

**DEVELOPMENT OF MULTIFUNCTIONAL ADDITIVES FOR
ENGINE OIL/FUELS AND ZIEGLER NATTA CATALYSTS
FOR POLYPROPYLENE SYNTHESIS**

SAMEEKSHA RAIZADA



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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ENGINE OIL/FUELS AND ZIEGLER NATTA CATALYSTS
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by

SAMEEKSHA RAIZADA

Submitted

**In fulfilment of the requirements of the degree of Doctor of Philosophy
to the**



**DEPARTMENT OF CHEMISTRY
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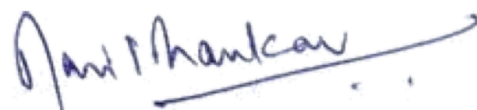
Dedicated to My Heavenly Parents

CERTIFICATE

This is to certify that the thesis entitled “**DEVELOPMENT OF MULTIFUNCTIONAL ADDITIVES FOR ENGINE OIL/FUELS AND ZIEGLER NATTA CATALYSTS FOR POLYPROPYLENE SYNTHESIS**” being submitted by Ms. Sameeksha Raizada to the Department of Chemistry, 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 her.

She has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis, which to my knowledge has reached the requisite standard.

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.



Prof. Ravi Shankar

Department of Chemistry

Indian Institute of Technology Delhi

New Delhi-110016, India



Dr. G. S. Kapur

Former Executive Director

Indian Oil R&D Centre,

Faridabad, Haryana-121007, India

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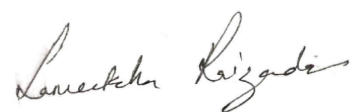
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गुरुर्ब्रह्मा गुरुर्विष्णुः गुरुर्देवो महेश्वरः।

गुरुः साक्षात् परं ब्रह्म तस्मै श्री गुरवे नमः ॥



Sameeksha Raizada

ABSTRACT

The thesis is devoted to a systematic study on three important aspects of petrochemical industry, namely, the development of lubricity improvers for ultra-low sulfur diesel (ULSD), multifunctional additives for engine oil formulations, and polymerization of propylene using Ziegler Natta catalyst. The former two aspects are relevant to meet the standard norms and regulations to limit the emission of polluting elements such as S and polar trace components from fossil fuels without compromising fuel efficiency. In this context, the application of poly(isobutylene succinic anhydride) derivatives tethered with functionally substituted discrete siloxanes/polydimethylsiloxanes have been examined for their efficacy as lubricity improvers in ultra-low sulfur diesel as well as multifunctional additives in base oil. Blends with varying concentrations of additives have been studied to evaluate physical parameters such as viscosity index, kinematic viscosity, and density. These blends are found to be useful in improving the anti-wear and anti-friction attributes of ULSD or base oil. A few examples among the multifunctional additives under study have shown significant dispersion efficiency of the blends on carbon soot in the base oil and exhibit superior activity as compared to the commercial additive. The results are included in Chapters 3 and 4 of the thesis. In Chapter 5, polypropylene with characteristic properties has been synthesized using ZN catalyst with an emphasis on understanding the role of siloxanes/alkoxysilanes as external donors.

सार

थीसिस पेट्रोकेमिकल उद्योग के तीन महत्वपूर्ण पहलुओं पर एक व्यवस्थित अध्ययन के लिए समर्पित है, अर्थात्, अल्ट्रा-लो सल्फर डीजल (यूएलएसडी) के लिए चिकनाई सुधारकों का विकास, इंजन तेल फॉर्मूलेशन के लिए बहुक्रियाशील एडिटिव्स और ज़िग्लर नट्टा उत्प्रेरक का उपयोग करके प्रोपलीन का पोलिमेराइजेशन। पहले के दो पहलू ईंधन दक्षता से समझौता किए बिना जीवाश्म ईंधन से एस और ध्रुवीय ट्रेस घटकों जैसे प्रदूषणकारी तत्वों के उत्सर्जन को सीमित करने के लिए मानक मानदंडों और विनियमों को पूरा करने के लिए प्रासंगिक हैं। इस संदर्भ में, कार्यात्मक रूप से प्रतिस्थापित असतत सिलोक्सेन/पॉलीडिमिथाइलॉक्सेन के साथ जुड़े पॉलीसोब्यूटिलीन स्यूसिनिक एनहाइड्राइड डेरिवेटिव के अनुप्रयोग की अल्ट्रा-लो सल्फर डीजल में चिकनाई सुधारक के साथ-साथ बेस ऑयल में बहुक्रियाशील एडिटिव्स के रूप में उनकी प्रभावकारिता के लिए जांच की गई है। चिपचिपाहट सूचकांक, गतिक चिपचिपाहट और घनत्व जैसे भौतिक मापदंडों का मूल्यांकन करने के लिए एडिटिव्स की अलग-अलग सांद्रता वाले मिश्रणों का अध्ययन किया गया है। ये मिश्रण यूएलएसडी या बेस ऑयल के घर्षण-रोधी और घर्षण-रोधी गुणों को बेहतर बनाने के लिए उपयोगी पाए गए हैं। अध्ययनरत मल्टीफंक्शनल एडिटिव्स के बीच कुछ उदाहरणों ने बेस ऑयल में कार्बन कालिख पर मिश्रणों की महत्वपूर्ण फैलाव दक्षता दिखाई है और वाणिज्यिक एडिटिव की तुलना में बेहतर गतिविधि प्रदर्शित की है। परिणाम थीसिस के अध्याय 3 और 4 में शामिल हैं। अध्याय 5 में, बाहरी दाताओं के रूप में सिलोक्सेन/अल्कोक्सीसिलेन की भूमिका को समझने पर जोर देने के साथ ZN उत्प्रेरक का उपयोग करके विशिष्ट गुणों वाले पॉलीप्रोपाइलीन को संश्लेषित किया गया है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

General Abbreviations

ULSD	Ultra-Low Sulfur Diesel	ENDO	Endotherm
EU	European Union	EXO	Exotherm
MASCD	Maximum Allowed Permissible Sulfur Content in Diesel	Cat.	Catalyst
FAME	Fatty Acid Methyl Ester	CSTR	Continuous Stirring Tank Reactor
HFRR	High-Frequency reciprocating rig	ED	External donor
FBWT	Four Ball Wear Test		
SRV	Schwingung (Oscillating), Reibung (Friction), Verschleiß (Wear)	ID	Internal Donor
WSD	Wear Scar Diameter	I.I	Isotactic Index
TOFA	Tall Oil Fatty acids	PP	Polypropylene
COF	Coefficient Of Friction	XS	Xylene Soluble
LCN	Light Cracked Naphtha	TEAL	Triethylaluminum
PIB	Polyisobutylene	EDX	Energy Dispersive X-Ray
PIBSA	Poly(isobutylene succinic anhydride)	VI	Viscosity Index
PIBSI	Poly(isobutylene succinic imide)	KV	Kinematic Index
EC	Ethylene Carbonate	DV	Dynamic Viscosity
ZN	Ziegler Natta	ESI	Electrospray Ionization
ASTM	American Society for Testing and Materials	Mn	Number average molecular weight
NACE	National Association of Corrosion Engineers	Mw	Weight average molecular weight
XPS	X-Ray Photoelectron Spectroscopy	FT	Fourier Transformation
EDS	Energy-Dispersive X-ray spectroscopy	DSC	Differential Scanning Calorimetry

GPC	Gel Permeation Chromatography	PDI	Poly Dispersity Index
NMR	Nuclear Magnetic Resonance	MFI	Melt Flow Index
SEM	Scanning Electron Microscope	IR	Infra-Red
AW	Anti-Wear	BLI	Blend Lubricity Improver
LA	Lubricant Additive	BCP	Blend Commercial PIBSI
EAME	Eleostearic Acid Methyl Ester	EDA	Ethylenediamine
MA	Maleic Anhydride	TBA	Tert-butylamine
BTA	Benzotriazole	PY	Pyrogallol
BHT	Butylated-hydroxy-toluene	T _m	Melting Temperature
nBA	n-butylamine	T _c	Crystallization Temperature
<i>X</i>	Crystallinity		

General Units of measurements

eV	Electron Volt	ppm	Parts per million
keV	Kilo Electron Volt	μm	micrometers
nm	Milimeter	°	Degree
s	seconds	Δ	Difference
rpm	Rotation Per Minute	Å	Angstrom
v	wavenumber	λ	Wavelength
Kv mm ²	Kilo Volt Mili Meter Square	N	Newtons