoride
Barium hydroxide	Cadmium chloride
Cobalt chloride	Zirconium chloride
Lead chloride	Lead iodide
Boron nitride	Silver sulfate
Borax	Talc
Mica	

3. Boron nitride

Boron nitride is an artificial compound formed by 1:1 ratio of boron and nitrogen. Its chemical formula is BN and has three crystal structures resembling carbon polymorphs. Its crystal structures are; hexagonal structured hexagonal boron nitride (hBN), close packed hexagonal structure that is synthesized at high pressure, wursitic boron nitride (wBN) and cubic boron nitride (cBN) that is synthesized at high pressure and at high temperature. Every crystal structure of BN has different properties [29-31].

Boron nitride is produced by various methods by a small number of companies in the world. Production technology is kept secret by the owners of these technologies. Although BN was first produced by Balmain at 1842 by heating boron oxide with NaCN, until production of hot pressed hexagonal BN in mid. 20th century (1950), it was used just as a laboratory material [32].

hBN is an artificial material with layered crystal structure that has strong covalent bond between atoms in layers but weak Van der Waals between layers (Fig. 4) [33]. Because of its crystal structure and white color, it is also called white graphite. hBN has a density between 2.0 to 2.28 g/cm^3. Lattice parameters are measured as a= 2.5040 Å c= 6.6612Å at 300K. Bulk modulus at 300K is 36.5GPa and hardness at Mohs scale is 1.5 [34]. hBN is stable up to 900 °C in oxidizing conditions. Hexagonal boron nitride is used from metal industry to cosmetics because of its unique properties. hBN isn't wetted by molten metals or slags and show excellent solid lubrication properties. Also has low friction coefficient, high thermal conduction and electrical insulation properties [35, 36]. Unlike graphite hexagonal boron nitride does not need water vapor between crystal layers for lubrication. This property enables hBN to be used in vacuum or space research as a solid lubricant [38].

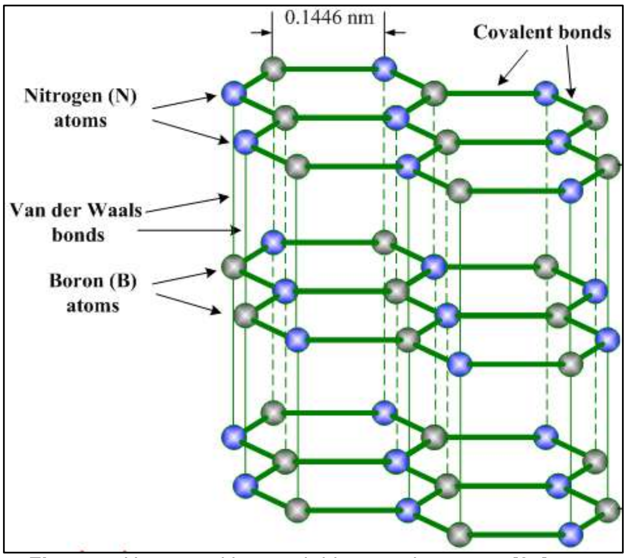

Figure 4. Hexagonal boron nitride crystal structure [37]

Although Turkey has more than 73% of world boron reserves, market share of boron end products of Turkey is not at desired levels. There are around 250 boron compounds and one of them is boron nitride. Boron nitride has two commercial forms; hexagonal and cubic boron nitride. hBN had not been produced industrially in Turkey until its production by BORTEK Inc. in 2006 with support of National Boron Research Institute (Project No: BOREN-2006-37-ÇG1-24). In addition, nano sized hBN was synthesized with support of

Republic of Turkey, Ministry of Science, Industry and Technology (Project No: SANTEZ, 00090-STZ.2007-1). Nano sized hBN is used as an oil additive to reduce friction and wear and it has no reaction with engine oil, engine parts, does not cause clogging in filters and does not breakdown. BORONMAX® is a registered trademarked of BORTEK. Various tests were conducted on BORONMAX® product and its performance was measured [39]. While the investigation of lubricity properties of hBN had been started in Turkey in 2007, US Department of Energy had gave the grant to Argonne National Laboratory (USA) with partners for research on “Development of Boron-Based Nanolubrication Additives for Improved Energy Efficiency and Reduced Emissions” in 2008 [8].

According to Abdullah et.al. [40], the coefficient of friction (COF) decreases with increasing hBN content in conventional diesel engine oil. They obtained the results by using signal-to-noise (SN) ratio and analysis of variance (ANOVA) as statistical technique. They found that the optimized values of 0.5 vol% hBN and 0.3 vol% surfactant decreased COF by 12-33% compared to conventional diesel engine oil.

Reeves et.al. [41] found that nano sized hBN particles enhanced tribological performance in canola oil compared to micron and submicron sized hBN.

A study by Çelik et.al. [42] investigated the effects of nano hBN particles on the friction and wear properties of AISI 4140 steel material when hBN particles were used as an oil additive. In this study, it was inferred that the amount of nano particles in the oil affects the friction and wear properties. It was indicated that the addition of the nano hBN particles did not change the viscosity of the lubricants. As a results of this study, 14.4% improvement in the friction coefficient (Fig. 5) and 65% decrease in the wear rate (Fig. 6) were achieved. Nanoparticles completely covered the asperities in samples; therefore, the mending effect occurred in these samples, and they exhibited the lowest wear rate and the wear-track widths (Fig. 7). The presence of sufficient nano hBN additives in oil prevents direct contact and results in a decrease in friction and wear.

Abdullah et.al. [43] studied the effect of hBN and alumina (Al_2O_3) nanoparticle additives, on the tribological performance of SAE 15W40 diesel engine oil by making a four-ball tribotester. According the study, the presence of hBN nanoparticles additive in the diesel engine oil lowered the material’s wear rate by 58%. They showed that the 15W40 diesel engine oil, containing hBN nanoparticle additives, could provide good anti-wear effects in the friction pairs.

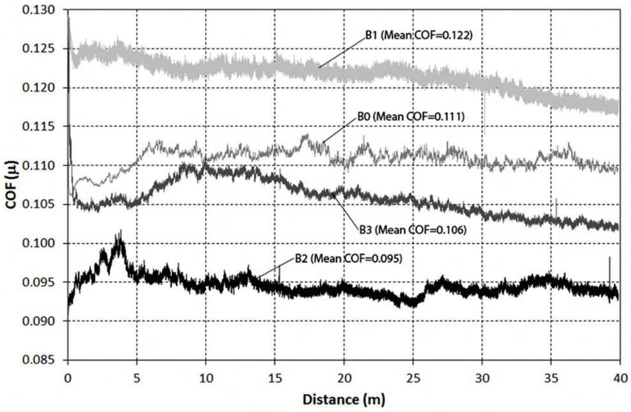

Figure 5. Coefficients of friction as functions of the sliding distance (2.5 cm/s sliding speed) [42]

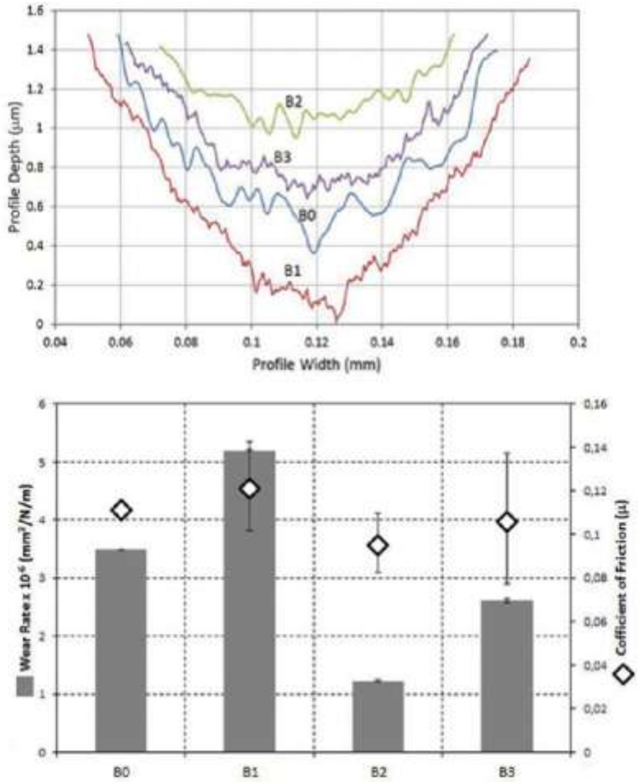

Figure 6. Wear profiles, the specific wear rates and the coefficient of friction of samples [42]

In another study of Abdullah et.al. [44], the effect of hBN nanoparticles on the engine performance was studied. They concluded that addition of optimal composition of hBN nanoparticles in conventional diesel engine oil effectively increase both maximum power and torque of the engine as well as reduce wear of the engine components.

Abdullah et.al. [45] investigated the potential of hBN nanoparticles as friction modifier and antiwear additive in engine oil. The study showed that the optimized nano-oil could reduce the coefficient of friction and increase wear resistance, as compared with conventional diesel engine.

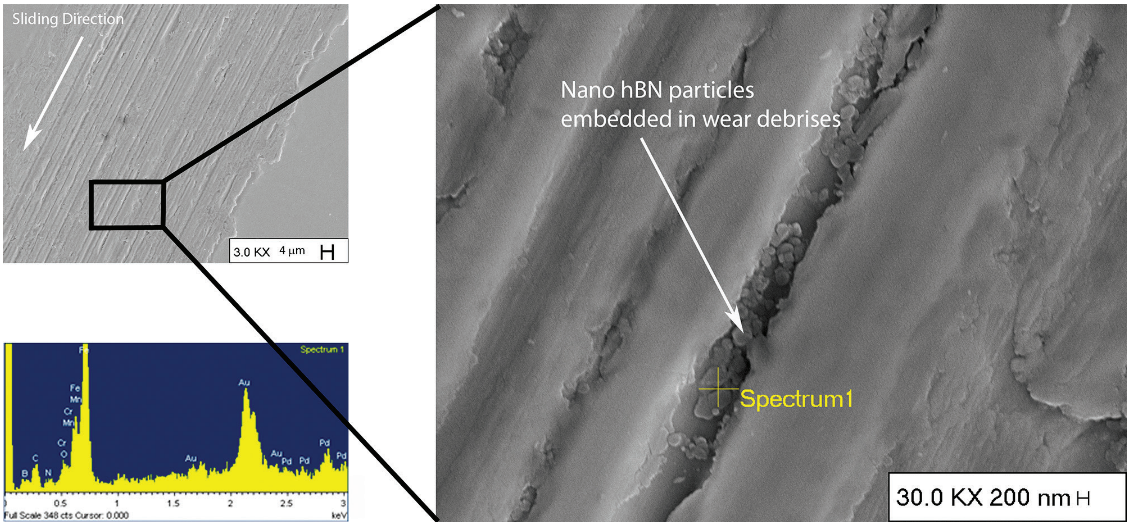

Figure 7. The wear track, the wear debris and the chemical analysis of the wear debris [42]

A similar study to that of Çelik was conducted by Wan et.al [46] and the mending effect that cause anti-friction and anti-wear properties of hBN particles was confirmed. The results showed that the BN nanosheets (BNNSs) can greatly reduce the friction coefficient and the wear scar diameter of the base oil. Fig. 8 shows the SEM images of worn ball surfaces used for testing the base oil and base oil containing BNNSs. The base oil gives the biggest scar (1mm) while the base oil containing BNNSs shows reduction in wear scar diameter (0.5mm). The reduction of wear scar literally means the good anti-wear property of BN nanosheets.

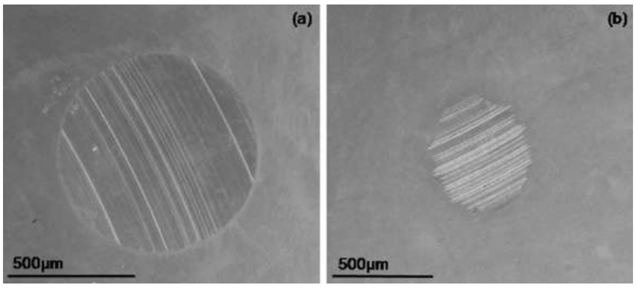

Figure 8. SEM images of worn-surfaces of the stationary balls tested for (a) neat base oil and (b) base oil with BN nanosheets [46].

Baş and Karabacak [47] investigated the effect of boron compounds (boric acid (BA) and hBN) on performance of engine oil. 2, 4, and 6 wt% BA and hBN were added to oil. The results showed that boron compound additives can reduce the friction coefficient and form a tribofilm in boundary or mixed lubrication conditions in engine oils.

Kumari et.al [27] studied the dispersibility of exfoliated and functionalized hBN in lube base oil and their effects on friction and wear properties. In this study, hBN powder was exfoliated into h-BN nanoplatelets (hBNNPs), and then long alkyl chains were chemically grafted. For functionalization of hBNNPs, octadecyltriethoxysilane (ODTES) were used. Micro- and macro tribology results showed that hBNNPs-ODTES, as an additive to synthetic polyol ester, significantly reduced both the friction and wear of steel disks. It is obvious that hBN concentration is effective on COF (Fig 9). This study depicts that thoroughly dispersed hBNNPs-ODTES can significantly improve the tribological properties of the lubricant by reducing the friction and wear.

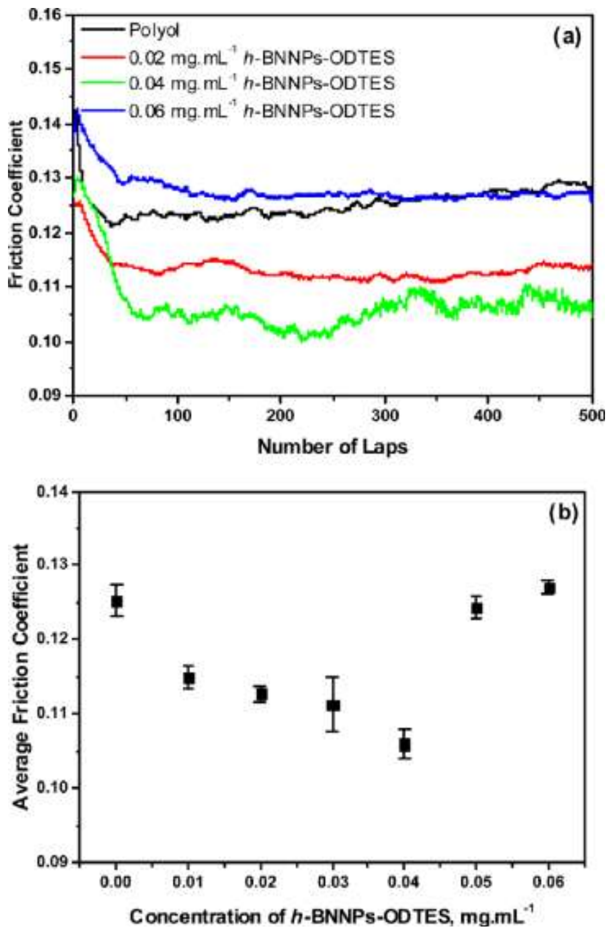

Figure 9. (a) Evolution of the friction coefficient with the number of laps. (b) Changes in the average friction coefficient for polyol ester as a function of increasing doses of hBNNPs-ODTES under unidirectional sliding contact. Conditions: load 250 mN; speed 1 cm/s; Hertzian contact pressure 864 MPa [27].

There are several researches on using hBN in greases. Podgornik et al. [48] investigated the possibility of replacing graphite with hBN in Al-forming lubricants. Three different hBN particle sizes (0.5 μm, 5 μm and 30 μm) with concentration of 5, 10 and 20% were used in commercially available NLGI class-2 lubrication grease for preparing the lubricants. The results of the investigation show that hBN is capable of successfully replacing graphite in Al-forming processes, while at the same time maintaining a clean surface without staining.

Wen et.al [49] investigated the effects of different additives and combinations of additives on the properties of polyurea grease. The research of several groups of experiments have shown that the Teflon, molybdenum disulphide and hBN, graphite fluoride is relatively more superior additive if compared with graphite.

The wind energy industry is a rapidly growing sector and gearbox failure has been declared. Considering the high cost of replacing a gearbox, improving the reliability of the wind turbine drivetrain is a critical issue. The failures were caused by micro pitting, spalling, scuffing, excessive abrasive wear, and corrosive wear. There have been several researches on solving this problems. hBN may be the solution with reducing friction and wear in wind turbine drivetrain.

Greco et.al. [50] studied the tribological performance of a boron based surface treatment and lubricant additive in a wind turbine gearboxes. The results indicated that nano-colloidal boron-nitride added into the gear oil formed a stable film which was important to achieve improved tribological performance.

4. Conclusion

Hexagonal boron nitride decreases friction and wear, reduces materials loss and energy usage. hBN applications in internal combustion engine oil, gear boxes oil, wind turbine drivetrains oils and greases etc. will save the energy by reducing friction and preserving the environment. A decrease in environmental footprint can be achieved by using hBN with oils and grease. Besides environmental contribution, with broad application of hBN in oils, national gross domestic product could be increased by 5–7% annually.

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