

NANOPARTICLES OF SOLID LUBRICANTS FOR TRIBO- PERFORMANCE ENHANCEMENT OF OILS

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by

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CERTIFICATE

This is to certify that the thesis entitled "*Nano-particles of solid lubricants for tribo-performance enhancement of oils*" being submitted by **Mr. Vinay Saini** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. Mr. Vinay Saini has worked under our guidance and supervision and has fulfilled the requirements for the submission of the thesis. The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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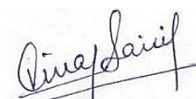
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Vinay Saini

ABSTRACT

Enhancement in the performance of lubricants and energy efficiency of the system continues to be a major challenge to the transportation and lubricant industries. The reduction of carbon emissions is a key to meeting sustainable development goals, especially for the transportation and industrial sectors. Lubricants play a vital role in efficiently keeping the crucial machine/equipment parts healthy running. However, the drive towards employing lower viscosity oils with low SAPS (Sulphated Ash, Phosphorous, and Sulphur) to enhance the fuel economy impacts the wear and durability of critical tribo-pairs operating under boundary lubrication (BL) regime. Thus, to comply with stringent norms, novel lubricants, especially nano oils (oils with nanoparticles), are currently the focus of research attention. In the past decade, nanoparticles (NPs) of several solid lubricants of various categories (polymeric, metallic, inorganic, and carbonaceous) have been explored as additives in oils and greases. Based on an extensive literature survey in this thesis work, research gaps were identified, which led to the objectives of the work. It was based on the NPs that were either not explored at all, such as Talc and Titanium, or inadequately researched. The concept of the shape of NPs of carbonaceous materials such as multi-wall carbon nanotubes (MWCNTs), multi-layer graphene (MLG), and graphite in oils on the tribo-performance was not addressed.

Moreover, the literature is silent on investigations on the suitability of base oil types such as Group I, II, III and IV for developing the most efficient nano-oils using selected NPs such as PTFE. Furthermore, in the case of NPs of PTFE (Polytetrafluoroethylene), some issues such as stability of oils, in-depth wear mechanisms, exploration of commercially available suspensions, etc., were not addressed.

Keeping all these in view, the objectives of the thesis work were defined. In the present work, NPs from four different categories viz. polymeric (PTFE), carbonaceous (multi-wall carbon nanotubes (MWCNTs), multi-layer graphene -MLG, and graphite-G), inorganic (Talc), and metallic (Titanium) were selected for the tribo-performance enhancement of API group III base-stock oil. Various series of nano-oils containing dispersant (PIBSI+PIBSA)-1 %) and theme NPs in increasing concentrations (0.5, 1, 1.5, 2, 3, and 4 wt.%) were developed, and the stability of formulated oils for the shelf life was studied using multiple techniques, i.e., dynamic light scattering (DLS), ultraviolet-visible spectroscopy, and visual photographs. They were also evaluated for performance (physical- density, viscosity, viscosity index, and tribological-extreme pressure-EP, anti-wear-AW, and anti-friction-AF). The tribo-performance evaluation, such as EP and AW, was carried on a Four-ball tester as per IP 239 and ASTM D4172 standard.

AF performance was evaluated on the Optimal SRV III under a reciprocating condition as per modified ASTM D5707 standard. The worn surface analysis was done by various techniques such as SEM (scanning electron microscopy), EDAX (energy dispersive X-ray analysis), AFM (atomic force microscope), XPS (X-ray photoelectron spectroscopy), and MRS (micro-Raman spectroscopy).

The thesis comprises eight chapters where each chapter mentions its theme, followed by a pertinent literature survey, materials, evaluation of oils, and study outcome.

Chapter 1 briefly explains the key aspects of tribology, lubrication, with a particular reference to mineral oil lubrication, additives, and their functions. Moreover, it addresses the need for novel additives. Nano lubricants, especially based on NPs of solid lubricants, (SLs) were discussed. Finally, it identifies the research gaps, objectives, and execution strategy.

Chapter 2 reveals the particulars of selected materials chosen for the investigations. Various techniques employed for the characterization, development of nano-oils, and performance evaluation and instruments/apparatus utilized) are discussed.

Chapters 3, 4, 5, 6, and 7 comprise the experimental investigations on nano-oils. Chapters 3-6 are on studies on solo oils, while chapter 7 is on combo-oils where combinations of NPs are used in oils.

Chapter 3 reveals the outcome of studies on investigating the most suitable oil among various API basestock oils (Group I, II, III, and IV) to develop nano-lubricant containing PTFE NPs in a fixed amount (3 %) as a tribo-additive in the oil. Furthermore, the amount optimization of PTFE for best tribo-performance as EPA and AWA is explored. Also, the plausible interfacial working mechanism of PTFE NPs is discussed. PTFE NPs in the form of nano-suspension (NanoFlon) proved to have significant potential as an EPA when used in group III oil. 6 wt. % of NPs proved to be the optimum concentration for the highest (392 %) improvement.

Chapter 4 investigates the influence of nano-oils containing Talc nanoparticles (NPs) (≈ 50 nm size) in varying amounts (0.5, 1, 2, 3, and 4 wt.%) in the presence of dispersant (1 %). Addition of 3 wt. % Talc NPs led to $\sim 40\%$, 122 % improvement in AW and EP properties of oil.

Chapter 5 investigates the effect of various shapes of carbonaceous NPs viz. (MLG, NG, MWCNTs) in dispersant with varying concentrations (0.5- 4 wt.%) on the performance of oils. MLG proved best as AWA (48%), EPA (89%), and AFA (27 %), followed by nano graphite. MWCNTs performed worst among carbonaceous NPs.

Chapter 6 deals with the study of Titanium metallic NPs in various amounts (0.1-2 wt.%) and their effect on the tribological performance of oils. Addition of just 0.5 wt. % of Ti NPs showed the nearly highest reduction in wear and friction compared to other metallic NPs in literature.

Chapter 7 explores the possible synergism while using various combinations of different NPs with PTFE in fixed amounts (3 wt.%) as a primary player. Other NPs (1 %) such as Talc, MLG, G, MWCNTs and Ti were used in each oil with PTFE, the total % being 4 always. The combination of MoDTC (1wt.%) and PTFE (3 wt.%) showed complete synergism in all tribological properties (AW, EP, AF).

Chapter 8 summarizes the salient conclusions of the research work in this thesis and recommends future work to be taken forward.

The major takeaway from the thesis work was as follows.

- The proper selection of base oils for preparing nano-oil with selected NPs is essential since it affects the performance significantly. Group III oil proved to be the most suitable for selected PTFE NPs as EPA.
- The comparative study on different NPs in Group III oil indicated that MLG proved to be the best AWA among the solo particles, followed by NPs of Talc and Titanium, while PTFE performed best as EPA. MWCNTs did not show promising results. The inclusion of a combination of NPs, keeping PTFE as primary NPs proved very beneficial in the case of MoDTC (a commercial lubricant) and NPs of Ti and MLG. A record increase (455 %) in EP property was observed using combination of 1 wt.% MoDTC with 3 wt.% PTFE NPs and 1 wt.% nanographite with 3 wt.% PTFE NPs.

सार

स्नेहक के प्रदर्शन में वृद्धि और प्रणाली की ऊर्जा दक्षता परिवहन और स्नेहक उद्योगों के लिए एक बड़ी चुनौती बनी हुई है। कार्बन उत्सर्जन में कमी सतत विकास लक्ष्यों को पूरा करने की कुंजी है, खासकर परिवहन और औद्योगिक क्षेत्रों के लिए। महत्वपूर्ण मशीन/उपकरण के पुर्जों को सुचारू रूप से चलाने में स्नेहक एक महत्वपूर्ण भूमिका निभाते हैं। हालांकि, ईंधन की बचत को बढ़ाने के लिए कम एसएपीएस (सल्फेटेड ऐश, फॉस्फोरस और सल्फर) के साथ कम चिपचिपाहट वाले तेलों को नियोजित करने की दिशा में सीमा स्नेहन (बीएल) शासन के तहत काम कर रहे महत्वपूर्ण ट्राइबो-जोड़े के पहनने और स्थायित्व को प्रभावित करता है। इस प्रकार, कड़े मानदंडों का पालन करने के लिए, उपन्यास स्नेहक, विशेष रूप से नैनो तेल (नैनोकणों वाले तेल), वर्तमान में अनुसंधान ध्यान का केंद्र हैं। पिछले एक दशक में, विभिन्न श्रेणियों (पॉलीमरिक, धात्विक, अकार्बनिक और कार्बोनेसियस) के कई ठोस स्नेहक के नैनोकणों (एनपी) को तेल और ग्रीस में एडिटिव्स के रूप में खोजा गया है। इस थीसिस कार्य में एक व्यापक साहित्य सर्वेक्षण के आधार पर, अनुसंधान अंतराल की पहचान की गई, जिससे कार्य के उद्देश्य सामने आए। यह उन एनपी पर आधारित था जिन्हें या तो बिल्कुल भी नहीं खोजा गया था, जैसे कि टैल्क और टाइटेनियम, या अपर्याप्त रूप से शोध किया गया था। बहु-दीवार कार्बन नैनोट्यूब (MWCNTs), बहु-परत ग्राफीन (MLG), और ट्राइबो-प्रदर्शन पर तेलों में ग्रेफाइट जैसे कार्बनयुक्त पदार्थों के एनपी के आकार की अवधारणा को संबोधित नहीं किया गया था। इसके अलावा, पीटीएफई जैसे चयनित एनपी का उपयोग करके सबसे कुशल नैनो-तेल विकसित करने के लिए समूह I, II, III और IV जैसे आधार तेल प्रकारों की उपयुक्तता पर जांच पर साहित्य चुप है। इसके अलावा, पीटीएफई (पॉलीटेट्राफ्लूओरोएथिलीन) के एनपी के मामले में, कुछ मुद्दों जैसे तेलों की स्थिरता, गहन पहनने की व्यवस्था, व्यावसायिक रूप से उपलब्ध निलंबन की खोज आदि को संबोधित नहीं किया गया था। इन सब को ध्यान में रखते हुए थीसिस कार्य के उद्देश्यों को परिभाषित किया गया। वर्तमान कार्य में, चार अलग-अलग श्रेणियों के एन.पी. पोलिमेरिक (PTFE), कार्बोनेसियस (मल्टी-वॉल कार्बन नैनोट्यूब (MWCNTs), मल्टी-लेयर ग्रेफीन-MLG, और ग्रेफाइट-), इनऑर्गेनिक (टैल्क), और मेटालिक (टाइटेनियम) को एपीआई ग्रुप III के ट्राइबो-परफॉर्मेंस एन्हांसमेंट के लिए चुना गया था। बेस-स्टॉक तेल। बढ़ती सांद्रता (0.5, 1, 1.5, 2, 3, और 4 wt.%) में फैलाव (PIBSI + PIBSA) -1%) और थीम NPs युक्त नैनो-तेल की विभिन्न श्रृंखला विकसित की गई, और शेल जीवन के लिए तैयार तेलों की स्थिरता का अध्ययन कई तकनीकों, यानी गतिशील प्रकाश बिखरने (डीएलएस), पराबैंगनी-दृश्यमान स्पेक्ट्रोस्कोपी और दृश्य तस्वीरों का उपयोग करके किया गया था। प्रदर्शन (भौतिक-घनत्व, चिपचिपाहट, चिपचिपापन सूचकांक, और आदिवासी-अत्यधिक दबाव-ईपी, एंटी-वेयर-एडब्ल्यू, और एंटी-घर्षण-एएफ) के लिए उनका मूल्यांकन भी किया गया था। ट्राइबो-प्रदर्शन मूल्यांकन, जैसे EP और AW, IP-239 और ASTM D-4172 और मानकों के अनुसार फोर-बॉल टेस्टर पर किया गया था। AF के प्रदर्शन का मूल्यांकन संशोधित ASTM D-5707 मानक के अनुसार एक पारस्परिक स्थिति के तहत इष्टतम SRV III पर किया गया था। पहना सतह विश्लेषण एसईएम (स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी), ईडीएक्स (ऊर्जा फैलाव एक्स-रे विश्लेषण), एएफएम (परमाणु बल माइक्रोस्कोप), एक्सपीएस (एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी), और एमआरएस (माइक्रो-रमन) जैसी विभिन्न तकनीकों द्वारा किया गया था। स्पेक्ट्रोस्कोपी)।

थीसिस में आठ अध्याय शामिल हैं जहां प्रत्येक अध्याय अपने विषय का उल्लेख करता है, उसके बाद एक प्रासंगिक साहित्य सर्वेक्षण, सामग्री, तेलों का मूल्यांकन, और अध्ययन परिणाम।

अध्याय 1 संक्षेप में खनिज तेल स्नेहन, योजक, और उनके कार्यों के विशेष संदर्भ में ट्राइबोलॉजी, स्नेहन के प्रमुख पहलुओं की व्याख्या करता है। इसके अलावा, यह उपन्यास एडिटिव्स की आवश्यकता को संबोधित करता है। नैनो स्नेहक, विशेष रूप से ठोस स्नेहक के एनपी पर आधारित, (एसएल) पर चर्चा की गई। अंत में, यह अनुसंधान अंतराल, उद्देश्यों और निष्पादन रणनीति की पहचान करता है।

अध्याय 2 जांच के लिए चुनी गई चयनित सामग्री के विवरण को प्रकट करता है। लक्षण वर्णन, नैनो-तेल के विकास, और प्रदर्शन मूल्यांकन और उपकरणों/उपकरणों के उपयोग के लिए नियोजित विभिन्न तकनीकों पर चर्चा की जाती है।

अध्याय ३, ४, ५, ६, और ७ में नैनो-ऑयल पर प्रायोगिक जांच शामिल है। अध्याय 3-6 एकल तेलों पर अध्ययन पर हैं, जबकि अध्याय 7 कॉम्बो-तेल पर है जहां एनपी के संयोजन तेलों में उपयोग किए जाते हैं।

अध्याय 3 विभिन्न एपीआई बेसस्टॉक तेलों (समूह I, II, III, और IV) के बीच सबसे उपयुक्त तेल की जांच पर अध्ययन के परिणाम का खुलासा करता है ताकि एक ट्राइबो-एडिटिव के रूप में एक निश्चित मात्रा (3%) में पीटीएफई एनपी युक्त नैनो-स्नेहक विकसित किया जा सके। तेल में। इसके अलावा, ईपीए और एडब्ल्यूए के रूप में सर्वश्रेष्ठ ट्राइबो-प्रदर्शन के लिए पीटीएफई की राशि अनुकूलन का पता लगाया गया है। इसके अलावा, PTFE NPs के प्रशंसनीय इंटरफेसियल वर्किंग मैकेनिज्म पर चर्चा की गई है। नैनो-निलंबन (नैनोफ्लोन) के रूप में पीटीएफई एनपी समूह III तेल में उपयोग किए जाने पर ईपीए के रूप में महत्वपूर्ण क्षमता साबित हुई। 6 वाट. एनपी का% उच्चतम (392%) सुधार के लिए इष्टतम एकाग्रता साबित हुआ।

अध्याय 4 में टैल्क नैनोकणों (एनपी) (≈ 50 एनएम आकार) वाले नैनो-तेल के प्रभाव की जांच अलग-अलग मात्रा (0.5, 1, 2, 3, और 4 wt.%) में फैलाव (1%) की उपस्थिति में की जाती है। 3 वाट का जोड़ा % टैल्क एनपी ने तेल के एडब्ल्यू और ईपी गुणों में $\sim 40\%$, 122% सुधार किया।

अध्याय 5 कार्बोनेसियस एनपी के विभिन्न आकारों के प्रभाव की जांच करता है। (एमएलजी, एनजी, एमडब्ल्यूसीएनटी) तेलों के प्रदर्शन पर अलग-अलग सांद्रता (0.5- 4 wt.%) के साथ फैलाव में MLG AWA (48%), EPA (89%), और AFA (27%) के रूप में सबसे अच्छा साबित हुआ, इसके बाद नैनो ग्रेफाइट का स्थान रहा। MWCNTs ने कार्बोनेसियस एनपी के बीच सबसे खराब प्रदर्शन किया।

अध्याय 6 विभिन्न मात्राओं (0.1-2 wt.%) में टाइटेनियम धातु एनपी के अध्ययन और तेलों के जनजातीय प्रदर्शन पर उनके प्रभाव से संबंधित है। सिर्फ 0.5 wt. % का जोड़ा साहित्य में अन्य धातु एनपी की तुलना में टीआई एनपी के% ने पहनने और घर्षण में लगभग उच्चतम कमी दिखाई।

अध्याय 7 एक प्राथमिक खिलाड़ी के रूप में निश्चित मात्रा (3 wt.%) में PTFE के साथ विभिन्न NPs के विभिन्न संयोजनों का उपयोग करते हुए संभावित तालमेल की पड़ताल करता है। अन्य एनपी (1%) जैसे टैल्क, एमएलजी, जी, एमडब्ल्यूसीएनटी और टीआई का इस्तेमाल पीटीएफई के साथ प्रत्येक तेल में किया जाता था, कुल% हमेशा 4 होता था। MoDTC (1wt.%) और PTFE (3 wt.%) के संयोजन ने सभी जनजातीय गुणों (AW, EP, AF) में पूर्ण तालमेल दिखाया।

अध्याय 8 इस थीसिस में शोध कार्य के मुख्य निष्कर्षों को सारांशित करता है और भविष्य के काम को आगे बढ़ाने की सिफारिश करता है। थीसिस के काम का प्रमुख अंश इस प्रकार था।

चयनित एनपी के साथ नैनो-तेल तैयार करने के लिए आधार तेलों का उचित चयन आवश्यक है क्योंकि यह प्रदर्शन को महत्वपूर्ण रूप से प्रभावित करता है। समूह III तेल ईपीए के रूप में चयनित पीटीएफई एनपी के लिए सबसे उपयुक्त साबित हुआ।

- समूह III के तेल में विभिन्न एनपी पर तुलनात्मक अध्ययन ने संकेत दिया कि एमएलजी एकल कणों में सबसे अच्छा एडब्ल्यूए साबित हुआ, इसके बाद टैल्क और टाइटेनियम के एनपी थे, जबकि पीटीएफई ने ईपीए के रूप में सर्वश्रेष्ठ प्रदर्शन किया। MWCNTs ने आशाजनक परिणाम नहीं दिखाए। एनपी के संयोजन को शामिल करना, पीटीएफई को प्राथमिक एनपी के रूप में रखना एमओडीटीसी (एक वाणिज्यिक स्नेहक) और टीआई और एमएलजी के एनपी के मामले में बहुत फायदेमंद साबित हुआ। EP संपत्ति में एक रिकॉर्ड वृद्धि (455%) देखी गई, जिसमें 3 wt.% PTFE NPs के साथ 1 wt.% MoDTC और 3 wt.% PTFE NPs के साथ 1 wt.% नैनोग्राफाइट का संयोजन किया गया।

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LIST OF ACRONYMS

AFA	Anti-friction Additive
AFM	Atomic Force Microscopy
API	American Petroleum Institute
AWA	Anti-wear Additive
DLS	Dynamic Light Scattering
EDAX	Energy Dispersive X-ray Analysis
EPA	Extreme Pressure Additive
FESEM	Field Emission Scanning Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
MLG	Multilayer Graphene
MRS	Micro-Raman Spectroscopy
NLs	Nano-lubricants
NPs	Nano-particles
PWL	Pre-weld Load
PTFE	Polytetrafluoroethylene
SL	Solid Lubricant
SMPs	Sub-micron sized particles
WL	Weld-Load
WSD	Wear Scar Diameter
UV-Vis	Ultraviolet Visible Spectroscopy
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
μ	Coefficient of friction