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Evaluation of EP Components for Gear Oil Packages

Presenter:

Date: May 2023

Introduction

The largest component in a gear oil additive package is the Extreme Pressure additive (EP)

- Properties of EP agents
  - Mixtures
  - Contain high amounts of sulfur
  - Can contain undesirable constituents
  - Prevent machinery from shock-bump damage
- Evaluation of EP agents
  - Performance tests – rig, field, OEM evaluation
  - Bench tests – wear, material combability etc.
  - Chemical tests
- Conventional Method
  - CCT bench test
  - Shown to predict ability of component to perform in CRC L-42 hypoid gear shock-bump test
  - No chemical composition information

Conventional Method

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Gravimetric method to evaluate EP components

- CCT Method (patented)
  - Immerse copper coupon in candidate compound
  - Measure weight loss
  - Copper corrosion test (CCT)

Test	A	B	C	D	E	F
HT Axle Fatigue	Fail	Fail	Pass	Fail	Pass	Pass
HT Axle EOT Wear	2800 ppm	2700 ppm	210 ppm	170 ppm	180 ppm	130 ppm
HT Bearing Test	Pass	Pass	Pass	Pass	Pass	Pass
L-42 Axle Shock Test	Fail	Fail	Pass	Fail	Pass	Fail
ISOT Cu weight loss	38%	30%	9%	19%	11%	19%
EP Additive	SIB	SIB	di-t-butyl polysulfide	di-tributyl trisulfide	di-t-butyl polysulfide	di-t-butyl trisulfide
CCT wt. loss, mg	55	55	126	4	126	4

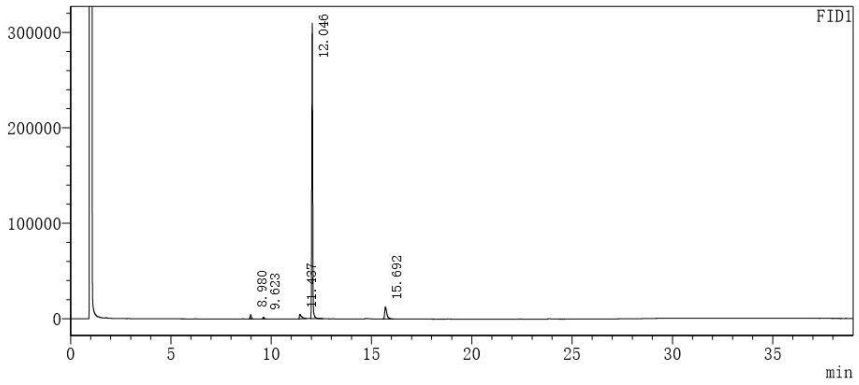
US patent 7,888,299

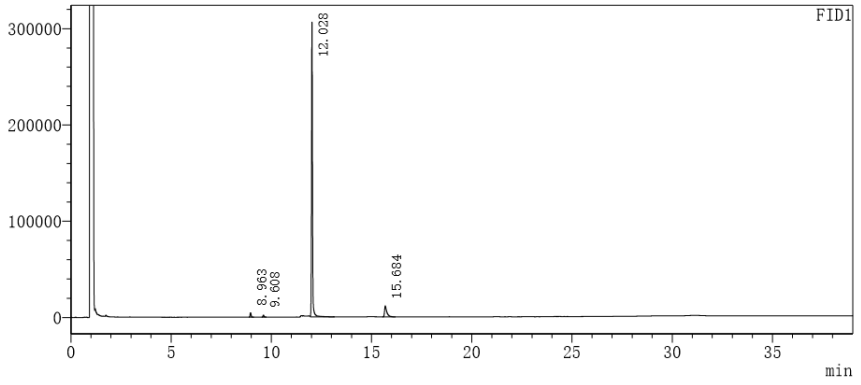
EP Component	CCT
SIB	55
Di-t-butyl polysulfide	126
Di-t-butyl disulfide	2
Di-t-butyl trisulfide	4
Di-t-butyl pentasulfide	466
Di-t-nonyl polysulfide	731

CCT Results

- T-butyl polysulfide
  - Passing rig test data
  - T-butyl polysulfide CCT > SIB CCT
  - T-butyl polysulfide CCT >> CCT for di-t-butyl disulfide and trisulfide
  - Di-t-butyl pentasulfide is very corrosive
  - What is structurally different comparing t-butyl polysulfide with pure t-butyl trisulfide?
  - Trade off between aggressiveness of sulfur toward copper corrosion and EP activity

Analysis





GC/MS data of t-butyl polysulfide from patent

- Two different lots – GC data
  - Sample 1 – One major peak and four minor peaks
  - Sample 2 – One major peak and three minor peaks
  - Sample compositions are different

MS analysis of t-butyl polysulfide

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	Retention time, min.	Mwt.	Likely identity	Sample 1, area %	Sample 2, area%
1	8.96	178	Disulfide or isomer	1.339	1.36
2	9.601	178	Disulfide or isomer	0.576	0.608
3	11.44	209	Suspected ring compound	3.148	
4	12.028	210	Tri sulfide	86.659	90.071
5	15.684	242	Tetra sulfide	8.278	7.961
Total				100	100

Analysis by MS

- MS detects molecular weight
  - Primarily t-butyl trisulfide
  - ~ 8% t-butyl tetra sulfide
  - Minor amount of disulfide and isomer
  - Implies that the t-butyl tetra sulfide has very good load-carrying capability.

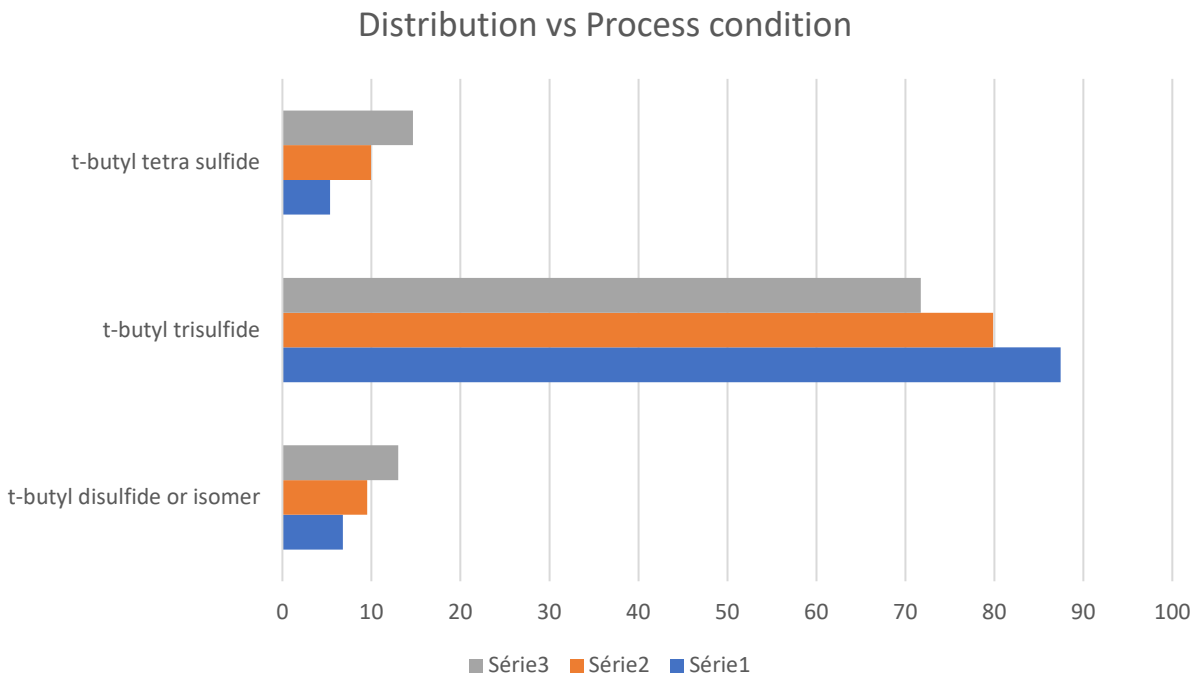
Application for process development

Identity	t-butyl polysulfide from patent, area %	Developmental t-butyl polysulfide A, area %	Developmental t-butyl polysulfide B, area %	Developmental t-butyl polysulfide C, area %
t-butyl disulfide or isomer	1.36	0.03	.06	0.08
t-butyl disulfide or isomer	0.608	6.80	9.52	13.02
t-butyl trisulfide	90.071	87.44	79.85	71.73
t-butyl tetra sulfide	7.961	5.33	9.95	14.66
t-butyl penta sulfide		0.05	.08	.12
t-butyl hexa sulfide		0.04	.08	.12
Sum	100	100	100	100
CCT, mg. weight loss	85	134	257	290

GC/MS analysis of three candidates

- Run under different reaction conditions
  - Similar to t-butyl polysulfide from patent
  - CCT is high – likely due to higher polysulfide impurities
  - Further process improvement is needed to remove heavy materials.

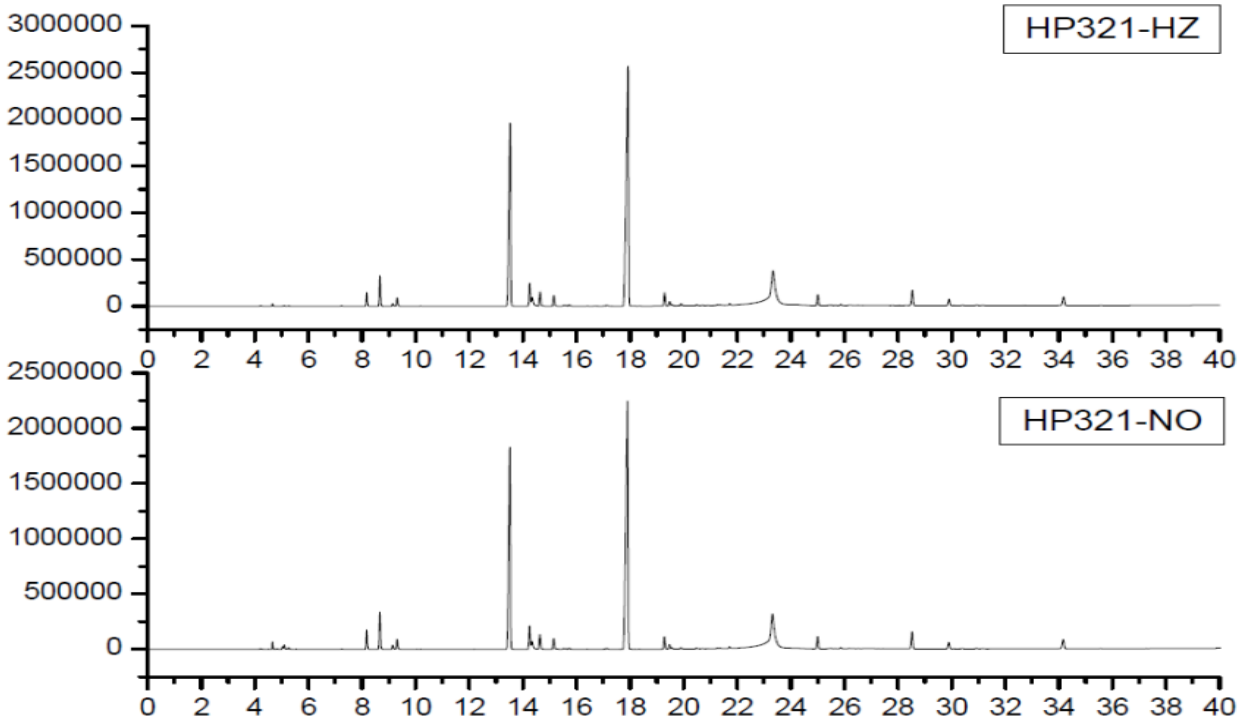
Application for process development



Three different process conditions

- Analysis by GC/MS
  - As –t-butyl trisulfide increases, the di and tri sulfides decrease
  - Can control composition of the product.

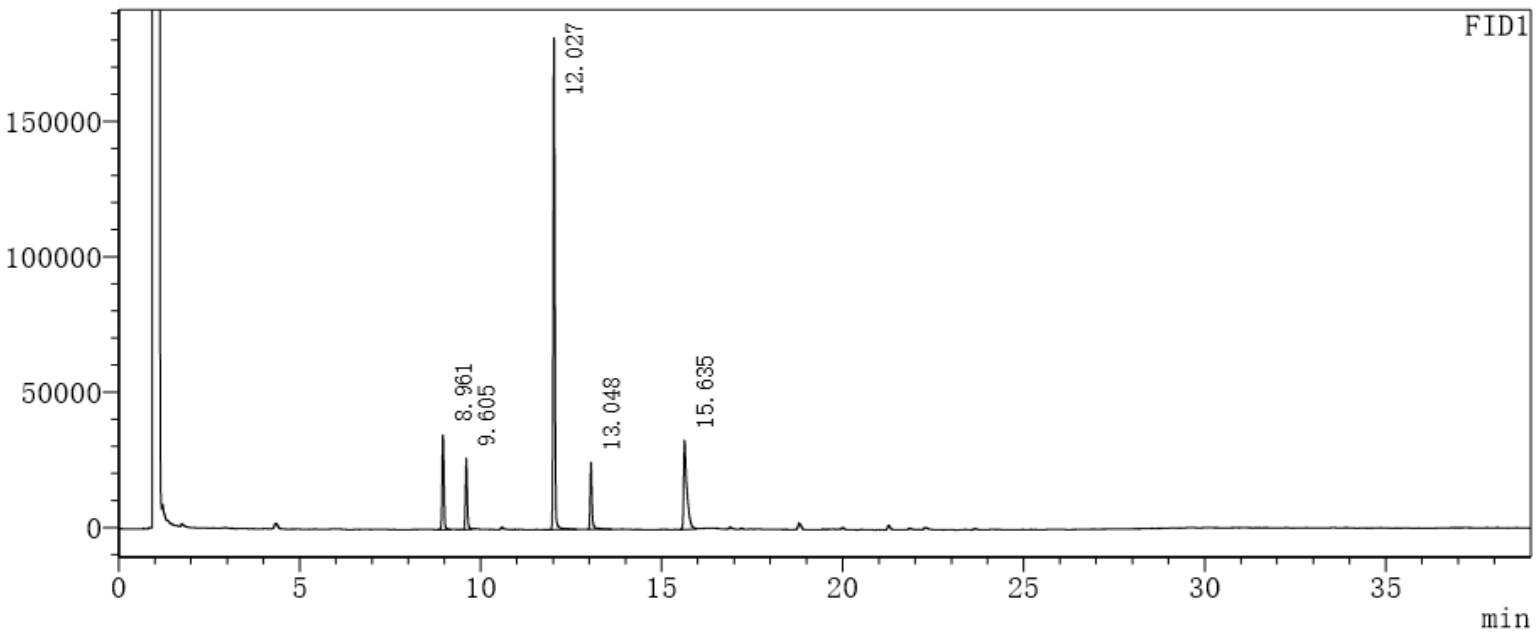
Evaluation of market samples



Two market samples

- Like developmental polysulfides except:
  - Strong odor of rotten eggs
  - Could only blend additive packages in a hood due to odor.
  - Heavy impurities – copper corrosion – penta and hexasulfide
  - Can see mercaptans, R-S-S-H etc. in GC trace - not acceptable.

Market Sample A



GC analysis

- Known component
  - Polysulfide
  - Used to formulate GL-5 quality oils
  - GC simple and clean
  - No heavy materials and no mercaptans.

MS analysis of market sample A

Peak No.	Retention Time	Area %	Identity	Mwt
1	8.961	11.369	t-butyl disulfide or isomer	178
2	9.605	8.450	t-butyl disulfide or isomer	178
3	12.027	53.036	t-butyl trisulfide	210
4	13.048	8.258	Isomer of t-butyl trisulfide	210
5	15.635	18.887	t-butyl tetra sulfide	242
Total		100		

Mass spec. analysis

- Only three molecular weights detected
  - 178 molecular weight – two species. Di-t-butyl disulfide and isomer
  - 210 molecular weight – two species. Di-t-butyl tri sulfide and isomer
  - 242 molecular weight – Di-butyl tetra sulfide

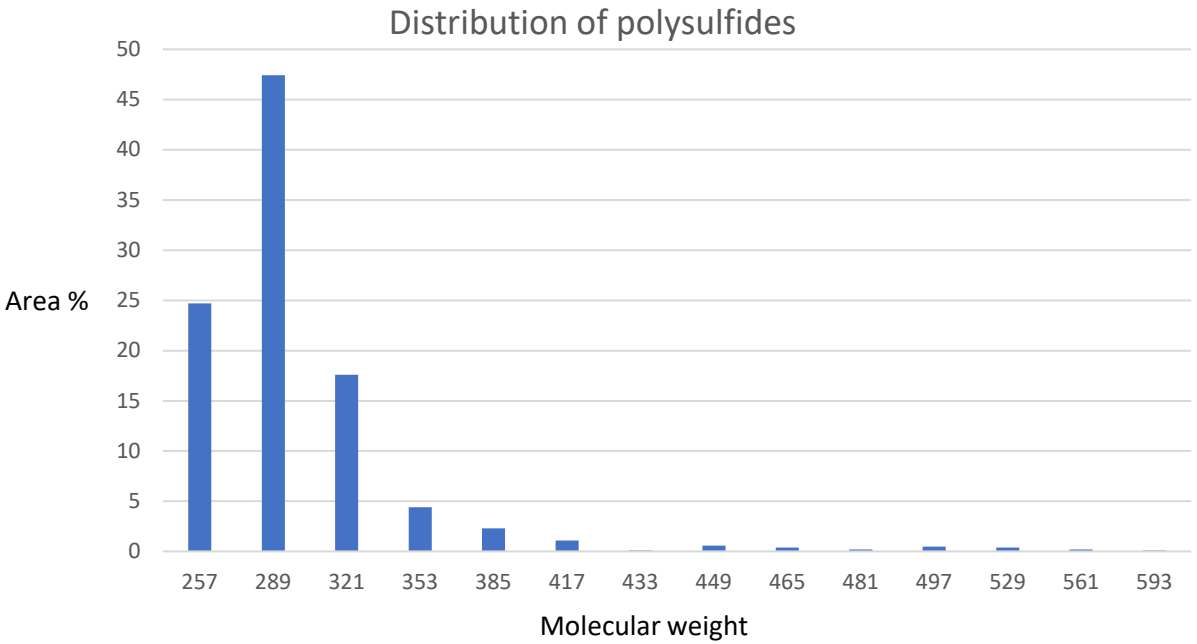
Soft ionization techniques

Ionization type	Ionizing species	Comment
Electrospray ionization (ESI)	Sample solution is aspirated across a high potential difference, heat, and gas flow desolvates clusters	Good for charged, polar or basic compounds, multiply charged species are common, good for LC-MS, mass range to 200 k
Matrix-assisted laser desorption ionization (MALDI)	Analyte dissolved in a matrix that is UV active, on a Laser target, matrix absorbs laser pulse	Very high mass range–up to 500,000 AMU, requires pulsed mass analyzer, not compatible with LC-MS

Soft ionization methods in MS

- Minimize fragmentation
  - No separation required
  - Successfully used for analysis of competitor's products.
  - Finished oil, additive packages, neat components.

Introduction



MALDI analysis of sulfurized di-isobutylene

- Metal working component offered by several suppliers
  - Minor amounts of heavy materials
  - Everything is isobutylene + sulfur
  - Major constituents are mono, di, tri, tetra, penta and hexa sulfide

Summary

- A wet chemical procedure exists (CCT) to screen sulfur compounds for their potential for inclusion at the EP additive for high quality gear oils. The procedure was published in the patent literature.
- The CCT has the drawback of not giving any chemical information.
- GC/MS gives detailed information about the chemical composition of a mixture of polysulfides. Performance can be inferred from the chemical composition.
- Taken together, the CCT and GC/MS are synergistic in providing insight into performance of polysulfides.

Summary

- GC/MS is a powerful tool to guide process development.
- GC/MS is a powerful tool to screen candidate components.
- Higher polysulfides (n > 4) are very corrosive toward copper
- If mercaptan can be detected by GC/MS, the odor is most likely unacceptable.
- Soft ionization techniques are demonstrated to be able to characterize candidate components.

Thank you for your attention