

Use Of Improved Methods For Studying Oxidation & Deposit Control In Low Phosphorus Engine Oils (Identifying Robust Antioxidant Systems)

Vince Gatto, Bill Moehle, Tyler Cobb



Presented At:
Additives 2005
April 6, 2005
Dublin, Ireland

Albemarle Corporation
P. O. Box 341
Baton Rouge, LA 70821
USA

Rapid Engine Oil Technology Changes Along Many Fronts

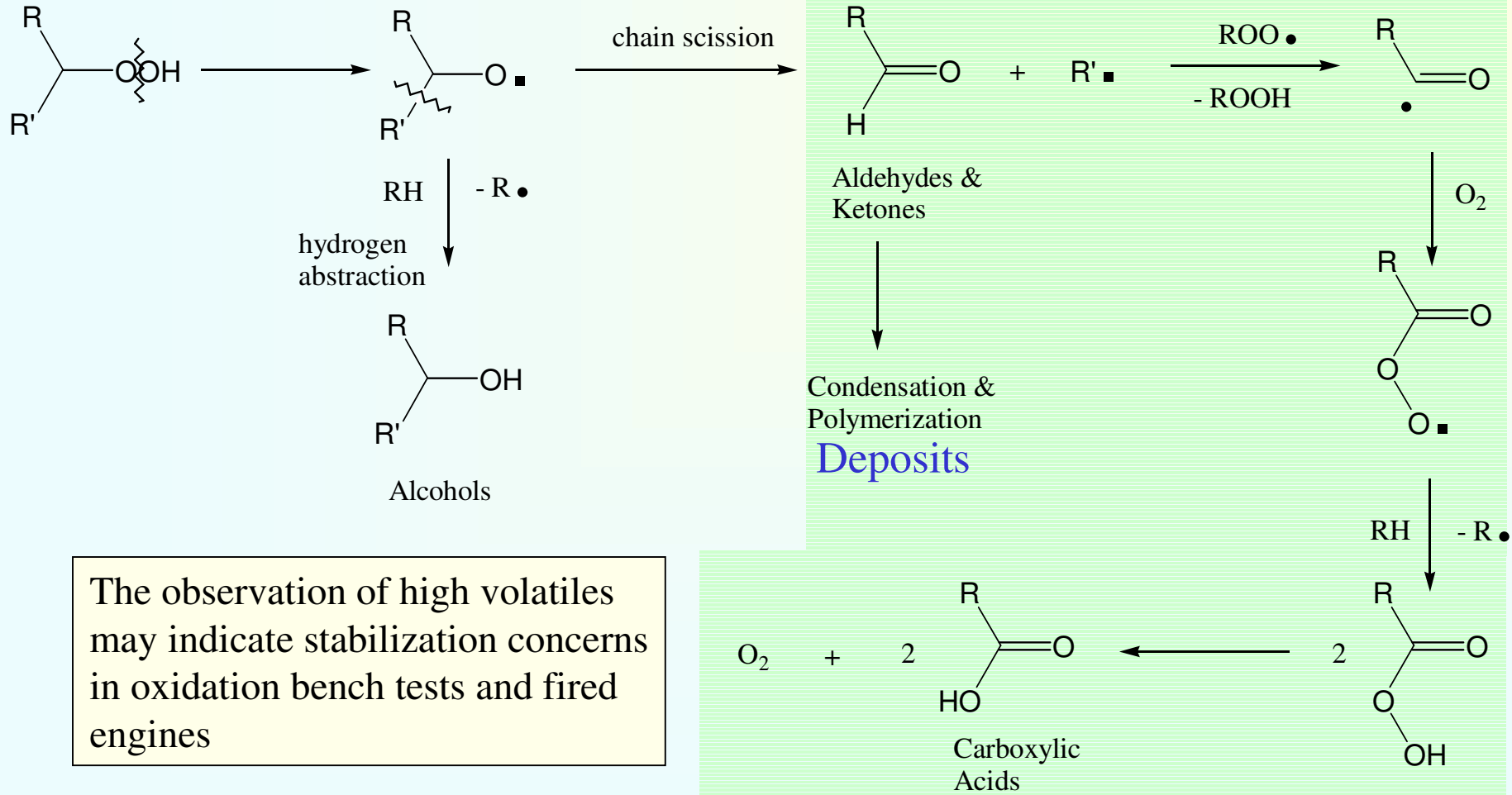
- Basestocks
- Tests
- Specifications
- Additives
 - phosphorus-free anti-wear replacements for ZDDP (EP 1 321 506)
 - use of organomolybdenum to solve specialized deposit and oxidation problems (TLT, October, 2003, p 40-47)
 - Robust antioxidants needed to address all aspects of lubricant degradation

Increased Use Of Organo-Molybdenum
Complements The Trend To Reduce
Phosphorus Levels In Gasoline Engine Oils

Robust

Controls Deposits
Minimizes Volatiles Formation
Controls True Oxidation
Controls Polymerization

Chemical Mechanism Of Lubricant Oxidation



The observation of high volatiles may indicate stabilization concerns in oxidation bench tests and fired engines

Objective Of This Study

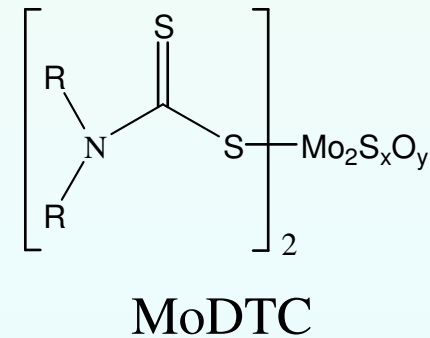
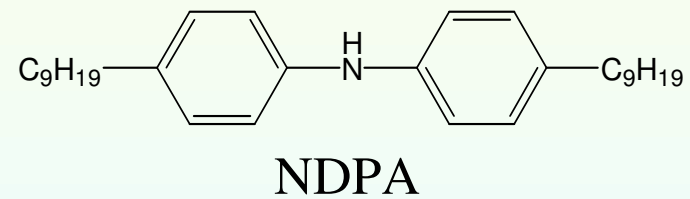
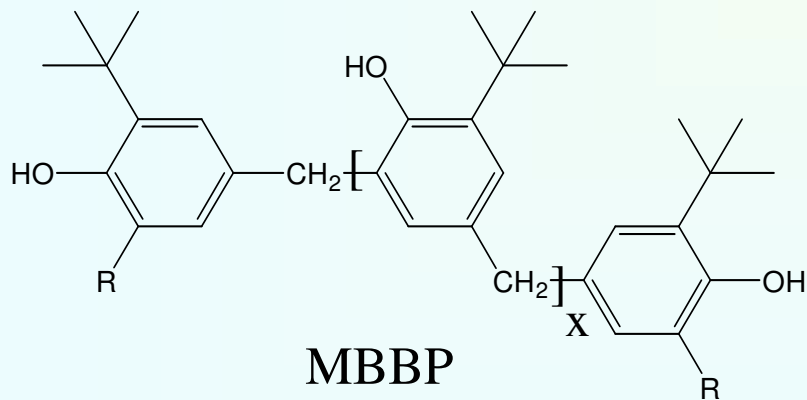
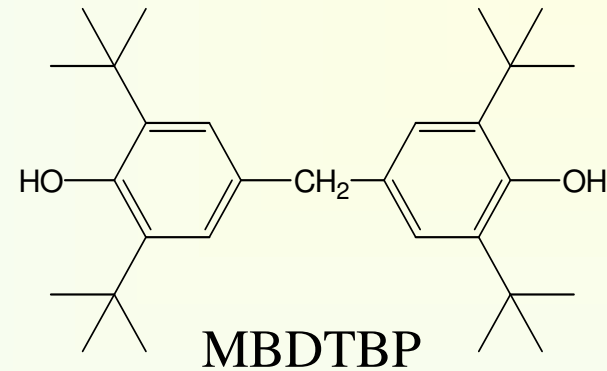
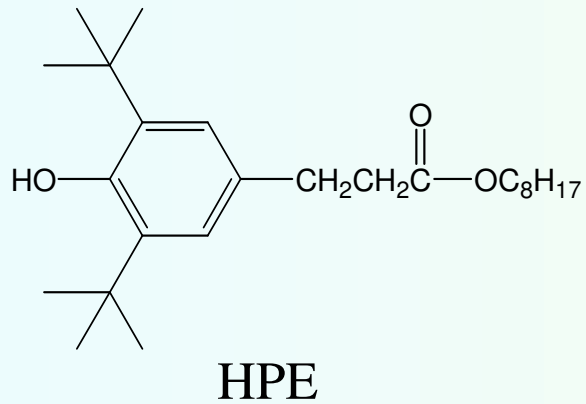
- Assess the antioxidant performance of different hindered phenolic types in low phosphorus engine oils containing molybdenum and alkylated diphenylamines
 - TEOST MHT-4
 - ALBOT

} Covers a broad range of oxidation environments
- Demonstrate Use Of The TEOST As A Tool To Obtain Valuable Information Beyond Deposit Formation
 - Oxidation Of Recovered Oil & Volatiles
 - Fundamental Understanding Of Oxidation Mechanisms Using FTIR Techniques

Testing Protocol

- TEOST MHT-4
 - Total Rod Deposits (mg)
 - Total Volatiles (g) – Oxidation Leading To Chain Scission
 - FT-IR Peak Area Of Volatiles, Used Oil and Rod – Carbonyl Oxidation (modification of JSAE 20030124)
- Detailed Oil Thickening Study (ALBOT)
 - Percent Viscosity Increase - Polymerization
 - FT-IR Peak Area Increase - Carbonyl Oxidation
- Baseline Engine Oil
 - Group II Basestock
 - Dispersant/detergents Additives
 - ZDDP (470 ppm P)
- Hindered Phenolic Types
 - Hindered Phenolic Ester (HPE)
 - Bis-Hindered Phenol (MBDTBP)
 - Hindered Phenol Oligomer (MBBP)
- Molybdenum Dithiocarbamate (MoDTC)
- Nonylated Diphenylamine (NDPA)

Antioxidants Used In Study



Simulated Engine Oils Used In Study

Table - Composition of Tested Engine Oils								
Oil #	Engine Oil Preblend (g)	MoDTC (g)	Mo (ppm)	NDPA (g)	MBBP (g)	MBDTBP (g)	HPE (g)	Diluent (g)
1	96.00	0.80	360			1.50		1.70
2	96.00	0.80	360	1.50				1.70
3	96.00	0.80	360	0.75				2.45
4	96.00	0.80	360	0.75	0.40			2.05
5	96.00	0.80	360	0.75	0.75			1.70
6	96.00	0.80	360	0.75		0.40		2.05
7	96.00	0.80	360	0.75		0.75		1.70
8	96.00	0.80	360	0.75			0.40	2.05
9	96.00	0.80	360	0.75			0.75	1.70

Finished Group II engine oil blends also contain:

4.8 wt. % dispersant,

1.8 wt. % overbased calcium detergent,

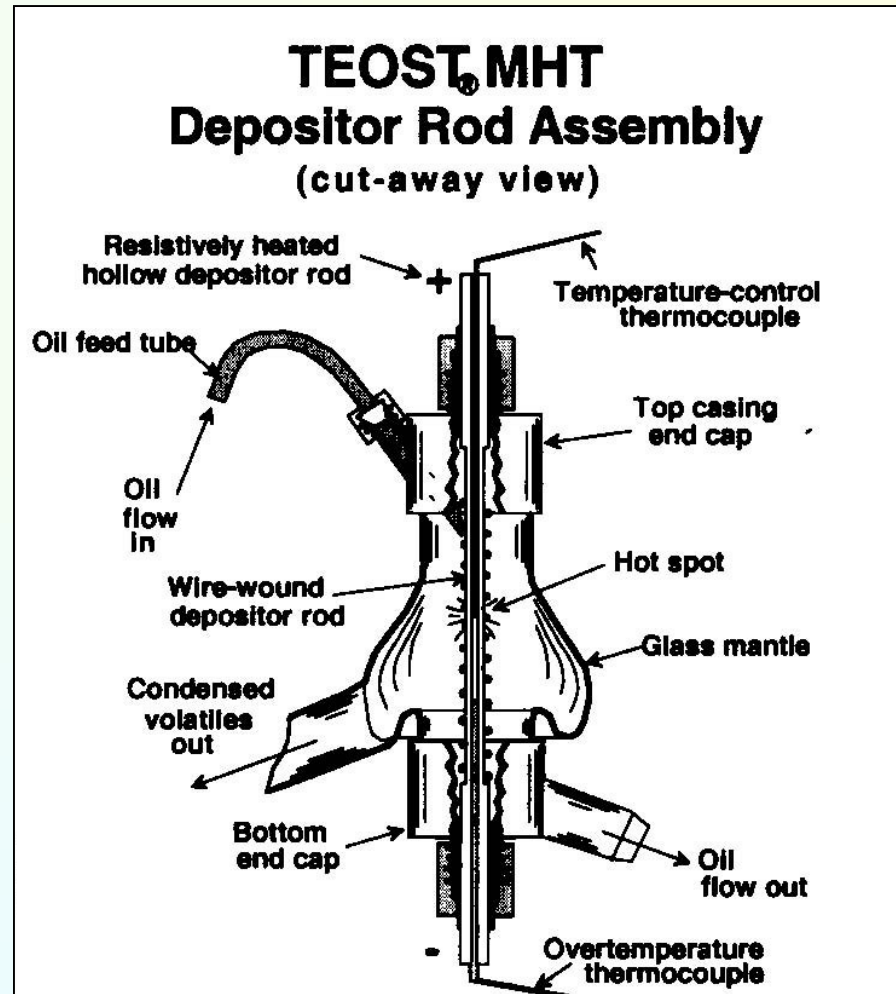
0.5 wt. % neutral calcium detergent

0.6 wt. % secondary ZDDP (470 ppm P)

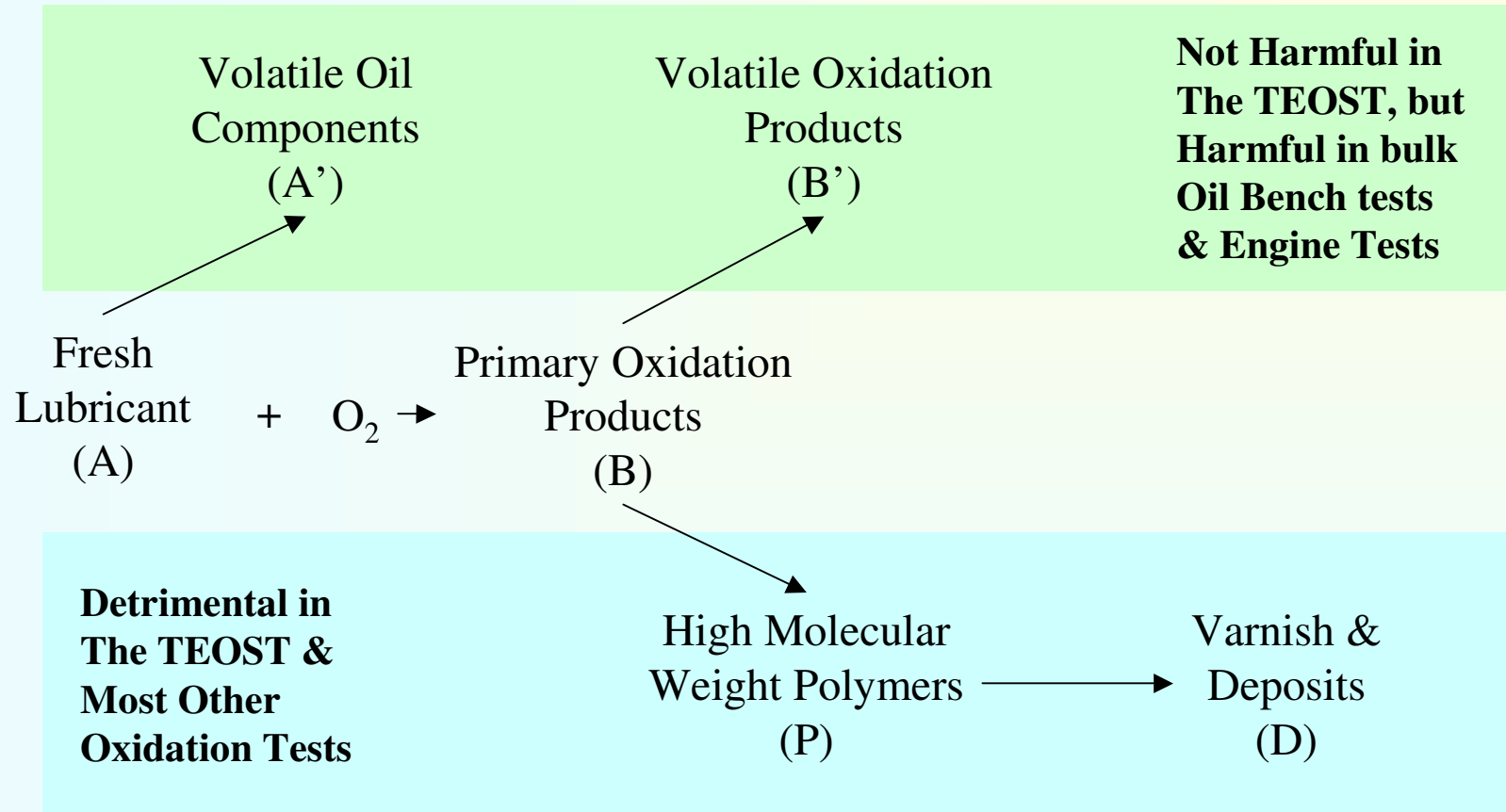
Thermo-Oxidation Engine Oil Simulation Test (TEOST MHT-4)

TEOST[®] MHT Conditions

- Rod Temperature – 285°C
- Test Time – 24 hours
- Oxidant – Air
- Air Flow – 10 mL/minute
- Sample Size – 8.5 grams
- Sample Flow – 0.25 g/minute
- Fe/Pb/Sn Catalyst System
- Wire-Wound Depositor Rod
- Measures:
 - Total Rod Deposits (mg)
 - Volatiles (grams)
 - FT-IR Peak Area (PA)

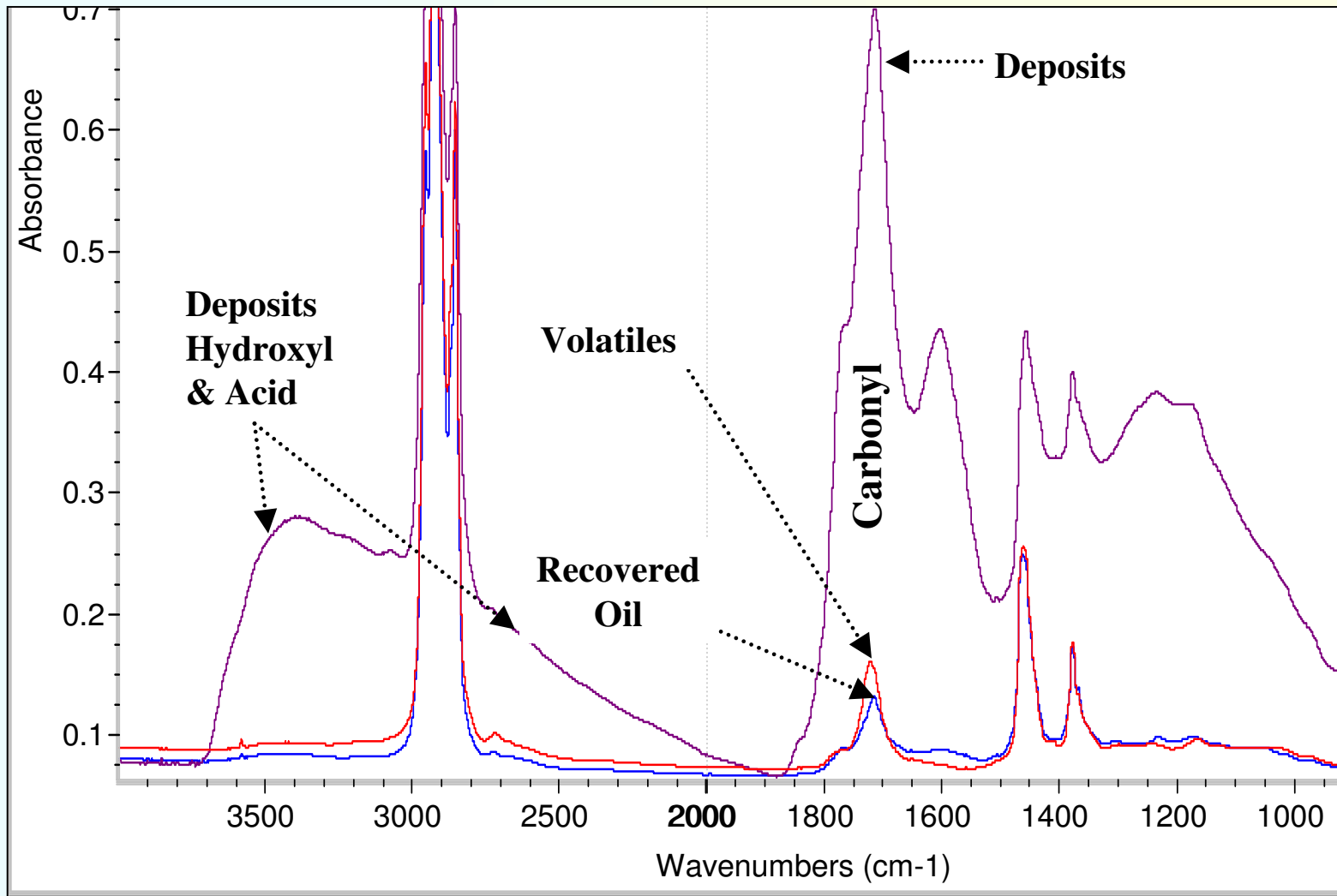


TEOST Physical Mechanism

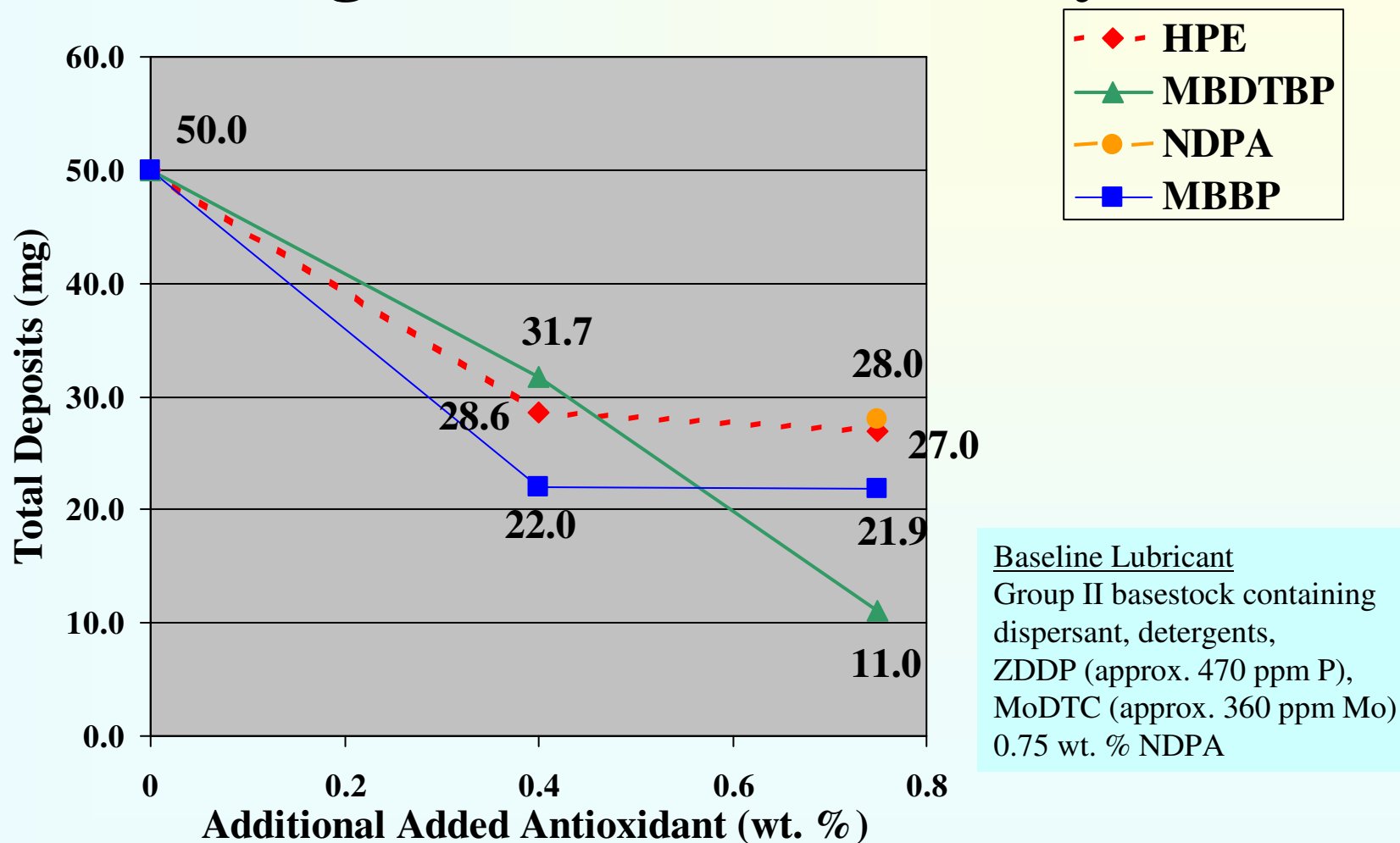


Tribology Transactions, 37 (1994), p 168-174

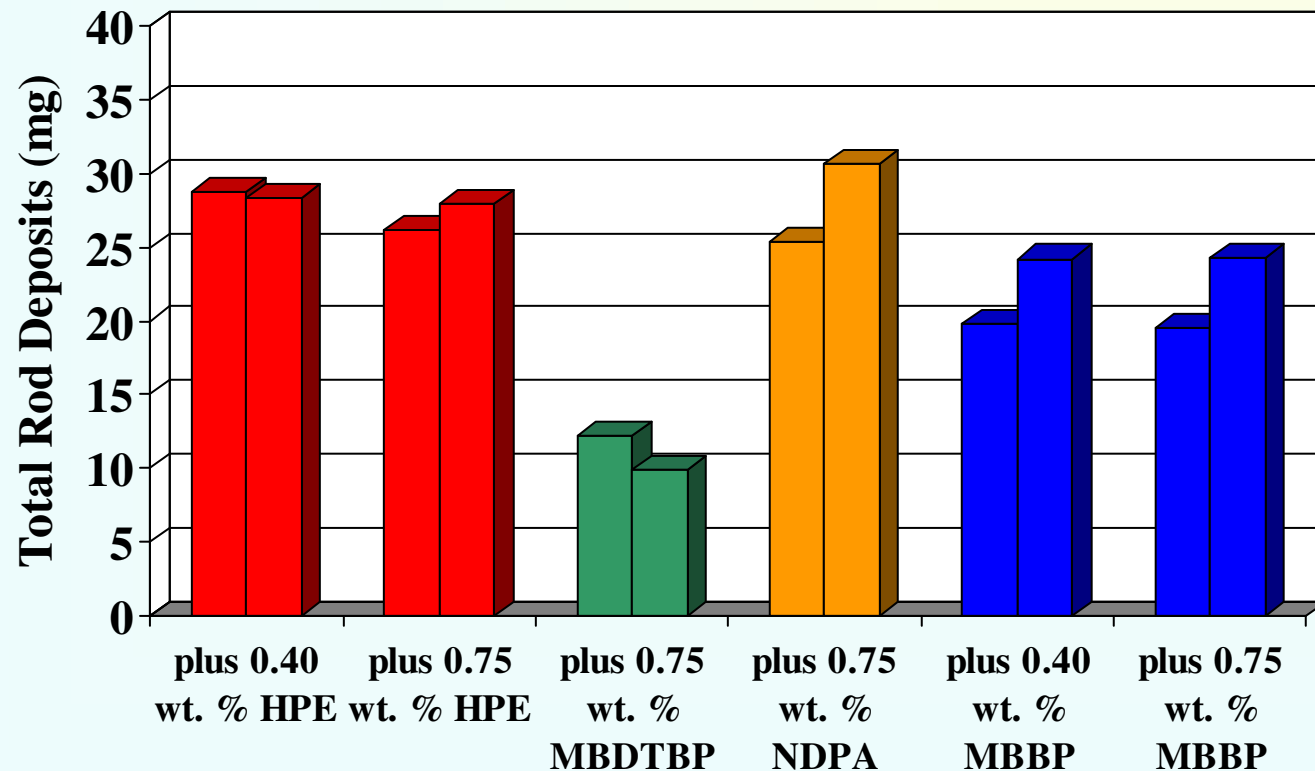
FT-IR Spectra Comparing TEOST Used Oil, Volatiles, and Deposits



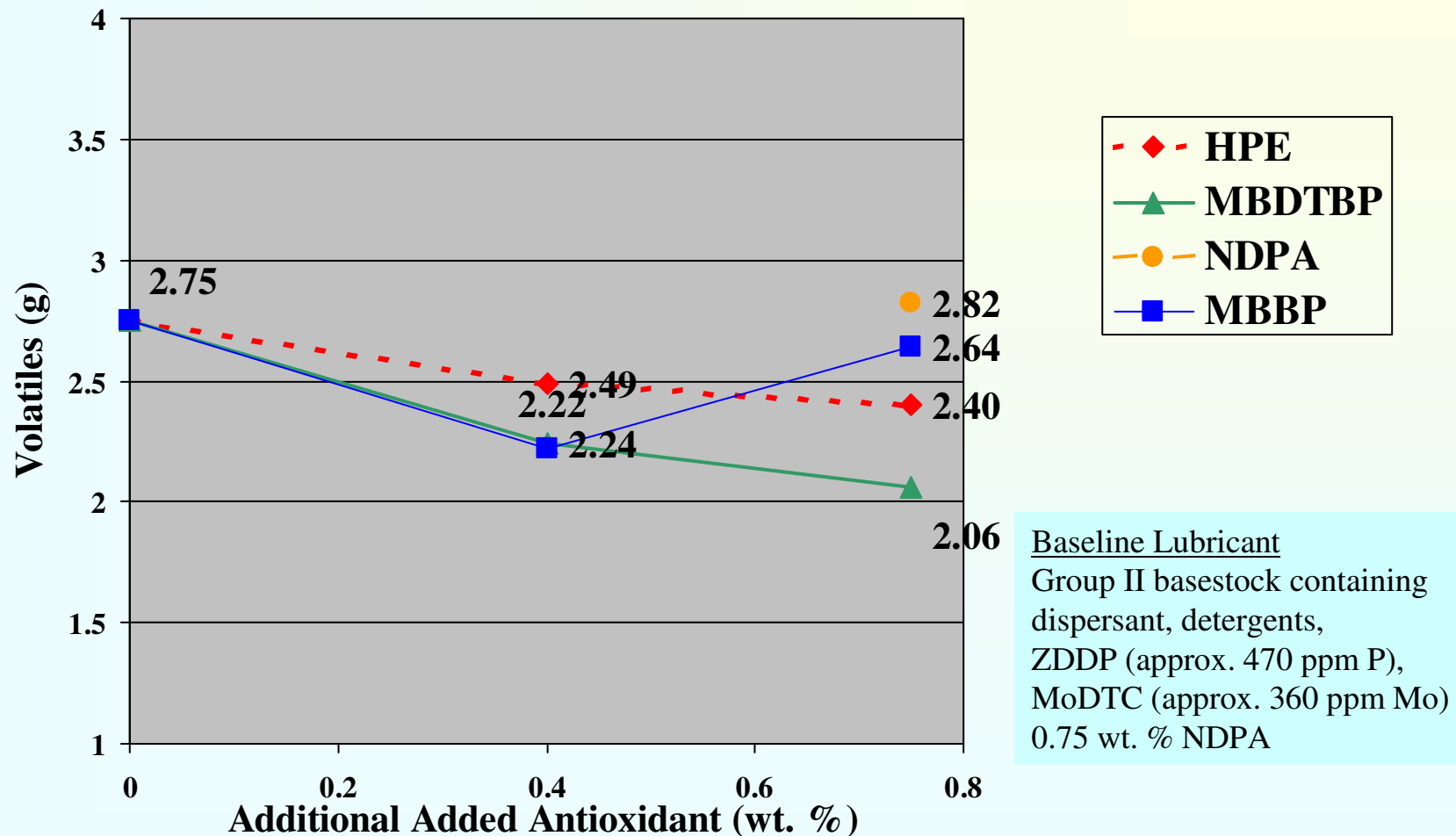
TEOST Evaluation Of Engine Oils Containing Various Antioxidant Systems



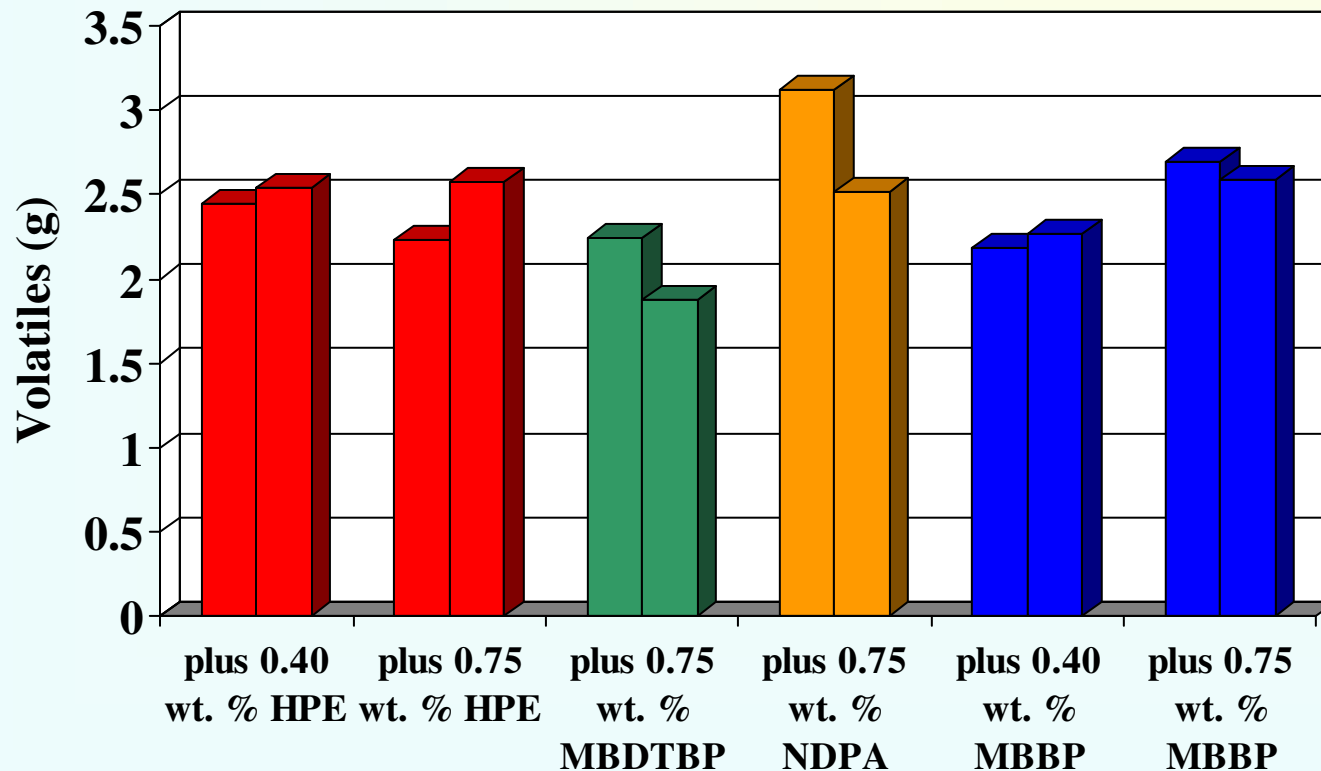
TEOST Repeatability - Deposits



TEOST Evaluation Of Engine Oils Containing Various Antioxidant Systems

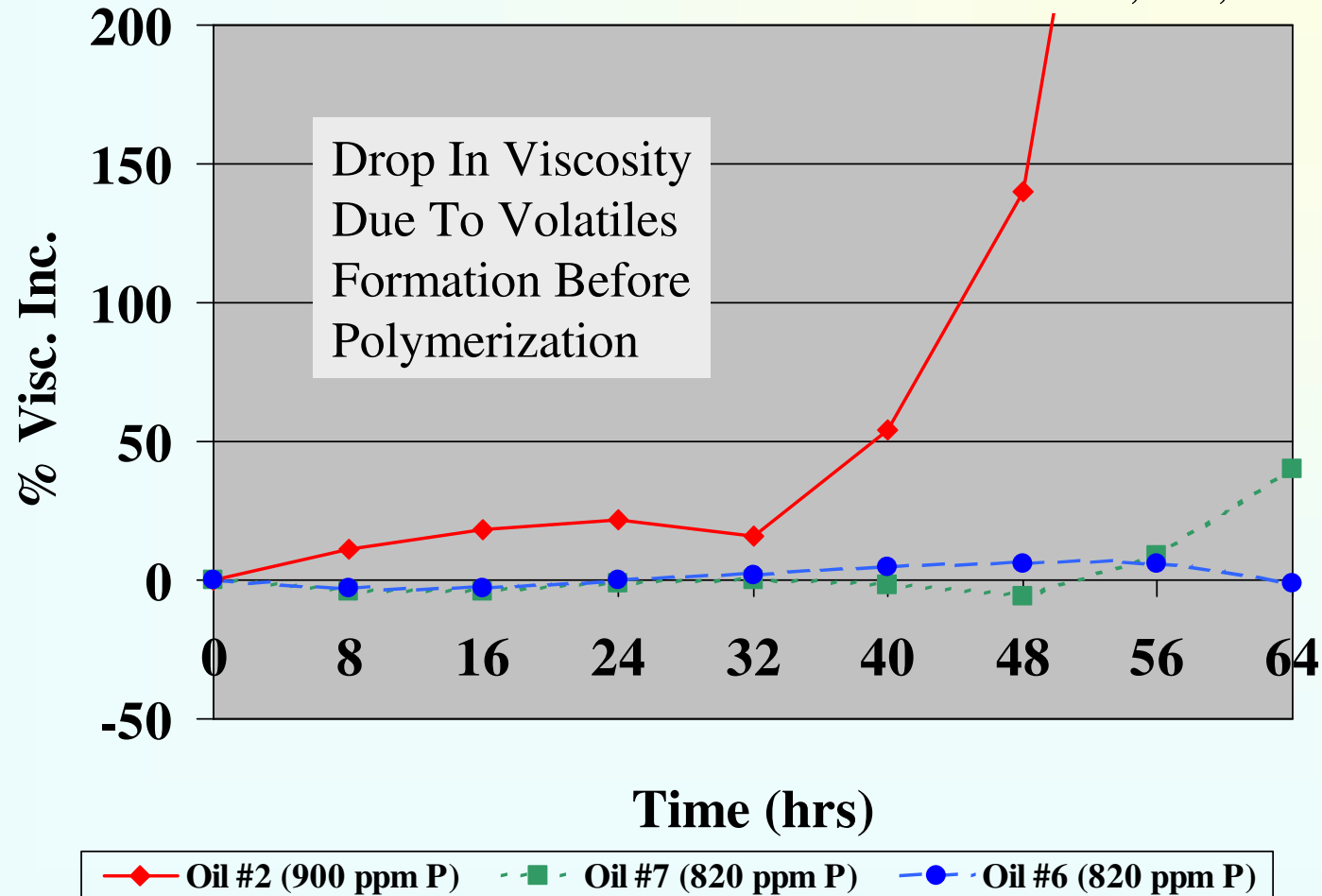


TEOST Repeatability - Volatiles

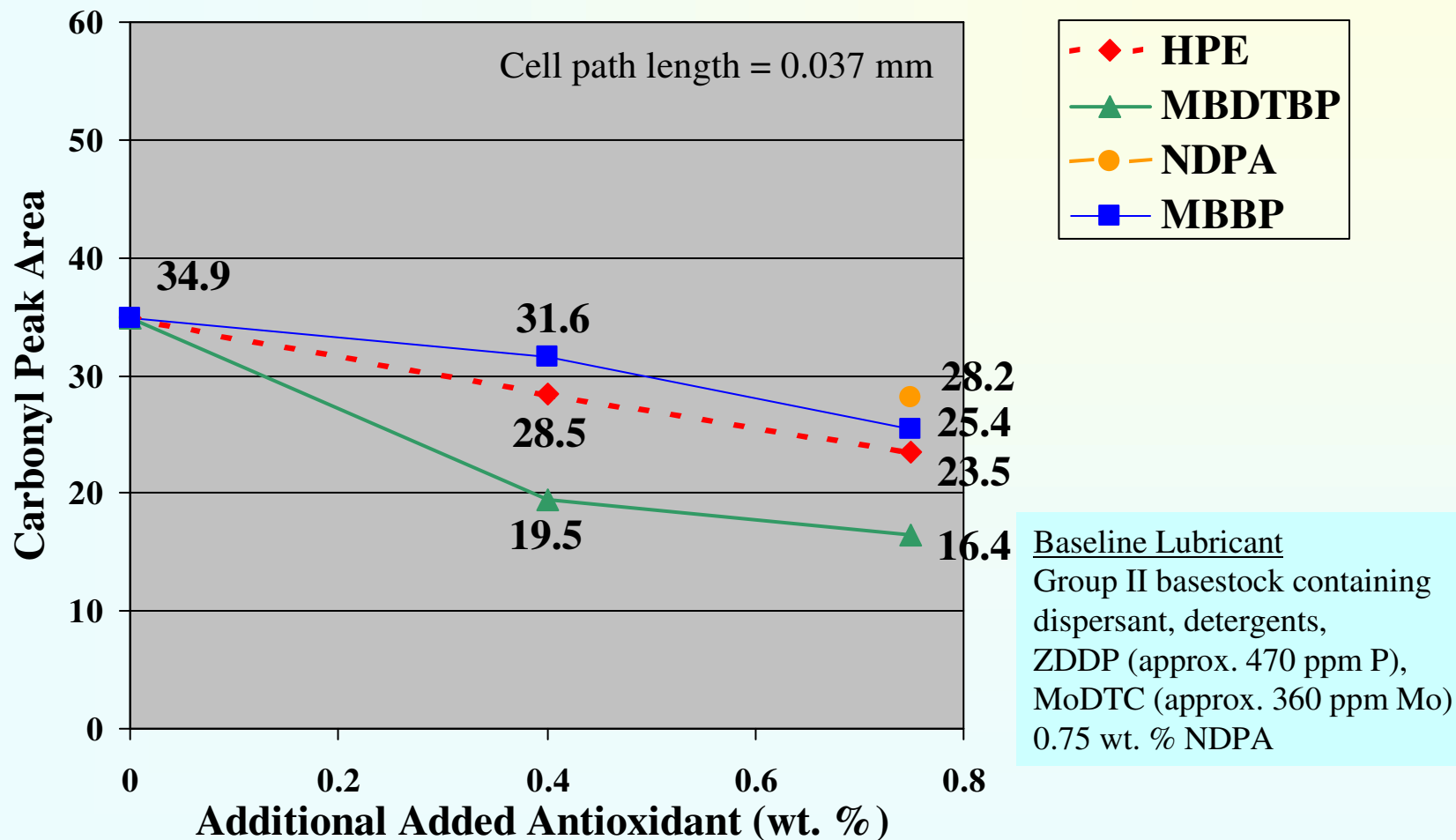


Observed Viscosity Drop Before Oil Thickening In The Sequence III E

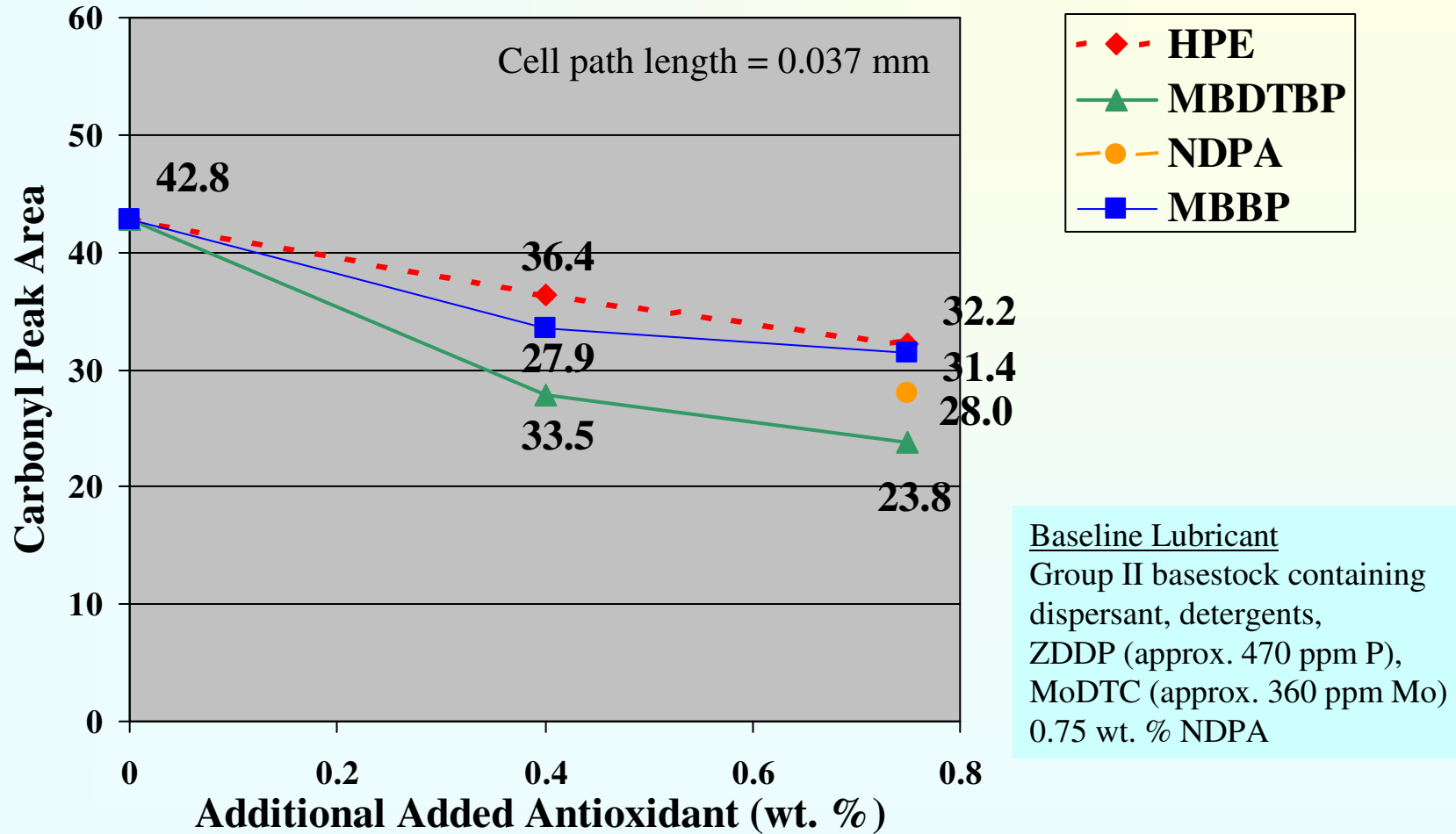
From U. S. Patent 5,840,672



FTIR Analysis Of Recovered TEOST Used Oils Containing Various Antioxidant Systems

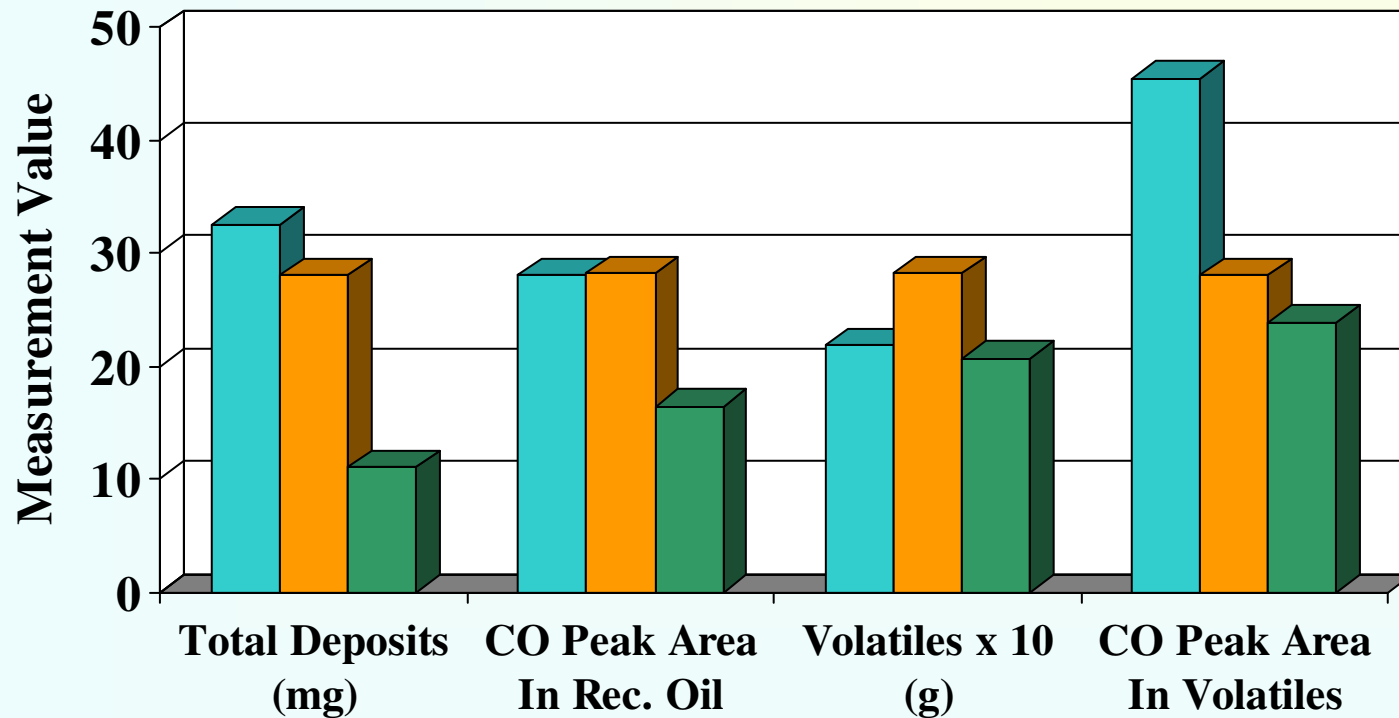


FTIR Analysis Of Collected TEOST Volatiles Containing Various Antioxidant Systems



Evaluating Antioxidant Synergy In All Aspects Of TEOST Lubricant Oxidation

Synergy Between MBDTBP and NDPA clearly seen in all TEOST Oxidation Test Parameters

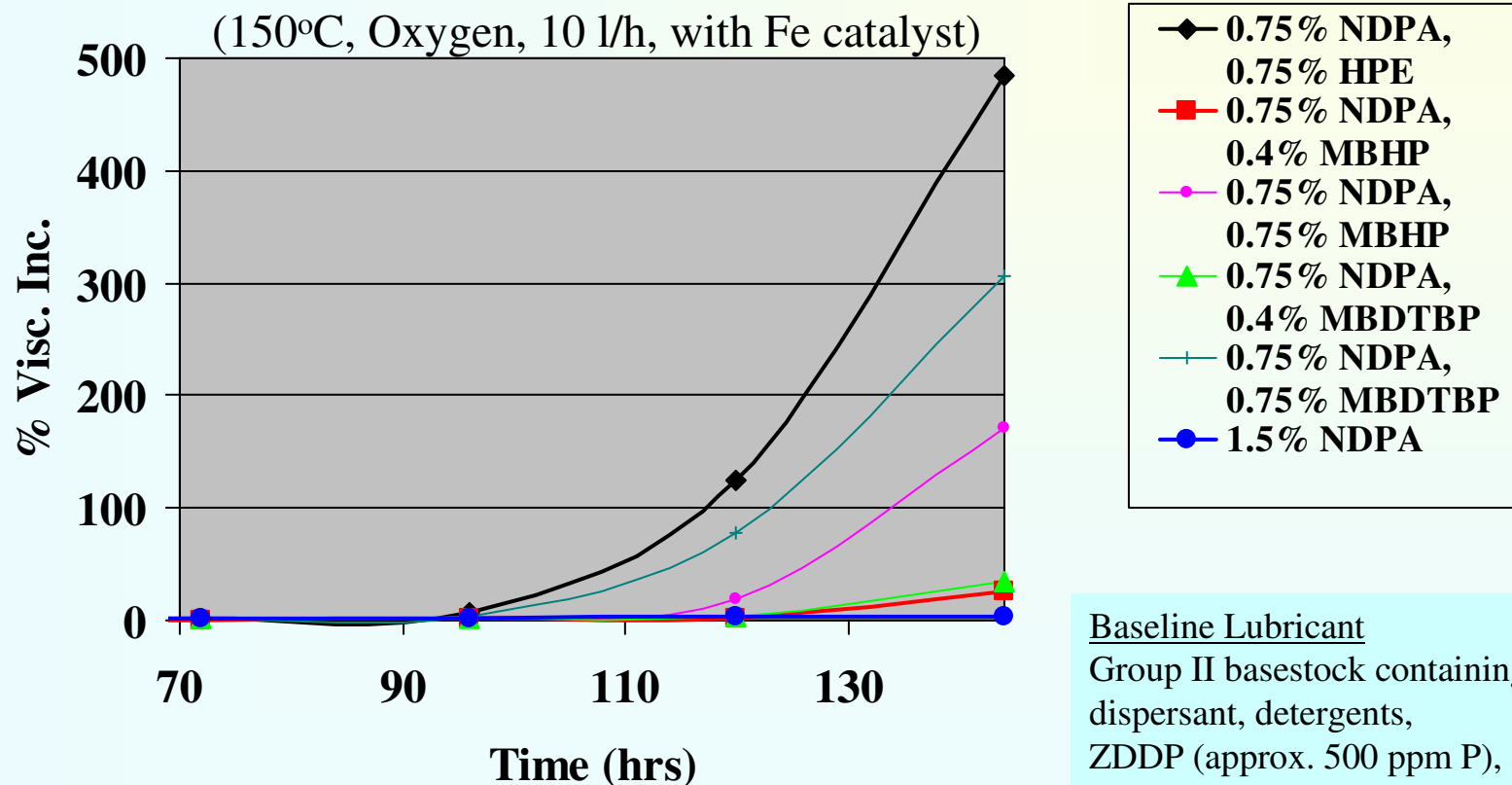


■ MBDTBP alone (1.5 %) ■ NDPA alone (1.5 %) ■ MBDTBP/NDPA (1:1 @ 1.5 %)

Albemarle Bulk Oil Oxidation Test (ALBOT) Conditions

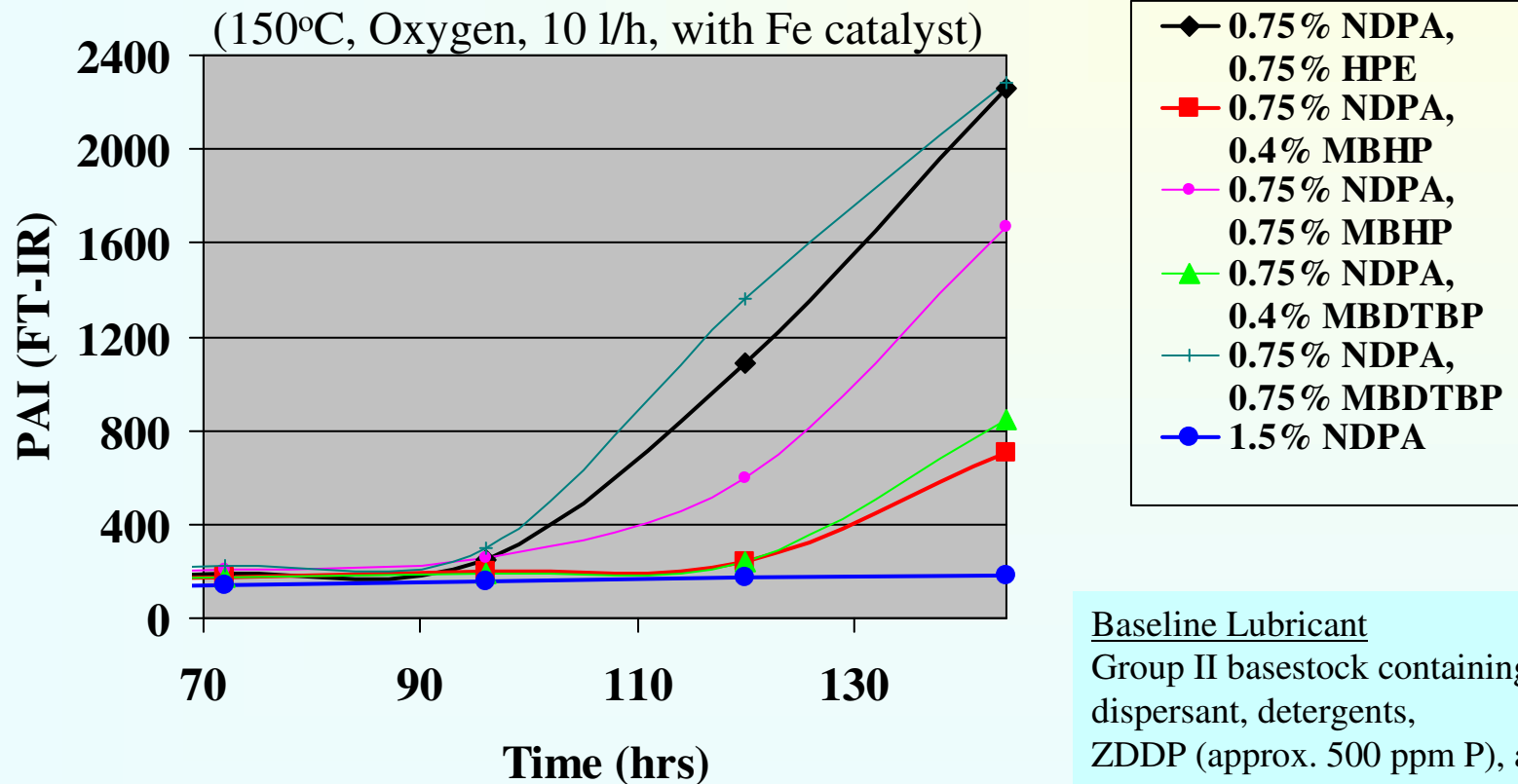
- Low Temperature – 150°C
- Test Time – 24, 48, 72, 96, 120, and 144 hours
- Oxidant – Oxygen
- Air Flow Through Oil – 167 mL/minute
- Oil Sample Size – 300 mL
- Fe Naphthenate Catalyst System
- Measures Viscosity Increase and FTIR Peak Area Increase (PAI)
- Viscosity Increase Relates To The Combined Effects Of Lubricant Oligomerization & Oxidation
- PAI Relates To True Oxidation

ALBOT Evaluation of Complex Engine Oil Antioxidant Systems

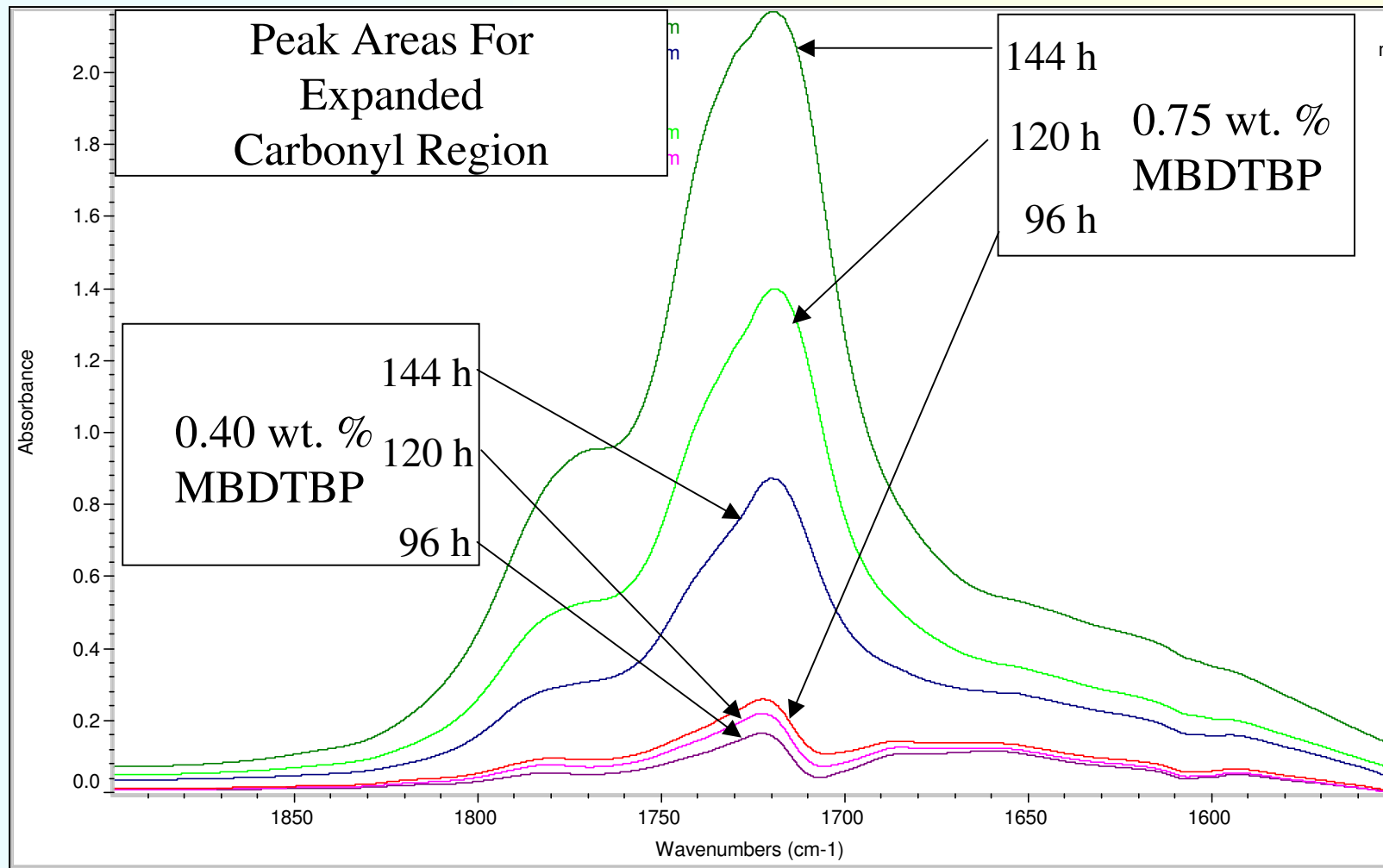


Baseline Lubricant
Group II basestock containing dispersant, detergents, ZDDP (approx. 500 ppm P), and MoDTC (approx. 360 ppm Mo)

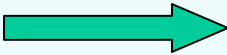
ALBOT Evaluation of Complex Engine Oil Antioxidant Systems



FT-IR Of Engine Oils Oxidized in the ALBOT

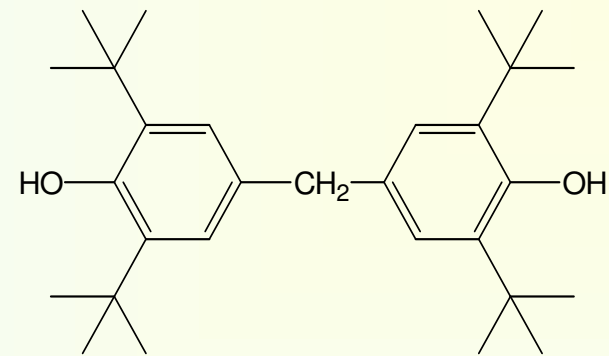


Conclusions “For This Molybdenum Containing Engine Oil”

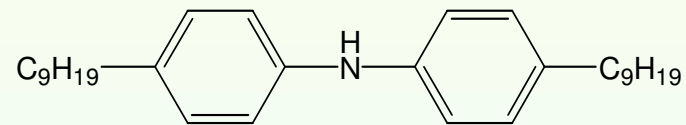
- 4,4'-Methylenebis(2,6-di-tert-butylphenol) (MBDTBP) is synergistic with alkylated diphenylamines for deposit, volatiles and oxidation control in the TEOST
- HPE does not show the same TEOST synergy
- All NDPA antioxidant systems are more effective than mixed NDPA/phenolic systems in the ALBOT
- Comprehensive or robust oxidation and deposit control can be achieved with combinations of MBDTBP, alkylated diphenylamines, and organomolybdenum
- Evaluation of TEOST volatiles may be useful for understanding fundamental oxidation pathways that can impact other bench and possibly engine tests
- These tools can be applied to the study of other antioxidant systems or additive combinations  STLE in May, 2005

Acknowledgements

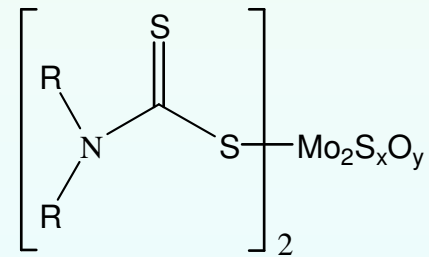
- Albemarle Corporation,
Baton Rouge, LA
- Asahi Denka Company,
Ltd., Tokyo, Japan
- Tannas Corporation,
Midland, MI
- Koehler Instrument
Company, Bohemia, NY



MBDTBP



NDPA



MoDTC