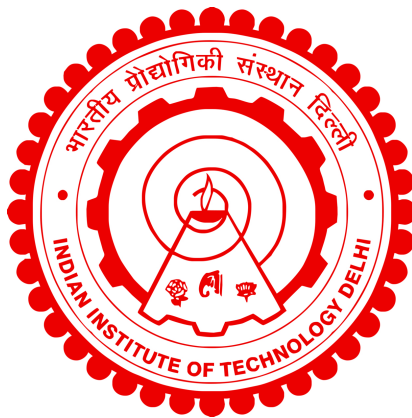


**DEVELOPMENT AND TRIBO-DYNAMIC  
PERFORMANCE OF ENVIRONMENTALLY  
FRIENDLY GREASES**

**ANKIT SAXENA**



**CENTRE FOR AUTOMOTIVE RESEARCH AND  
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**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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# DEVELOPMENT AND TRIBO-DYNAMIC PERFORMANCE OF ENVIRONMENTALLY FRIENDLY GREASES

by

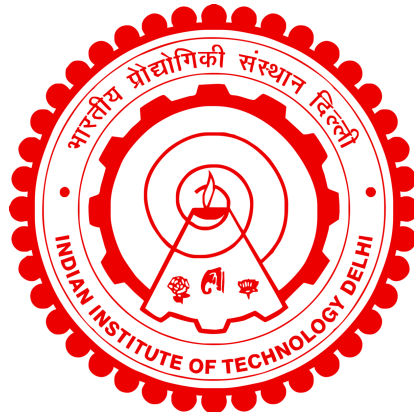
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**Submitted**

in partial fulfillment of the requirements of the degree of Doctor of Philosophy

to the



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*Dedicated to my parents,  
Smt. Sangita Saxena and Sri. Manish Saxena*

# Certificate

This is to certify that the thesis entitled “**Development and tribo-dynamic performance of environmentally friendly greases**”, submitted by **Ankit Saxena** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of the original, bonafide research work carried out by him under my supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results in this thesis have not been submitted in part or in full to any other University or Institute for awarding any degree or diploma to the best of our knowledge.

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# Abstract

*The grease industry is saturated with extensive use of non-renewable, non-biodegradable, toxic, and bioaccumulative entities as ingredients that satisfy the performance goals and jeopardize the environment simultaneously. The recurrent production and consumption of greases based on such ingredients pose high risks to the land and aquatic life, where the greases eventually end up. This has been the prime reason behind the stiffening of government regulations worldwide. Apart from this, such greases also significantly contribute to depleting non-renewable petroleum resources at a rapid rate. Further, they are impractical for industries with stringent safety standards like food, beverages, agriculture, medicine, supplements, cosmetics, etc., contributing to a significant fraction of the overall lubricant demand. Several permutations and combinations of environmentally benign ingredients have been tried to develop green alternatives to conventional mineral/petroleum oil-based greases; however, a potential solution is not yet reached. This highlights the pressing need for a potential, sustainable, and economical solution for environmentally friendly greases.*

*This thesis presents the use of soybean oil as the base oil and organoclay as the thickener to develop eco-friendly greases on a laboratory scale. Eco-friendly additives like calcium carbonate nanopowder (nano-CaCO<sub>3</sub>), gum acacia (GA), and guar gum (GG) are also incorporated to enhance the performance of greases. The prime*

*focus of enhancing the performance of developed greases up to the level of commercial greases is behind the choice of a diverse variety of additives; the quest ended when desired performances were achieved. The additives are doped in the greases at varying concentrations to obtain a series of nano-greases (0.1 - 4 %w/w) and gum-greases (0.5 - 10 %w/w).*

*These greases are then screened in the following order - basic characteristics, tribological characteristics (fail-safe assessment), and dynamic characteristics (actual rolling bearing). The performance of the formulated greases in every aspect is benchmarked with that of the commercial greases. The basic characteristics involve the determination of consistency, dropping point copper corrosion, and rheology. Deep exploration of the grease microstructures is also carried out using Transmission electron microscopy (TEM) and Field-emission scanning electron microscopy (FESEM) to understand the mechanism of formulated greases. Afterward, the greases are evaluated for tribological characteristics on a four-ball tester using two standard methods, the anti-wear (AW) test (ASTM D2266) and the extreme-pressure (EP) test (ASTM D2596) for their fail-safe assessment. The worn surfaces are investigated using FESEM, Energy dispersive x-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), and 3D optical profilometer to understand the tribo-mechanisms. Finally, the dynamic performance of the newly developed greases is evaluated on a rolling bearing at an array of speeds and radial loads using two techniques- vibrations and shock pulse method (SPM) carpet values.*

*The results indicate that the formulations exhibited typical grease-like characteristics in terms of consistency, dropping point, copper corrosion, and rheology. The concentration of additives appeared to influence grease behavior significantly in both nano-greases as well as gum-greases. Also, the behavior of the greases was closely associated with their microstructure. In gum-greases, the type of polysaccharide gum also appeared to play a role in the grease performance.*

*In tribological performance, the greases again display concentration-dependent behavior. For nano-greases, the participation of nanoparticles (NPs) as a third body seems to increase frictional coefficients under the AW test. At the same time, the interfacial deposition (physisorption) of nano-CaCO<sub>3</sub> (and nano-CaO) decreases wear. While under the EP test, the nano-greases displayed an enhanced response at all concentrations of the nanoparticles, and the performance improved with increasing concentration (up to 60% increment achieved, better than commercial greases). The enhanced EP performance is attributed to the calcination of nano-CaCO<sub>3</sub> into nano-CaO to form a more robust tribosintered film. The nano-grease containing 4% nano-CaCO<sub>3</sub> performed best under both tribological test methods.*

*For gum-greases, GG acts as a synergistic additive for the greases, whereas GA acts antagonistically in the AW test. The contradictory behavior of the two gums is associated with their distinct interfacial interaction tendencies with organoclay. Adding GG in greases at all concentrations augments AW characteristics (up to ≈ 22% improvement achieved) and frictional response (up to ≈ 42% improvement achieved). Optimal performance at 4% GG is almost equivalent to the lithium-based*

commercial grease used as the benchmark. The formation of a physisorbed tribofilm at the interface is attributed to the enhanced performance. According to analysis of variance (ANOVA), the type of gum influences the tribological characteristics more than the gum concentration. In the EP test, both GA and GG prove beneficial to the greases. The performance ameliorates with the gum's concentration showing impressive results at higher concentrations (up to  $\approx 60\%$  better than lithium-based commercial grease). The superior performance is attributed to an in-situ formed polymer-layered silicate nanocomposite tribofilm at the interface via chemisorption (for GA) or physisorption (for GG).

Both the series of greases generally display acceptable performances on the rolling bearing; however, the performance varies with the concentration and type of additive. The RMS vibrations and the SPM carpet values give insight into the frictional behavior and film thickness of greases on the bearing. Where a combined effect of rheology and additive size seems to influence the vibrations, the entrainment of additives governs the carpet values. In nano-greases, a significant decrement in vibrations is observed at concentrations  $\geq 1\%$  w/w, where the greases performed almost equivalent to the commercial lithium grease. The rolling effect of nanoparticles is ascribed to enhanced performance. At the same time, comparable carpet values are observed for nano-greases indicating only a slight influence of nanoparticles over the film thickness. In gum-greases, the vibrations generally indicate a stable performance of GA-based greases at different GA concentrations, whereas a decline in the performance of GG-based greases with an increase in GG concentration. Regarding carpet

*values, except for GA1, every gum-grease performs either equivalent to or better than the grease without additives. Based on the research, it can be well summarized that the formulated greases display immense scientific prospects as a sustainable and potential alternative to the existing harmful commercial greases.*

## सारांश

ग्रीज़ उद्योग गैर-नवीकरणीय, अजैव निम्नीकरणीय, विषाक्त, और जैव-संचयी अवयवों के व्यापक उपयोग से संतृप्त है जो कि प्रदर्शन लक्ष्यों को पूरा करते हैं और इसके साथ ही पर्यावरण को खतरे में डालते हैं। इस तरह के अवयवों पर आधारित ग्रीज़ का आवर्तक उत्पादन और खपत भूमि और जलीय जीवन के लिए उच्च जोखिम पैदा करता है, जहां ग्रीज़ अंततः समाप्त हो जाती है। यह मुख्य कारण है दुनिया भर में सरकारी नियमों की कठोरता के पीछे। इसके अलावा, इस तरह के ग्रीज़ तेज दर से गैर-नवीकरणीय पेट्रोलियम संसाधनों को कम करने में महत्वपूर्ण योगदान भी देते हैं। इसके अलावा, वे कड़े सुरक्षा मानकों वाले उद्योगों के लिए अप्रयोगात्मक हैं, जैसे कि खाद्य, पेय पदार्थ, कृषि, चिकित्सा, पूरक, सौंदर्य प्रसाधन, आदि, जो कि समग्र स्नेहक मांग का एक महत्वपूर्ण अंश हैं। पर्यावरणीय रूप से सौम्य अवयवों के कई क्रमपरिवर्तनों और संयोजनों से पारंपरिक खनिज / पेट्रोलियम तेल आधारित ग्रीज़ों के हरित विकल्प को उत्पन्न करने की कोशिश की गई है; हालांकि, एक सशक्त समाधान तक अभी कोई नहीं पहुंचा है। यह पर्यावरण के अनुकूल ग्रीज़ों के लिए एक सशक्त, स्थायी, और किफायती समाधान की अति-आवश्यकता पर प्रकाश डालता है।

यह थीसिस पर्यावरण के अनुकूल ग्रीज़ों को प्रयोगशाला पैमाने पर उत्पन्न करने के लिए सोयाबीन तेल के उपयोग को आधार तेल के रूप में और ऑर्गेनोक्ले को प्रगाढक के रूप में प्रस्तुत करती है। पर्यावरण के अनुकूल एडिटिव्स जैसे कैल्शियम कार्बोनेट नैनोपाउडर (नैनो- $\text{CaCO}_3$ ), एकेसिया गोंद (GA), और ग्वार गोंद (GG) को भी ग्रीज़ों के प्रदर्शन को बढ़ाने के लिए शामिल किया गया है। उत्पन्न ग्रीज़ों के प्रदर्शन को व्यापारिक ग्रीज़ों के प्रदर्शन स्तर तक बढ़ाने का प्रधान केंद्र ही विभिन्न प्रकार के एडिटिव्स के चयन के पीछे का कारण है; खोज समाप्त की गई जब अभिलषित प्रदर्शन हासिल किए गए। एडिटिव्स को ग्रीज़ में अलग-अलग सांद्रता पर मिलाया गया जिससे की नैनो-ग्रीज़ (0.1 - 4% भार/ भार) की और गोंद-ग्रीज़ (0.5 - 10% भार / भार) की एक- एक श्रृंखला प्राप्त की जा सके।

इन ग्रीज़ों को फिर निम्नलिखित क्रम में जांचा गया - मूल विशेषताएं, ट्राइबोलॉजिकल विशेषताएं (असफल-सुरक्षित मूल्यांकन), और गतिशील विशेषताएं (असल रोलिंग बियरिंग)। उत्पन्न ग्रीज़ों का प्रदर्शन हर पहलू में व्यापारिक ग्रीज़ों के प्रदर्शन के साथ बेंचमार्क किया गया है। मूल विशेषताओं में गाढ़ापन, ड्रॉपिंग पॉइंट, कॉपर संक्षारण, और रियोलॉजी का निर्धारण शामिल हैं। ग्रीज़ की सूक्ष्म-संरचना की गहरी खोज भी संचरण इलेक्ट्रॉन माइक्रोस्कोपी (TEM) और क्षेत्र-उत्सर्जन क्रमवीक्षण इलेक्ट्रॉन माइक्रोस्कोपी (FESEM) का उपयोग करके की गयी है जिससे की तैयार ग्रीज़ों की क्रियाविधि को समझा जा सके। बाद में, ग्रीज़ों का ट्राइबोलॉजिकल विशेषताओं के लिए चार-गेंद परीक्षक पर मूल्यांकन किया गया है जिसमें दो मानक विधियों का उपयोग करके, एंटी-वियर (AW) परीक्षण (ASTMD2266) और चरम दबाव (EP) परीक्षण (ASTMD2596) द्वारा उनका असफल-सुरक्षित मूल्यांकन किया गया है। घिसी हुई सतहों की जांच FESEM, ऊर्जा फैलाने वाली एक्स-रे स्पेक्ट्रोस्कोपी (EDS), फूरियर रूपांतरण इन्फ्रारेड स्पेक्ट्रोस्कोपी (FTIR), और 3D प्रकाशीय प्रोफाइलोमीटर का उपयोग करके की गयी है जिससे की ट्राइबो- क्रियाविधि को समझा जा सके। अंत में, नए उत्पन्न ग्रीज़ों के गतिशील प्रदर्शन का मूल्यांकन रोलिंग बियरिंग पर गति और रेडियल भार की एक सरणी पर दो तकनीकों – कंपन और शॉक पल्स विधि (SPM) कालीन मान का उपयोग करके किया गया है।

परिणाम बताते हैं कि योगों ने गाढ़ापन, ड्रॉपिंग पॉइंट, कॉपर संक्षारण, और रियोलॉजी के संदर्भ में प्ररूपी ग्रीज़ जैसी विशेषताओं का प्रदर्शन किया। एडिटिव्स की सांद्रता नैनो-ग्रीज़ अथवा गोंद-ग्रीज़ दोनों में ग्रीज़ के बर्ताव को काफी प्रभावित करती दिखाई दी। इसके अलावा, ग्रीज़ों का बर्ताव बारीकी से उनकी सूक्ष्म-संरचना के साथ जुड़ा हुआ पाया गया। गोंद-ग्रीज़ों में, बहुशर्करा गम का प्रकार ग्रीज़ प्रदर्शन में भी एक भूमिका निभाते हुए दिखाई दिया।

ट्राइबोलॉजिकल प्रदर्शन में, ग्रीज़ों ने फिर से सांद्रता-निर्भर बर्ताव प्रदर्शित किया। नैनो-ग्रीज़ों के लिए, नैनोकणों

(NPs) की भागीदारी तीसरे शरीर के रूप में AW परीक्षण के अंतर्गत घर्षण गुणांक में वृद्धि करती दिखाई देती है। इसके साथ ही, नैनो-CaCO<sub>3</sub> (और नैनो-CaO) का इंटरफेशियल जमाव (भौतिक अधिशोषण) घिसाव कम कर देता है। वहीं EP परीक्षण के अंतर्गत, नैनो-ग्रीज़ नैनोकणों की सभी सांद्रताओं पर प्रदर्शन में वृद्धि दिखती हैं, और प्रदर्शन में बढ़ती सांद्रता के साथ सुधार होता है (60 % तक की वृद्धि हासिल की गई है, व्यापारिक ग्रीज़ों से बेहतर)। बढ़े हुए EP प्रदर्शन के लिए नैनो-CaCO<sub>3</sub> के नैनो-CaO में कैल्सीनेशन को जिम्मेदार ठहराया जाता है जिसकी वजह से एक अधिक मजबूत ट्राइबोसिंटर्ड परत बनती है। नैनो-ग्रीज़ जिसमें 4% नैनो-CaCO<sub>3</sub> होता है उसने दोनों ट्राइबोलॉजिकल परीक्षण विधियों के अंतर्गत सबसे अच्छा प्रदर्शन किया।

गोंद-ग्रीज़ों के लिए, AW परीक्षण में GG एक सहक्रियात्मक योजक के रूप में कार्य करता है, जबकि GA विरोधी रूप से कार्य करता है। दोनों गोंद का परस्पर विरोधी बर्ताव ऑर्गेनोक्ले के साथ उनकी भिन्न इंटरफेशियल इंटरैक्शन प्रवृत्तियों से जुड़ा हुआ है। सभी सांद्रताओं में ग्रीज़ में GG डालने से AW विशेषताओं ( $\approx 22\%$  तक सुधार हासिल किया गया) और घर्षण प्रतिक्रिया ( $\approx 42\%$  तक सुधार हासिल किया गया) में वृद्धि होती है। 4% GG पर सर्वोत्तम प्रदर्शन लगभग लिथियम-आधारित व्यापारिक ग्रीज़ के बराबर है जिसे बेंचमार्क के रूप में उपयोग किया गया है। इंटरफ़ेस पर एक भौतिक अधिशोषण द्वारा गठित ट्राइबो-परत को प्रदर्शन के लिए जिम्मेदार ठहराया जाता है। विचरण के विश्लेषण (ANOVA) के अनुसार, गोंद का प्रकार ट्राइबोलॉजिकल विशेषताओं को अधिक प्रभावित करता है, गोंद सांद्रता की तुलना में। EP परीक्षण में, GA और GG दोनों ग्रीज़ के लिए फायदेमंद साबित होते हैं। गोंद की सांद्रता के साथ प्रदर्शन में सुधार होता है और उच्चतर सांद्रता पर प्रभावशाली परिणाम दिखाई पड़ते हैं (लिथियम-आधारित व्यापारिक ग्रीज़ की तुलना में  $\approx 60\%$  तक बेहतर)। बेहतर प्रदर्शन का श्रेय इंटरफ़ेस पर रासायनिक शोषण (GA के लिए) या भौतिक शोषण (GG के लिए) के माध्यम से गठित स्वस्थानी बहुलक-स्तरित सिलिकेट नैनोकम्पोजिट ट्राइबो-परत को दिया जाता है।

ग्रीज़ों की दोनों श्रृंखलाएं रोलिंग बियरिंग पर सामान्यतः स्वीकार्य प्रदर्शन प्रदर्शित करती हैं; हालांकि, प्रदर्शन सांद्रता

और ऐडिटिव के प्रकार के साथ तबदील होता है। RMS कंपन और SPM कालीन मान ग्रीज़ों के बियरिंग पर घर्षण बर्ताव और परत मोटाई में अंतर्दृष्टि प्रदान करते हैं। जहां रिओलॉजी और ऐडिटिव माप का एक संयुक्त प्रभाव कंपन को प्रभावित करता प्रतीत होता है, एडिटिव्स का प्रवेश कालीन मूल्यों को नियंत्रित करता है। नैनो-ग्रीज़ों में, 1% भार/ भार या उससे अधिक सांद्रताओं पर कंपन में महत्वपूर्ण गिरावट देखी जाती है, जहां ग्रीज़ों का प्रदर्शन लगभग व्यापारिक लिथियम ग्रीज़ के बराबर रहता है। नैनोकणों के रोलिंग प्रभाव को बेहतर प्रदर्शन के लिए जिम्मेदार ठहराया गया है। इसके साथ ही, नैनो-ग्रीज़ों के लिए तुलनीय कालीन मूल्य देखे जाते हैं जो नैनोकणों के परत की मोटाई पर केवल मामूली प्रभाव को दर्शाता है। गोंद-ग्रीज़ों में, कंपन सामान्यतः GA- आधारित ग्रीज़ों का विभिन्न GA सांद्रताओं पर एक स्थिर प्रदर्शन, जबकि GG सांद्रता में वृद्धि के साथ GG-आधारित ग्रीज़ों के प्रदर्शन में पतन का संकेत देते हैं। कालीन मान में, GA1 को छोड़कर, प्रत्येक गोंद-ग्रीज़ एडिटिव्स-हीन ग्रीज़ के या तो बराबर या उससे बेहतर प्रदर्शन करती है। अनुसंधान के आधार पर, यह अच्छी तरह से संक्षिप्त किया जा सकता है कि तैयार किए गए ग्रीज़ मौजूदा हानिकारक व्यापारिक ग्रीज़ों के एक स्थायी और सशक्त विकल्प के रूप में विशाल वैज्ञानिक संभावनाओं को प्रदर्शित करते हैं।

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# Abbreviations

<b>NPs</b>	Nanoparticles
<b>GA</b>	Gum Acacia
<b>GG</b>	Guar Gum
<b>FTIR</b>	Fourier Transform Infrared Spectroscopy
<b>SEM</b>	Scanning Electron Microscopy
<b>FESEM</b>	Field Emission Scanning Electron Microscopy
<b>TEM</b>	Transmission Electron Microscopy
<b>EDS</b>	Energy Dispersive X-ray Spectroscopy
<b>XRD</b>	X-Ray Diffraction
<b>TGA</b>	Thermogravimetric Analysis
<b>FBT</b>	Four Ball Tester
<b>WSD</b>	Wear Scar Diameter
<b>COF</b>	Coefficient Of Friction
<b>EHL</b>	Elasto-hydrodynamic Lubrication
<b>AW</b>	Anti-wear
<b>EP</b>	Extreme-pressure
<b>NLGI</b>	National Lubricating Grease Institute
<b>PV</b>	Pressure-Velocity
<b>RPM</b>	Revolutions Per Minute
<b>BL</b>	Boundary Lubrication
<b>ML</b>	Mixed Lubrication
<b>SPM</b>	Shock Pulse Method
<b>ANOVA</b>	Analysis of Variance
<b>AISI</b>	American Iron and Steel Institute
<b>ASTM</b>	American Society for Testing and Materials
<b>BSE</b>	Back-scattered electrons
<b>ATR</b>	Attenuated Total Reflectance

## *Abbreviations*

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<b>WL</b>	Weld load
<b>PWL</b>	Pre weld load
<b>DAQ</b>	Data Acquisition
<b>DC</b>	Direct Current
<b>RMS</b>	Root Mean Square
<b>SN</b>	Signal-to-noise
<b>a.u.</b>	Arbitrary units

# Symbols

$R_a$	Surface roughness
$V$	Volts
$\Delta$	Change
$\alpha$	Alpha
$\lambda$	Wavelength
$\text{\AA}$	Angstrom
$^\circ$	Degree
$C$	Celsius
$Pa$	Pascal
$GPa$	Giga pascal
$\omega$	Angular speed
$kHz$	Kilohertz
$h$	Hour
$s$	Second
$min$	Minute
$m$	Meter
$\mu m$	Micrometer
$nm$	Nanometer
$dBm$	Decibel maximum value
$dBc$	Decibel carpet value
$N$	Newton
$g$	Gram
$kg$	Kilogram
$ml$	Millilitre
$\%w/w$	Percentage weight by weight
$\Theta$	Angle