SYNTHESIS OF PETROLEUM EXTREME PRESSURE (EP) ADDITIVES USING SOME INORGANIC MATERIALS

A Thesis

Submitted by Hisham Mohamed Salah Youssef (M. Sc. Inorganic Chemistry)

> For the drgree of Ph.D. In Chemistry

> > To

Department of Chemistry Faculty of Science Cairo University

2010

APROVAL SHEET FOR SUMISSION

Thesis Title: Synthesis of petroleum extreme pressure (EP) additives using some inorganic materials.

Name of candidate: Hisham Mohamed Salah Youssef

This thesis has been approved for submission by the supervisors:

- 1- Prof. Dr. / Amin Mahmoud Baraka Signature:
- 2- Prof. Dr. / Ahmad El-Sayed Salem Signature:

Prof. Dr. Mohamed M. Shoukry

Chairman of Chemistry Department Faculty of Science- Cairo University

ABSTRACT

Student Name: Hisham Mohamed Salah Youssef

Title of the thesis: Synthesis of petroleum extreme pressure (EP)

additives using some inorganic materials

Degree: Ph. D. (Chemistry)

The objective of this work aim ed at synthesize of petroleum extrem e pressure additives which used in industrial gear oils and in engine lubrication through sulfurization and phosphorization of nine different neat vegetable oils, and to their mixtures with castor oil. The synthesized products was evaluated for solubility in mineral oils and for absence of corrosive active sulfur. Reactions were monitored through measuring the viscosity, FTIR spectra, and the sulfur and phosphorus percentage in the products. The synthesized products after blending with mineral base oils were evaluated for extreme pressure properties, oxidation stability, and for rust-preventing characteristics.

Keywords: extreme pressure additive, sulfurization, phosphorization, vegetable oils, mineral oils.

Supervisors: signature:

1- Prof. Dr. / Amin Mahmoud Baraka

2- Dr. / Ahmad El-Sayed Salem

Prof. Dr. Mohamed M. Shoukry

Chairman of Chemistry Department Faculty of Science- Cairo University

Acknowledgement

First and foremost, the author feels indebted to God.

I would like to express my hearty thanks for my supervisor, **Prof, Dr, Amin M. Baraka**, Professor of Physical Chemistry, Faculty of Science,
Cairo University, for his fatherly guidance, valuable supervision and his
personal interest in my work. The guidance and support given by him were
indispensable to the completion of this work.

My indebtedness and gratitude are also to **Dr. Ahmad El-Sayed Salem,** General Manager of Technical Affairs, Member of Board, Misr
Petroleum Co., for his great effort in suggesting the point investigated,
continuous encouragement and his valuable discussion of the obtained
results, without which this work has not been done.

I wish to express my special thanks for my dear parents for non stop encouragement. I must not deny the power of my devoted wife and my little three daughters for encouragement and putting up with my absence. I also want to thank my brothers for their efforts with me. Obviously, without them, this work would not exist.

Hisham Mohamed Salah Youssef

CONTENTS

	<u>Page</u>
List of Abbreviations	
List of Figures	
List of Tables	
AIM OF THE WORK	
I- INTRODUCTION	1
I-1- Lubrication is Essential	1
I-2- Lubricating Base Oil Classifications	3
I-2-1- Mineral Base Oils	3
I-2-2- Synthetic Base oils	4
I-2-3- Vegetable-Based Base Oils	5
I-3- Mineral Base Oils Manufacturing	5
I-3-1- Vacuum Distillation	6
I-3-2- Deasphalting	7
I-3-3- Dearomatization	7
I-3-4- Dewaxing	8
I-3-5-Hydrofinishing	8
I-4-Modern Catalytic Processes	9
I-4-1- Severe Hydrotreatment	9
I-4-2- Special Base Oils From Hydrocracking	10
I-4-3- Catalytic De-waxing	10
I-4-4- Iso-De-waxing	10
I-5- Base Oil Classifications	10
1-6- Lubricating Oils Classifications	12
1-6-1- Classification by Viscosity Grade	12
1-6-2- Classification by Additives	12

	<u>Page</u>
1-6-3- Classification According to Producer Brand Names	13
1-6-4- Classification According to Application	13
1-6-4-1- Engine Oil Classification and Requirements	13
I-6-4-2- Industrial Oils Classifications	20
I-6-4-2-1- Compressor Lubricants	21
I-6-4-2-2- Refrigerator Lubricants	22
I-6-4-2-3- Hydraulic Lubricants	22
I-6-4-2-4- Turbine Lubricants	22
I-6-4-2-5- Metal Working Lubricants	23
I-6-4-2-6- Gear Lubricants	23
I-6-4-2-6-1- Load and Speed Conditions During Tooth	
Engagement	24
I-7- Additives	27
I-7-1- Lubricant Protective Additives	27
I-7-2- Performance Additives	28
I-7-3- Surface Protective Additives	28
I-8- Lubrication Regimes	30
I-9- The Basic Mechanism of Lubrication and Wear	
and The Influence of Additives	34
I-10- The Function of Lubricity additives	36
I-11- Types of Antiwear (AW) and Extreme Pressure	
(EP) Additives	37
I-11-1- Phosphorus Compounds	37
I-11-2- Compounds Containing Sulfur and Phosphorus	40
I-11-3- Compounds Containing Sulfur and Nitrogen	42
I-11-4- Sulfur Compounds	42
I-11-5- Overbased Sulfonates	45
I-11-6- Chlorine Compounds	45

	Page
	4.6
I-11-7- Solid Lubricating Compounds	46
I-12- The Action Mechanism of Lubricity Additives	46
I-12-1- Sulfur Compounds	47
I-12- 2- Chlorine Compound Types	48
I-12-3- Phosphorus Compounds	49
I-12-4- Organo-metallic Compounds	50
II-EXPERIMENTAL	56
II-1- Specification of The Used Chemicals and Materials	56
II-2-Synthesis Method	62
II-2-1- Synthesis of Sulfurized Vegetable Oils	62
II-2-1-1- Synthesis of Sulfurized Neat Vegetable Oils	62
II-2-1-2- Synthesis of Co-sulfurized Mixture of Vegetable Oil	
And Castor oil	66
II-2-2- Synthesis of Sulfurized-Phosphorized Vegetable Oils	69
II-2-2-1- Synthesis of Sulfurized-Phosphorized Neat Vegetable Oils	69
II-2-2-2 Synthesis of Co-sulfurized-Phosphorized Mixtures	
of Vegetable Oils with Castor Oil	71
II-3-Evaluation of The Synthesized Additive for industrial gear	73
II-3-1-Solubility of The Synthesized Additive	74
II-3-2-Detection of Copper Corrosion From Petroleum Products by	
The Copper Strip Tarnish Test According to ASTM D 130	74
II-3-3-Uptaken Sulfur by Energy-Dispersive X-Ray Fluorescence	
Spectrometry According to ASTM D 4294	76
II-3-4- Oxidation Stability of Steam Turbine Oils by Rotating	
Pressure Vessel According to ASTM D 2272	79

	<u>Page</u>
II-3-5- Rust-Preventing Characteristics of Inhibited Mineral Oil	
in The Presence of Water	83
II-3-6- Extreme Pressure Properties: Friction and Wear Tests for	
Lubricants Four-Ball Machine According to IP 239	86
III- RESULTS & DISCUSSION	91
III-1- Synthesis of Extreme Pressure Additives	91
III-1-1- Synthesis of Sulfurized Vegetable Oils	91
III-1-1- Synthesis of Sulfurized Neat Vegetable Oils	92
III-1-1-2- Synthesis of Co-sulfurized Mixtures of Vegetable Oil	
and Castor Oil	107
III-1-2- Synthesis of Sulfurized-Phosphorized Vegetable Oils	119
III-1-2-1- Synthesis of sulfurized-phosphorized neat vegetable oils .	119
III-1-2-2- Synthesis of Cosulfurized-Phosphorized Mixtures	
of Vegetable Oils and Castor Oil	129
IV- SUMMARY	141
V- REFERENCES	148
VI- ARABIC SUMMARY	

List of Abbreviations

ACEA : Association des Constructeurs Européens d' Automobile

(Association of the European car Manufacturers).

AGMA : American Gear Manufacturers Association (USA)

API : American Petroleum Institute.

ASTM : American Society for Testing and Materials.

ATIEL : Association Technique de L'Industrie Européenne des

Lubrifiants.

(Technical Association of the European Lubricant Industry).

AW : Anti-Wear.

DBS : Di-n-butyl sulfide.

DMTD : Dialkyl-2,5-dimercapto-1,3,4- thiadiazole.

EHL : Elastohydrodynamic Lubrication.

EP : Extreme Pressure.

FTIR : Fourier Transform Infrared

FZG : Forschungsstelle Fur Zahnrader Und Getriebebau (D),

Performance Test Method for Determination of Load

Capacity of Lubricants According To FZG Method.

HSAB : Hard and soft acids and bases.

IP : Institute of Petroleum (UK).

I.S.L. : Inetial Seizure Load.

ISO : International Standard Organization.

ISO VG: ISO Viscosity Grade.

Kin. Vis. : Kinematic viscosity.

MHL : Mean Hertz Load.

MO : Mineral Oil.

MoDTC : Molybdenum dithiocarbamate.

MoDTP : Molybdenum dithiophosphate.

NMP : N-methyl-2-pyrrolidone.

OEMs : Original Equipment Manufacturers.

PEP : Passive Extreme Pressure.

PMMA : Poly methyl methacrelate.

PTFF : Polytetrafluorethylene.

R.I. : Refractive Index.

RO : Rust and Oxidation Inhibited.

SAE : Society of Automotive Engineers.

Sp. gr. : Specific gravity.

TAN : Total Acid Number in mg KOH/g sample.

TCP : Tricresyl phosphate.

TPPT : Triphenyl phosphorothionate.

ZDDP : Zinc dialkyldithiophosphate

ZDTP : Zinc dithiophosphate.

VI : Viscosity Index.

HVI : High Viscosity Index.

VHVI : Very High Viscosity Index.

List of Figures

	<u>Page</u>
Figure (I-1): The US "Tripartite" of API, ASTM, and SAE	16
Figure (I-2): Important gear types	24
Figure (I-3): Coefficient of friction as a function of viscosity,	
velocity and load	31
Figure (I-4): Temperature Effect on EP additive Activity	33
Figure (I-5): The mechanism proposed by Forbes and Reid	47
Figure (II-1): Copper Strip Corrosion Test Bomb	75
Figure (II-2): Schematic Drawing of the Rotary Vessel Test	
Apparatus	80
Figure (II-3): Chart of Recording Pressure Gage	82
Figure (II-4): Rusting Test Apparatus	84
Figure (II-5): Four-Ball Test Arrangement	88
Figure (II-6): Sectional View of Four-Ball Tester	89
Figure (II-7): Wear Load Curve Showing Hertz Line and I.S.L	90
Figure (III-1): FTIR spectra of cotton seed oil before (—) and	
after () sulfurization	95
Figure (III-2): FTIR spectra of corn seed oil before (—) and	
after () sulfurization	96
Figure (III-3): FTIR spectra of sunflower oil before (—) and	
after () sulfurization	97
Figure (III-4): FTIR spectra of soybean oil before (—) and	
after () sulfurization	98
Figure (III-5): FTIR spectra of castor oil before (—) and	
after () sulfurization	99