

# **Part III**

## **Nano Blended Polyacrylate as Lube Oil Additive**

# **Chapter-I**

## **Background of the Present Investigation**

The most revolutionary technology of the 21<sup>st</sup> century is nanotechnology. It has versatile application in many fields and ushers material science into a new era. Usually particles size between 1 and 100 nanometers are referred as nanoparticles. The term 'nanoparticle' is not generally applied to individual molecules. The exciting panorama of nanotechnology has potential application in almost every area of life. Synthesis and processing of nano materials and exploring their probable applications are essential aspects of nanotechnology. Research and development in this field helps in understanding, emerging and creating superior, as well as revised forms of devices, materials and systems for upcoming applications. Every field from electronics and medicine to apparels and manufacturing flourish from the advances in nanotechnology, which is versatile in its application. This technology has engrossed strong interest from the researchers across the world. Nanotechnology exercises breakthrough in fields such as- medicines, agriculture, catalysts, healthcare and energy. For instance, the understanding of cost effective power harvest by means of solar and fuel cells with better competency is a contemporary challenge. It can be used to undertake environmental troubles and may be used to develop proficient drug delivery processes. Genetic development enhances agricultural productivity and can facilitate to make crops resistant to heat and water logging. Nanotechnology has lots of future applications and potential that will become well-known with further development. Nanomaterials with desired morphology, size and chemical composition are necessary in order to learn their physical properties and application. Usually nanoparticles are defined as particles of less than 100 nm in size, which as a small object behaves as a whole unit in terms of its physical properties. The materials are more effective at nanoscale dimensions than their larger sized counterparts for two reasons: first, their small size results a very high surface area to volume ratio; second, when such materials are fabricated on the nanoscale, they attain

interesting surface properties owing to their active surface atoms that are not found inside their large-sized counterparts. Nanomaterials including nanowires, carbon nanotubes, semiconductor quantum dots, metal, and other inorganic nanoparticles (such as copper, silver and gold) are formed through different methods and are being tested for their potential applications.

Nanoparticles can be classified into two classes:

1. Organic nanoparticles

2. Inorganic nanoparticles

Carbon nanostructures such as graphene, fullerenes and nanotubes are organic nanoparticles, while inorganic nanoparticles may consist of noble metal nanoparticles (like silver and gold), metal oxide nanostructure, semiconducting nanoparticles (like titanium dioxide and zinc oxide) and magnetic nanoparticles. There is an emerging interest on inorganic nanoparticles, which show advanced material properties with processing and efficient flexibility. Inorganic nanomaterials have been extensively used in diverse fields; in medicine field owing to their versatile biocompatibility (for example, hydroxyapatite based artificial bones, titanium based dental implants) and their possibility to get functionalize helps in targeted drug delivery and controlled release of drugs. Glass and paint industries take advantage of the interesting properties of inorganic nanoparticles.

The inorganic nanoparticles are being added into lubricant formulations by oil companies exclusively to improve the extreme pressure (EP), anti-wear (AW) and anti-friction properties, in that way improving the efficiency and service life of machinery.<sup>1</sup>

With advanced machinery and equipment of the speed, load, temperature and other parameters of increasing the lubricating oil's anti-wear agent has not entirely meet their antifrication and anti-

wear performance requirements. Due to this, oil-soluble additives with anti-wear and anti-friction capabilities have been studied widely in recent years.<sup>2-4</sup>

The widespread studies on tribological characteristics of nanoparticles as lubricating oil additives have been carried out.<sup>5-7</sup> Unfortunately, insolubility and the obscurity of stable dispersion of inorganic material hold down their application in lubricating oil. The dispersion stability of nanoparticles is superior to micron particles in base oil. Therefore, it is essential to study lubricating oil additives based on nanoparticles.

The main benefit of using nanolubricants is that they are comparatively insensitive to temperature and that tribochemical reactions are limited, compared to traditional additives. One more advantage of the addition of nanoparticles in lubricating oil is that they cannot be retained by the filters. Furthermore, roughness of sliding surfaces is often a several micrometers so that nanoparticles can deposit in troughs on the rubbing surface.<sup>8-12</sup>

Numerous papers have reported that the incorporation of nanoparticles to lubricant is effective in dropping wear and friction. The friction-reduction and anti-wear behaviors are reliant on the characteristics of nanoparticles, such as size, shape, and concentration. One important property that makes nanoparticles different from other materials is the fact that they have a massive surface area. Due to their very high surface area, nanoparticles are exceptionally reactive compared to its larger form. The first key step in experimental studies with nanofluids is their preparation. Nanofluids are not merely liquid-solid mixtures. Some special requirements are vital, e.g., stable and durable suspension, negligible agglomeration of particles, no chemical change of the fluid, etc. Now a days, generally used nanoparticles are Oxide Ceramics-  $\text{Al}_2\text{O}_3$ ,  $\text{CuO}$ , Metal Carbides – $\text{SiC}$ , Nitrides –  $\text{AlN}$ ,  $\text{SiN}$ , Metals –  $\text{Al}$ ,  $\text{Cu}$ , Nonmetals – Graphite, Carbon nanotubes, Layered –  $\text{Al}+\text{Al}_2\text{O}_3$ ,  $\text{Cu}+\text{C}$ , PCM-S/S, functionalized nanoparticles.

Agglomeration is become a major problem during synthesis of nanofluids. Generally, ultrasonic equipment is used to intensively disperse the particles and reduce the agglomeration of particles. Numerous nanoparticles have recently been investigated for use as oil additives. Nano-powders of some metals and their compounds exert an especially effective influence on the characteristics of lubricants. The application of nanoparticles that include Cu, CuO, Fe, Ni, TiO<sub>2</sub> and other metallic nanoparticle additives in lubricating oils provides good friction reduction and anti-wear behavior.<sup>9, 10, 13-17</sup>

Juozas Padgurskas, Raimundas Rukuiza et. al. Investigated the tribological behaviour of mineral oil having Fe, Cu and Co nanoparticles and their combinations. The tribological tests revealed that each set of nanoparticles significantly decreased the friction coefficient and wear of friction pairs. The use of Cu nanoparticles showed the most effectual reduction of friction and wear in each combination of nanoparticles. Surface analysis shows that the constituent elements of nanoparticles precipitated on the contact surface during the use of the oils with nano-additives.<sup>18</sup>

The friction reduction and anti-wear mechanism (**figure: 3a**) of nanoparticles in lubricant have been reported as protective film, rolling effect and third body.

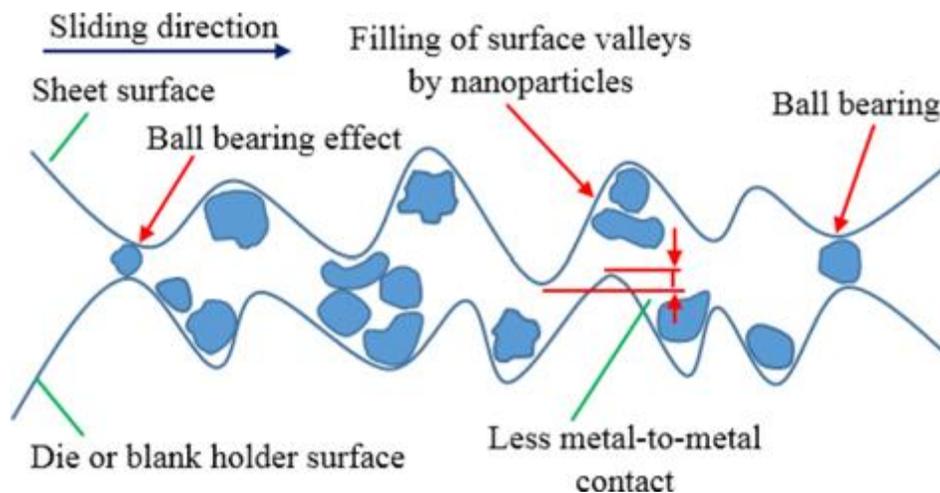


Figure 3a: Action mechanism of nanoparticles between lubrication surfaces

A variety of mechanisms (**figure:3b**) have been proposed to explain the lubrication enhancement of the nanoparticles suspended lubricating oil (i.e., nano-oil), including the ball bearing effect,<sup>19-21</sup> protective film,<sup>12,14, 22-24</sup> mending effect,<sup>25</sup> polishing effect.<sup>26</sup> The nanoparticles hovering in lube oil play the role of ball bearings between the frictional surfaces. In addition to that, they also create a protective film to some extent by covering the rough friction surfaces. The nanoparticles deposit on the friction surface and compensate for the loss of mass which is known as mending effect. Again the roughness of the lubricating surface is reduced by nanoparticle-assisted abrasion which is known as polishing effect. Among the above mentioned lubrication mechanism ball bearing and protective film are the direct effect of nanoparticles on lubrication enhancement and the other two are the secondary effect of the nanoparticles on surface enhancement.

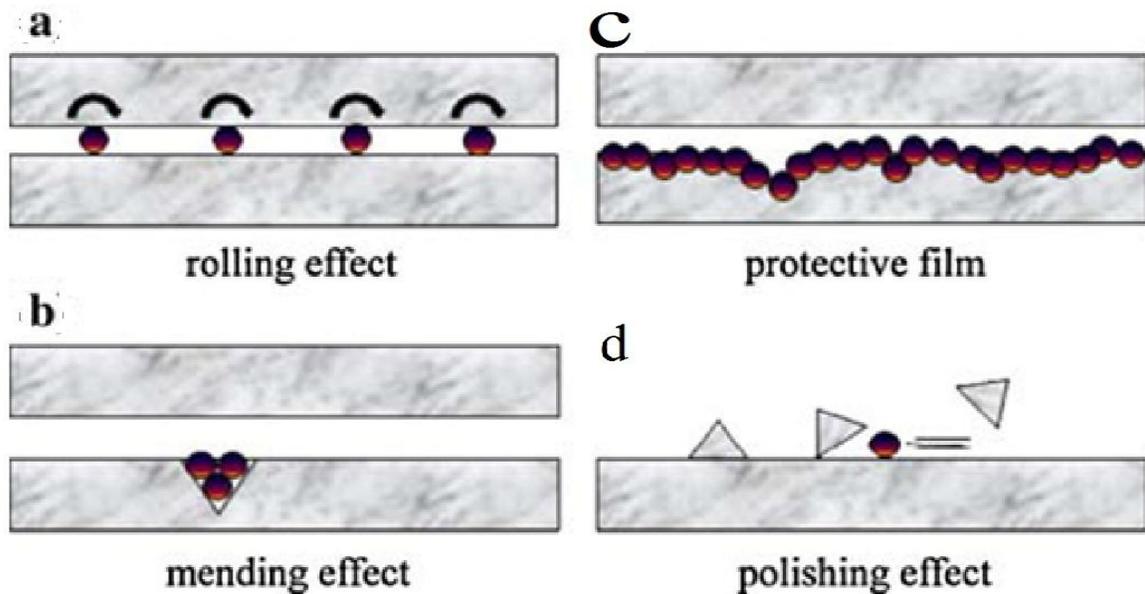


Figure 3b: Possible lubrication mechanisms between the frictional surfaces by the application of nanoparticle added lube oil.

J.L. Viesca , A. Herna´ ndez Battez investigated the influence of the incorporation of carbon-coated copper nanoparticles (25 nm) on the tribological behavior of a polyalphaolefin (PAO6)

and compared this behavior with the case of non-coated copper nanoparticles, determining the influence of coating. The study concludes that the addition of carbon-coated copper nanoparticles decreases wear and increases the load-carrying capacity of PAO6. This tribological improvement is due to the deposition of nanoparticles on the rubbing surfaces and probably by their action as tiny bearings. The copper nanoparticles coated with carbon did not perform better than non-coated ones.<sup>27</sup>

R. Chou, A. Hernandez Battez examined the influence of addition of 20 nm diameter nickel nanoparticles on the tribological behavior of synthetic oil (polyalphaolefin, PAO6). A TE53SLIM tribometer for testing at medium loads and a four-ball machine (ASTM D2783) were used in this research. The study leads to the conclusion that the addition of nickel nanoparticles to PAO6 results in a decrease in friction and wear and an increase in the load-carrying capacity of base oil. This tribological activity is strongly related to the deposition of nanoparticles on the rubbing surfaces.<sup>28</sup>

Sudeep Ingole, Archana Charanpahari studied the effects of titanium dioxide nanoparticle additives on the lubricated friction and wear performance of self-mated E52100 bearing steel were investigated by a reciprocating pin-on-disk apparatus. The additives were (a) nano-sized titanium dioxide ( $\text{TiO}_2$ ) and (b) commercially available  $\text{TiO}_2$  (P25). The friction and wear characteristics were tested at a constant applied load and rate of reciprocation. At all concentrations, P25 increased the coefficient of friction, but the addition of  $\text{TiO}_2$  nanoparticles reduced the variability and stabilized the frictional performance.<sup>29</sup>

Y.Y. Wu, W.C. Tsui study investigated the tribological properties of two lubricating oils, a Base oil and API-SF engine oil, with  $\text{TiO}_2$ , CuO, and Nano-Diamond nanoparticles used as additives. The friction and wear experiments were carried out using a reciprocating sliding tribotester. The

experimental outcome showed that nanoparticles, mainly CuO, exhibit good friction-reduction and anti-wear properties in oil. The addition of CuO nanoparticles in the Base oil and in the API-SF engine oil decreased the friction coefficient by 18.4 and 5.8%, respectively, and reduced the worn scar depth by 16.7 and 78.8%, respectively, as compared to the standard oils devoid of CuO nanoparticles.<sup>20</sup>

D.X. Peng Y. Kang investigates the tribological properties of liquid paraffin to which diamond and SiO<sub>2</sub> nanoparticles had been added, which prepared by the surface modification method using oleic acid and observed by scanning electron microscopy (SEM) and infrared (IR) spectroscopy. Also, the dispersion capacity and stability dispersivity of both modified nanoparticles in liquid paraffin were studied using a spectrophotometer. The study shows the dispersion capability and the dispersing stability of oleic acid-modified diamond and SiO<sub>2</sub> nanoparticles in liquid paraffin. The tribological properties are evaluated using a ball-on-ring wear tester. The results show that both nanoparticles have better anti-wear and antifriction properties at a tiny concentration in liquid paraffin.<sup>30</sup>

Jingfang Zhou, Zhishen Wu studied the LaF<sub>3</sub> nanoparticle surface coated by organic compounds containing S and P were synthesized by the chemical surface modification method. The particle size and structure were characterized and tribological behaviors were evaluated on a four-ball machine. The results showed that LaF<sub>3</sub> nanoparticles as an oil additive can strikingly improve the load-carrying capacity and anti-wear property of the base oil and had better friction-reduction when compared to that of ZDDP. It can be found that the boundary film on the worn surface was composed of LaF<sub>3</sub> nanoparticles depositing film and tribochemical reaction film of the elements of S and P, which contributed to excellent tribological properties of LaF<sub>3</sub> nanoparticle modified by compound containing S and P as an additive in liquid paraffin.<sup>31</sup>

Z.S. Hu, J.X. Dong studies the Nanoparticle amorphous lanthanum borate with a particle size of 20–40 nm was prepared with a Replacing Solvent Dry technique and characterized using TEM and XRD. Its tribological properties as a wear resistance additive of lubricating oil were evaluated with a four-ball tribotester. The wear scar was characterized with XPS. The wear resistance and load carrying capacity of 500SN base oil was improved by the lanthanum borate. The Diboron trioxide and FeB were formed on the wear scar surface. These tribochemical reaction products as well as some depositions formed a wear resistance film on the rubbing surface, which provided the oil with an excellent load carrying capacity.<sup>32</sup>

Cai-xiang et al. Investigated the tribological properties of lubricating oil (500SN Base Oil) containing TiO<sub>2</sub> and CeO<sub>2</sub> nanoparticles with appropriate surfactants such as Span-20, Tween-20, Tween-60, and Sodium sodecylbenzenesulfonate. In the study 40 kinds of lubricating oils were prepared, according to different weight fractions (0.2%, 0.4%, 0.6%, 0.8%, 1.0%, respectively) and different weight proportions of CeO<sub>2</sub> and TiO<sub>2</sub> nanoparticles ( 0:1, 1:1, 1:2, 1:3, 1:4, 3:1, 2:1, 1:0, respectively). The morphology and size of CeO<sub>2</sub> and TiO<sub>2</sub> nanoparticles were tested with a transmission electron microscope (TEM). The tribological properties of the oils were examined with an MRS-1J four-ball tribotester. The research results showed that when the amount by weight of CeO<sub>2</sub> nanoparticles to TiO<sub>2</sub> nanoparticles is 1:3, and the total weight portion is 0.6%, the lubricating oil showed the best anti-wear and friction reducing properties. The incorporation of CeO<sub>2</sub> nanoparticles reduces the requisite amount of TiO<sub>2</sub> nanoparticles.<sup>33</sup>

Kalakada et al.<sup>34</sup> developed the mathematical model for relationship between viscosity and temperature for the lubricant SAE 15W40 multi grade engine oil having Al<sub>2</sub>O<sub>3</sub> and ZnO nanoparticles. The incorporation of nanoparticles on commercially accessible lubricant noticeably enhances the viscosity of lubricant and also changes the performance characteristics.

Peng et al.<sup>35</sup> studied the antifriction and anti-wear properties of lubricating oil containing nano-ZnO and nano-TiO<sub>2</sub>. The study reveals that both the nanoparticles as additive in lubricating oil exhibit good anti-wear property. Veerandra et al.<sup>36</sup> discloses the synthesis of mixed metal oxide (MMO) nanoparticle of CuO-ZnO by co-precipitation method and friction and wear properties were studied by using pin on disc tester in SAE 20W50 oil which contain dispersed nanoparticle at different level of concentrations ( 0.5%, 1.0% and 2.0% wt). The study showed that the wear scar diameter (WSD) decreases with increasing the concentration of nanoparticles in SAE 20W50.

Nano scale ZnO has been attracting significant interest because of its unique structure and performance.<sup>37-39</sup> This is due to the fact that nano ZnO has large surface area, high surface energy, strong adsorption, high diffusion, easy sintering, low melting point and other outstanding characteristics. When the nano ZnO is used as the additive in base oil, there will be different friction reduction and wear resistant effects on lube oils. In this investigation another nanoparticle was chosen namely magnetic nanoparticle. Magnetic nanoparticles have been extensively studied because of their attractive properties, and ample scope of potential applications in ferrofluids, information storage, medicine, pigment, biomedical and bioengineering etc.<sup>40</sup>

From the above literature survey regarding the application of nanoparticles as lubricating oil additives, it is found that they are mainly used as anti-wear and anti friction agents. But they are not reported to use as other kind of additive. Moreover, polyacrylates were known to perform as effective viscosity modifier additive and pour point depressant additive. Hence to develop multifunctional performance additives for lube oil, authors were interested to develop

multifunctional additives by blending suitable proportion of different oxide based nanoparticles with acrylate based polymers and their performance as lube oil additives were studied.

### **References**

References are given in BIBLIOGRAPHY under Chapter I of Part III (PP 168-172).