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This review focused on the effects of nanoparticles on tribological performance in oil lubrication. Spe-

cifically, chemical, physical, and morphological parameters of nanoparticles were studied through sta-

tistical comparison. The influence of those particles on friction and wear was analyzed. Mechanisms of

lubrication involving nanoparticles were discussed via collected data in literature. More than a replen-

ishment of the current knowledge, this review facilitates the fundamental understanding of lubrication

that enables us to design and develop nanolubricants with superior tribological performance.



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## Roles of nanoparticles in oil lubrication $\frac{1}{2}$

### Wei Dai<sup>a</sup>, Bassem Kheireddin<sup>b</sup>, Hong Gao<sup>b</sup>, Hong Liang<sup>a,\*</sup>

<sup>a</sup> Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, United States <sup>b</sup> Shell Technology Center, Houston, TX 77082, United States

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#### ABSTRACT

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#### 1. Introduction

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In mechanical systems, consistent performance and energy saving demand eco-friendly and highly efficient lubricants. In today's market, 90% of lubricants are composed of hydrocarbon molecules and the rest are additives governing their behavior. For decades, organic phosphorous and sulfide compounds have played important roles in friction modification and wear resistance [1]. Lubrication mechanism stems from the physical and chemical interactions between lubricant molecules, material surfaces, and environment. In recent years, nanoparticles have started to play more important roles as lubricant additives for their potential in emission reduction and improving fuel economy. Their characteristic size, normally less than 100 nm, will allow them to enter the contact region. In comparison with organic additives, nanoparticles are considered thermal stable at elevated temperatures that makes them favorable as lubricant additives.

There are some reports about lubrication mechanisms of nanolubricants. When nanoparticles were used as friction modifiers, they displayed four behaviors [1]: rolling of nanospheres [2-4]; tribofilm formation as results of tribochemical reactions [5–9];

<sup>\*</sup>This manuscript was reviewed in the double-bland process.

<sup>\*</sup> Corresponding author.

E-mail address: hliang@tamu.edu (H. Liang).

mending effect because of the minimal size [10]; and polishing [11]. In addition, nanoparticles could be used as additives in diesel and biodiesel [12–15]. They were effective in improving fuel efficiency, engine performance, exhaust emission, combustion, and evaporation characteristics at different operating conditions. Moreover, nanorefrigerants were able to reduce energy consumption and enhance heat transfer rate [16–19].

The aforementioned reviews raised several questions: How can one optimize the tribological performance of nanolubricants? What are the characteristics of nanoparticles that are important to lubrication? Can we quantize their effects? During the review of literature of several hundreds of publications, we found that each study has been based on unique conditions, such as base stock. additive concentration, nanomaterials and their surface functionalization, workpiece materials, test parameters, lubrication regimes, etc., among many others. There is no one standard condition that can be used for fair comparison. The majority reports have been based on steel-steel contact. The non-steel metals will not be the focus due to lack of statistically sufficient data to conduct a fair comparison. In order to make the best use of available data for better comparison and prediction, we applied the following strategy for this review study. First, frictional performance. We chose the minimum friction coefficient reached (MFC) and maximum friction reduction (MFR) in order to reveal fuel efficiency. Using such an approach the lubrication regimes from boundary to hydrodynamic will be discussed together. Second, wear performance. We selected the maximum wear reduction percentage (MWR) to exhibit anti-wear capability, regardless of the working conditions. In this case, most wear studies were conducted in the boundary and mixed lubrication regimes that we do not separate in order to maintain sufficient data for statistic analysis. Thirdly, statistic analysis was conducted based on the experimental results collected from about 70 papers that were related to nanolubricant additives, as listed in Table 1. Correlation between the parameters and performance was calculated using the JMP software. Using this approach, not only we could identify the key factors such as chemical composition and morphology to improve the tribological performance, but also we could establish a relationship between the key factors and lubrication mechanisms. In this study we defined morphological parameters as the molecular structure and shape of nanoparticles. In addition, we defined the size as a separate factor that belonged to the physical properties of nanoparticles. This review is more than a replenishment of the current knowledge. As a result, it substantially facilitates our fundamental understanding in nanolubrication that enables us to design nanolubricants with superior tribological performance.

### 2. Effects of chemical composition of nanoparticles on lubricating performance

Nanoparticles with various chemical compositions possess different chemical and physical properties, affecting the interaction between lubricants and surfaces. There are three questions to be answered. Which elements are favorable for nanolubrication? What are lubrication mechanisms of the specific element (the role it played) in each lubricating regime? How important is the chemical composition in determining a nanolubricant's tribological performance? As discussed earlier, we focus on three aspects, the minimum friction coefficient (MFC), maximum friction reduction (MFR) and maximum wear reduction (MWR). Through this literature review and statistical correlation coefficient analysis, we aim to reveal insight from nanolubricants.

Based on the Table 1, we divided reported nanoparticles into seven types based on their characteristic chemical elements:

Table	1
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Summary of nanolubricant additives.

Nanoparticle	Reference
Ag doped MoS <sub>2</sub> nanoparticles	[20]
Ag nanoparticle	[21,22]
Al <sub>2</sub> O <sub>3</sub>	[23,24]
Al <sub>2</sub> O <sub>3</sub> and CuO	[25]
Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> composite	[26]
Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> nanocomposites	[27]
Bismuth nanoparticles	[28]
DIN Calcium carbonato nanonarticlos	[29]
	[30]
	[32-36]
Cu nanoparticles in serpentine powders	[37]
Cu/SiO <sub>2</sub> nanocomposites	[38]
CuO	[39]
CuO, TiO <sub>2</sub> and nanodiamond	[40]
CuS	[41]
Diamond and SiO <sub>2</sub>	[42]
Diamond nanoparticles	[43]
Fe, Cu, Co NPs	[44]
$Fe_3O_4$ magnetic nps	[45]
Fullerene-like MoS <sub>2</sub> nanoparticles	[46]
b pN	[47]
II-DIN Hydroxides NDs (Mg/A1/Ce IDHs)	[40]
IF-MoS <sub>2</sub> nanonarticles	[50 51]
IF-WX2	[52]
La doped Mg/Al lavered double hydroxide (LDH)	[53]
LaF <sub>3</sub>	[54]
MoS <sub>2</sub>	[55-59]
MoS <sub>2</sub> and SiO <sub>2</sub>	[60]
Diamond and graphene	[61]
Nano-Cu/graphene oxide composites	[62]
Nano-PTFE	[63]
NI NiMao S	[64]
NIMOU $_2$ S $_2$ Ni based papelubricants	[66]
	[67]
Pd	[68]
Pd and Au nanoparticles	[69]
PTFE	[70,71]
Rhenium doped MoS <sub>2</sub>	[72]
SA/CeBO <sub>3</sub>	[73]
Serpentine ultrafine powders	[74]
Serpentine, $La(OH)_3$ and their composites	[75]
Single wall carbon nanohorns (SWCNH) and $TiO_2$	[76]
SiO <sub>2</sub>	[77]
Sn and Fe nanoparticles	[78]
IBP-LaF <sub>3</sub> TiO	[/9]
$TiO_2$ TiO_ CuO_Al_O_ MWNTs	[84]
Titanium nanonarticle	[85]
Zeolite	[86]
$ZnAl_2O_4$	[87]
ZnO	[88]
ZnO and CuO	[89]
ZrO <sub>2</sub>	[90]
ZrP	[91]

carbon and its derivatives, metals, metal oxide, sulfides, rare earth compounds, nanocomposites and others. Detailed information about each category is listed in Table 2. For carbon and its derivatives, molecular structures (sheet, tube, onion) played a dominant role in determining their tribological behavior. The effects of carbon-containing additives would not be elaborated in this section. For metals and metal oxides, the majority elements were located in the transition metal group. For sulfides, the representative one was MoS<sub>2</sub>, others included WS<sub>2</sub>, CuS, and NiMoO<sub>2</sub>S<sub>2</sub>. For rare earth elements, Y, La, and Ce were considered as favorable elements for lubricant additives. For nanocomposites, they were the combinations of the aforementioned several categories. Others

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