ACTIVITY AND STRUCTURE OF SULFURIZED OLEFINS

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6th International Metalworking Fluids Conference

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Overview

The most common question asked when selecting a sulfurized additive is:

Is this an active sulfur product meaning it will stain copper?

So at what chain length of sulfur *does* sulfur transition from inactive to active? Historic data suggests 3-4 sulfur monomer units.

To answer this problem we sulfurized C18 alpha olefin at various mol ratios of sulfur (0.5 to 1.0 to 1.5 to 2.0 mol S:AO)

We reviewed theoretical reaction mechanisms.

We developed analytical testing to determine the resulting adducts

Performed ASTM D130 Cu staining on known and synthesized samples.

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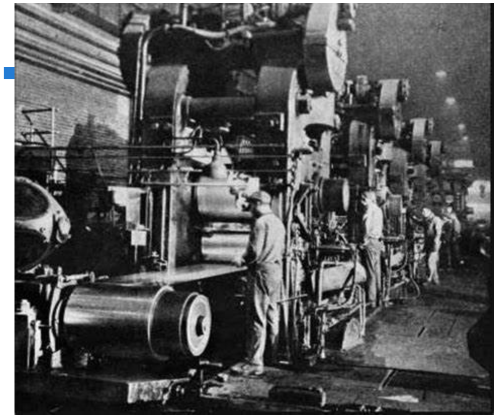
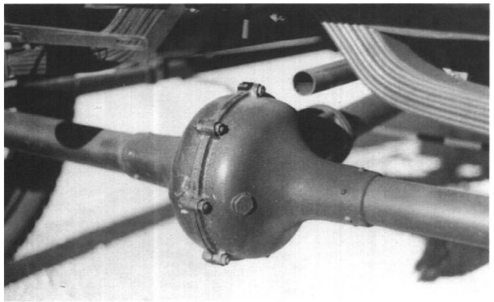
Uses and History behind Sulfurized Materials

Commercial industrial applications of sulfurized additives date back over 100 years; from the compounding of gear and axle oils to rolling and pickling oils for sheet steel production.





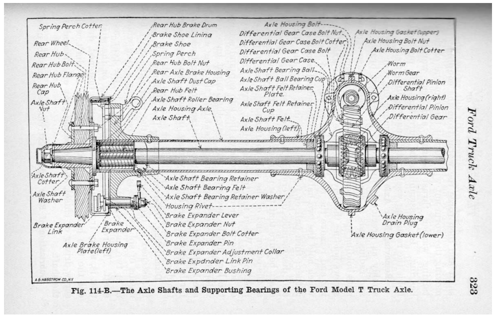


Fig. 114-B.—The Axle Shafts and Supporting Bearings of the Ford Model T Truck Axle.

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Uses and History behind Sulfurized Materials

Today sulfurized materials are an integral part of the industrial economy. Some better known applications are:

- AW and/or EP component in greases & gear oils to improve wear.
- Secondary AO in Powertrain lubes like PCMO.
- EP & AO in metal sheet rolling and pickling oils resolving carbon edge and improving surface morphology.
- EP for machining oils to improve tool life and cut quality.
- EP for drilling and coiled tubing service in the Oilfield.

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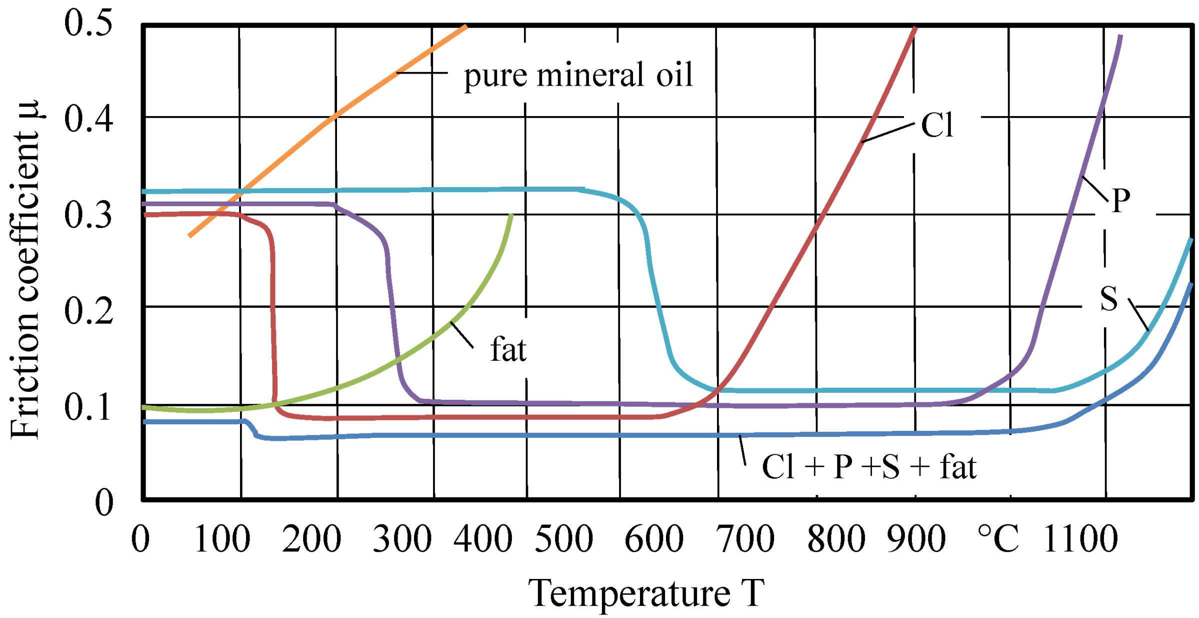
EP Activation Chart



H. Landau, "Chlorparaffine als EP-Additive in Metallbearbeitungsflüssigkeiten," Proceedings of the 5th International Lubricant-Colloquium, Esslingen, Germany, 20 January 1986.

Common Classifications of Sulfur Derivatives

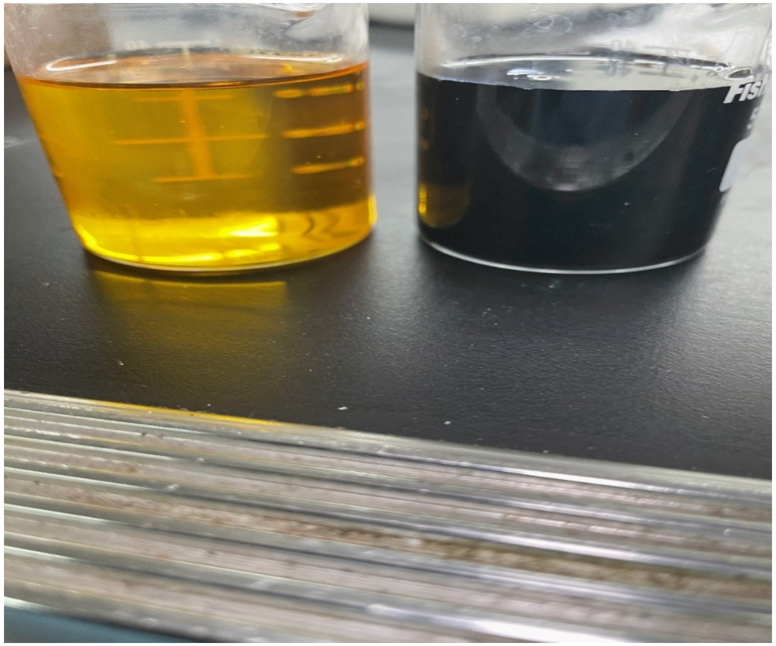
% Sulfur by weight

"Dark" vs "Light" color of the additive.

Corresponding unsaturated carrier

- Olefin alkenes
- Triglycerides
- Esters
- Fatty Acids

Active vs Inactive Sulfur



Light Sulfur(Left) vs Dark Sulfur(Right)

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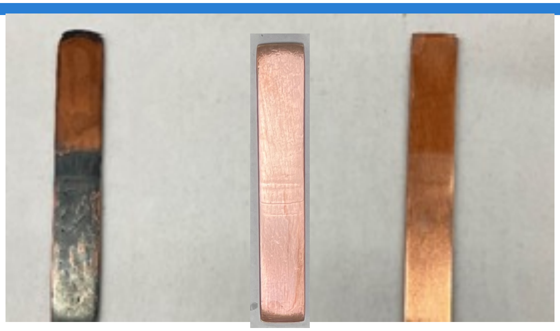
Sulfur Activity

- **Active** sulfur refers to a sulfur carrier that has a sulfide structure that will stain copper
- **Inactive** sulfur refers to a sulfide structure that will not stain copper.
- Active sulfur can also be **inhibited** or nonstaining through addition of inhibitors
- Inhibitors are compounds that inhibit copper staining at treat rates of 0.1-0.2% in the final formula or 0.6-1.0% directly added to the sulfur carrier



A B C

A Staining Sulfur
B Freshly polished copper strip
C Non Staining Sulfur

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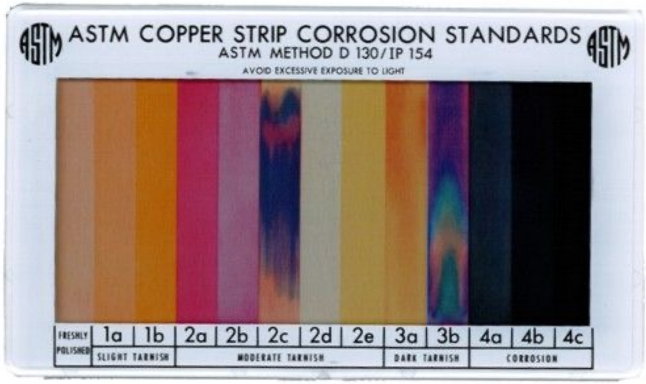
Copper Staining Test Standards ASTM D130

- The copper Strip Post Corrosion Test is compared to the chart
- The color of the surface is graded from a number and letter.
- Any rating other than a “1” indicates the sulfur product is active or staining.
- Not part of the test but vapor phase corrosion can be qualitatively assessed.



DC Scientific. “.” D130 ASTM Copper Strip Corrosion Standard, 2023
, https://shop.dcscientific.com/products/d130-astm-copper-strip-corrosion-standard

Proposed Mechanisms of the Elemental Sulfurization Reaction

There are several types of sulfurization, the hydrogen sulfide and sulfur method, and monosulfur chloride plus elemental sulfur reaction.

This presentation will cover the elemental sulfur mechanism

Elemental sulfurization generates many different products

Before we started analytical techniques, we reviewed established literature, these proposed mechanisms are based on the literature search.

Elemental sulfurization generates products through both nucleophilic and free radical mechanisms.

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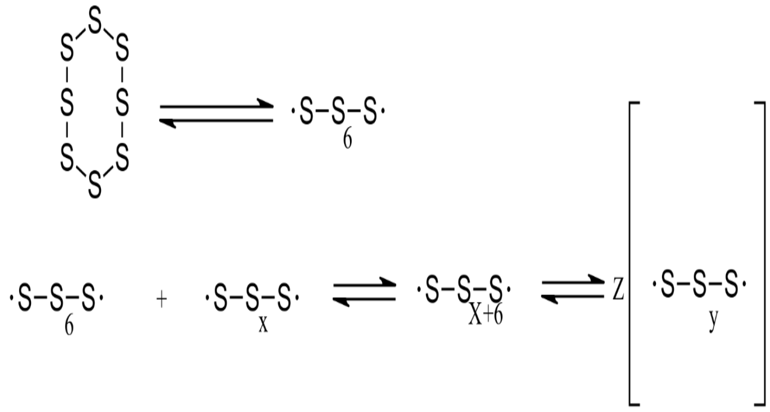
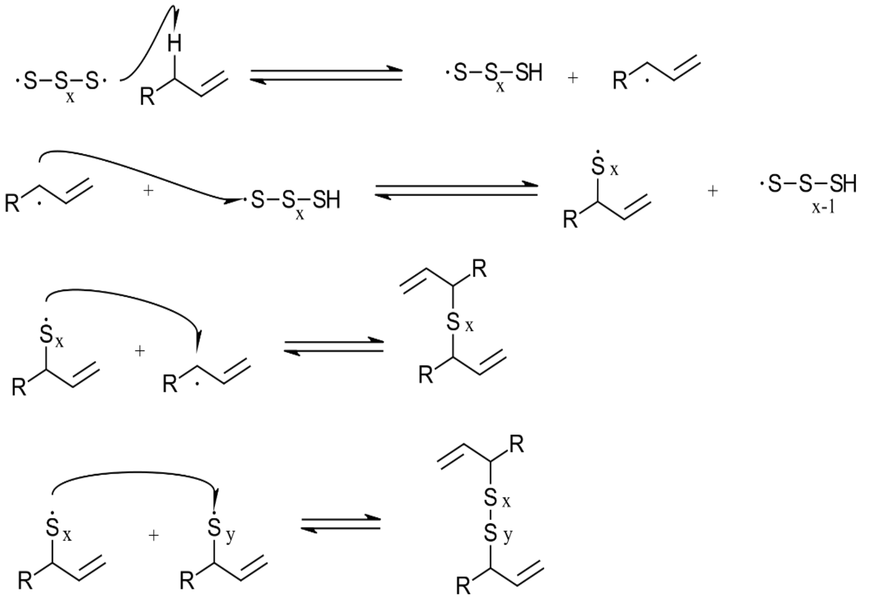
Generation of Radicals- Sulfur Polymer

- Sulfur consists of an eight member ring at room temperature.
- At around 120^{O}C the ring opens up and starts forming a biradical
- These radical units then start reacting to form a polymer chain
- At higher temperatures the sulfur polymer chain fragments generating radical sulfur chains. Fragmentation increases with temperature
- Increasing reactivity with increased radical formation
- This sulfur polymer formed also will cause the dark color in the final product



Free Radical Mechanism of Elemental Sulfurization at 130^{O}C

This is the mechanism how sulfur is added to the carbon chain of a compound through the elemental sulfur method
Free radical sulfurization at 130^{O}C or so occurs at the allylic hydrogen.



Leslie R. Rudnick(ed) 2017. *Lubricant Additives Third Edition*. Taylor and Francis Group

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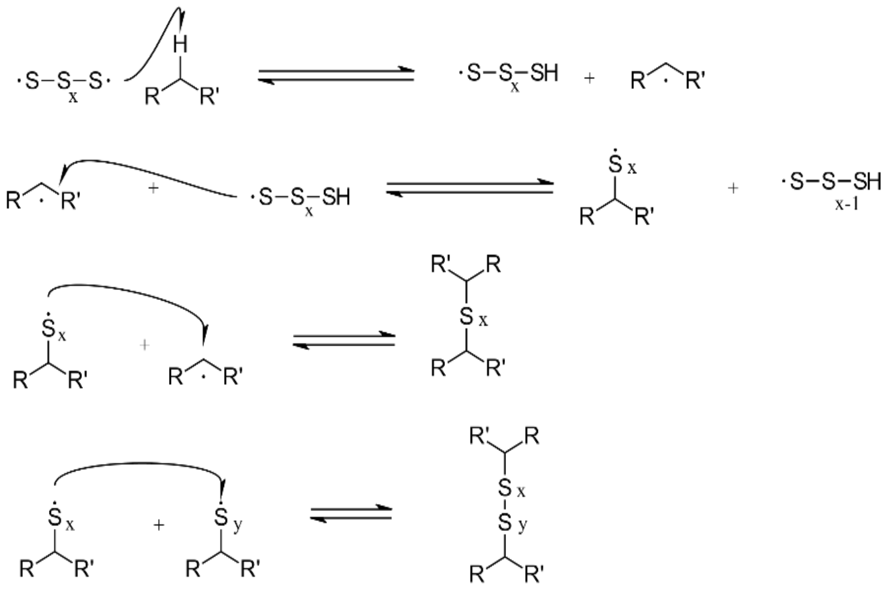
Free Radical Mechanism of Elemental Sulfurization at 160^{O}C and above

At higher temperatures 160^{O}C and above, this reaction can occur at other aliphatic hydrogen positions at the olefin.



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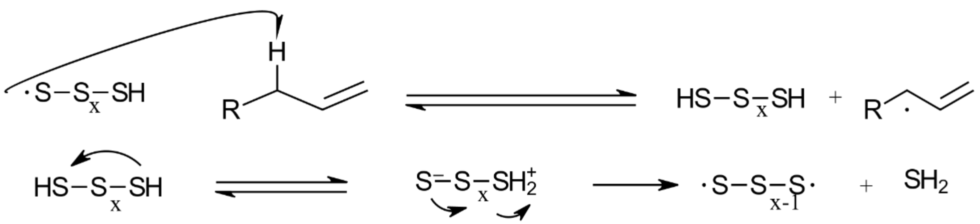
Hydrogen Sulfide Formation

Hydrogen abstraction by sulfur from the olefin

Then polysulfide rearrangement can also lead to the intramolecular formation of hydrogen sulfide



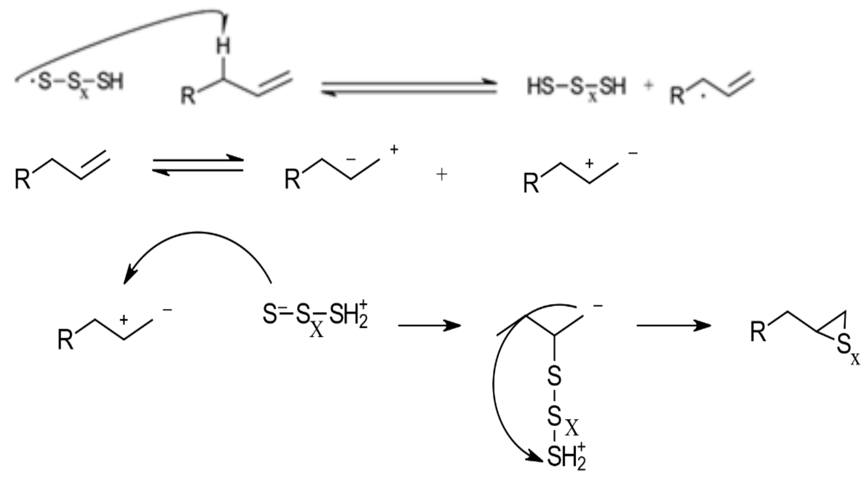
Nucleophilic Mechanism of Elemental Sulfurization At 160^{O}C and Above

The Olefin has a resonance structure where the carbon will have an area of high electron density and an area of low electron density

The sulfur chain can also form a version that has both sulfonium ions(SH2+) and polysulfide ions(S-)

These ions can react across the double bond in a nucleophilic reaction followed by electrophilic to close the ring

The mechanism is a source of the episulfides

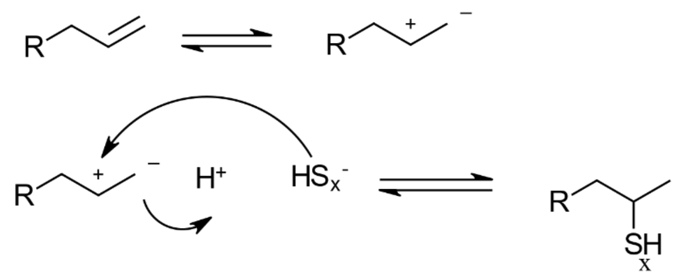


Mercaptan Formation

- Nucelophlic attack by HS_x^- generated by sulfur acting as a base with hydrogen sulfide
- This polysulfide then will then proceed with nucleophilic attack the olefin
- Can also form from radical reaction post radical hydrogen abstraction

$$S_8 + SH_2 \rightleftharpoons HS_8^+ + HS^-$$

$$HS^- + S_8 \rightleftharpoons HS_x^- + S_{9-x}$$



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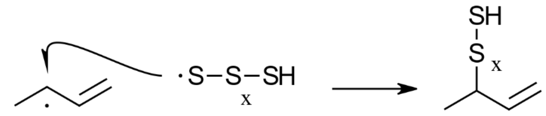
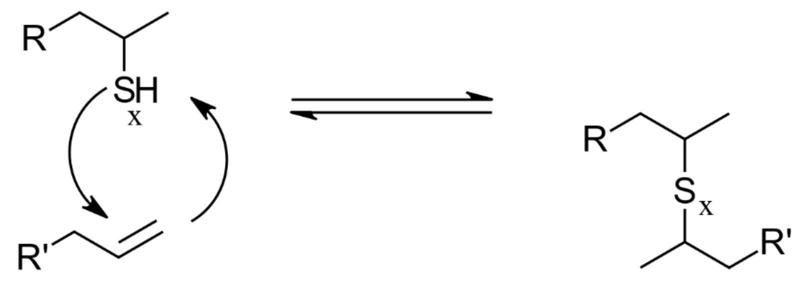


Intramolecular Polysulfide Formation Through Nucleophilic & Electrophillic Mechanism

Mercaptans can continue to react across other olefins, generating new polysulfides



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Polysulfide products and further Radical Generation

Polysulfides are generated as the primary product in the elemental sulfur reaction. These sulfides have a limit of stable chain length.

Polysulfides (RSxR') chains will breakdown releasing sulfur radicals which will then react . Eventually we see these forms of polysulfides as observed during analytical structural analysis

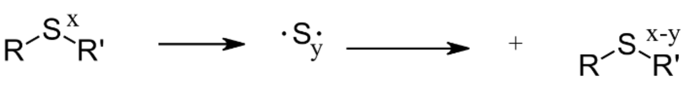
Mono Sulfides (RSR')

Di Sulfides (RS2R')

Tri Sulfides (RS3R')

Tetra Sulfides (RS4R')

Stability decreases with increase in chain length of sulfur



EXPERIMENTAL RESULTS

Sulfurization Reactions

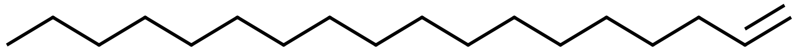
C18 Alpha-olefin reacted with elemental sulfur at different molar ratios of sulfur to olefin. Reactions @ 190°C

We chose these olefins as they are pure with one saturation at the same location to ensure the most accurate structure determination

Experiments performed based on the predicted free radical mechanism

Sulfur does not add at a 1:1 ratio of olefin to sulfur

- Molar Ratios:
  - 1 mole C18AO : 0.5 moles Sulfur
  - 1 mole C18AO : 1.0 moles Sulfur
  - 1 mole C18AO : 1.5 moles Sulfur
  - 1 mole C18AO : 2.0 moles Sulfur



+ Elemental Sulfur (S_8)

Analytical Goals

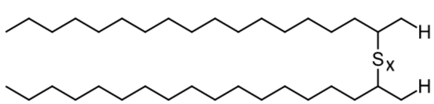
- Ratio of mono-, di-, tri- (and greater) sulfurized olefins
- Amount and arrangement of sulfur

What is ratio for each sample?

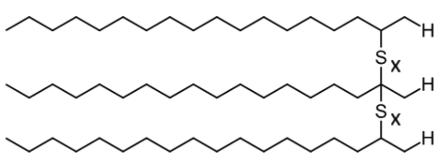
How many sulfurs on each olefin?
How are they connected?

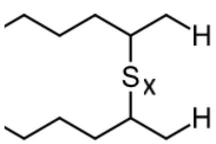
Sulfurized Mono-olefin

Sulfurized Di-olefins



Sulfuized Tri-Olefins (and higher)





What is "x"?

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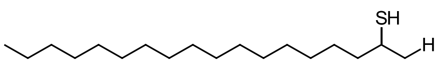
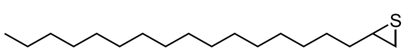
Analysis of Sulfurized Olefins

- Complex chemistry, with a multitude of final species
- Direct Analysis (FTIR, APCI-MS)
- Separation Analysis (GPC, GC-MS)
- Examples of proposed structures from literature

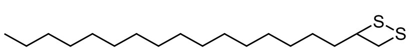
“Mono-Olefins”



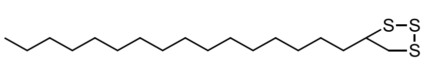
(MW 286.6, 11.2% S)



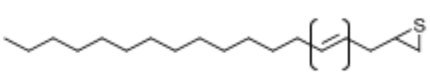
(MW 284.6, 11.3% S)

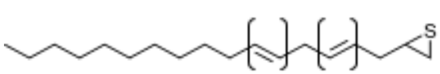


(MW 316.6, 20.3% S)

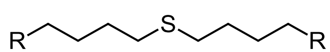


(MW 348.7, 27.6% S)

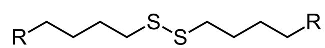




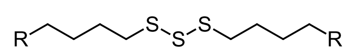
“Di-Olefins”



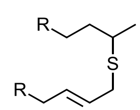
(MW 539.0, 5.9% S)

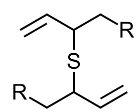


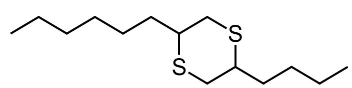
(MW 571.1, 11.2% S)



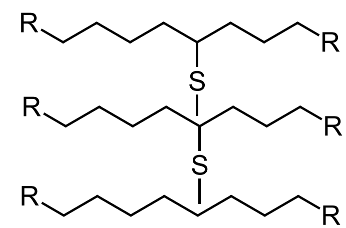
(MW 603.2, 16.0% S)







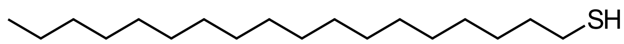
“Tri-Olefins”



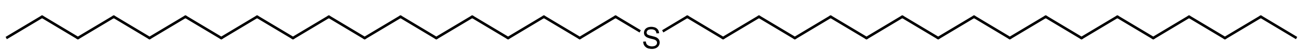
Analysis of Sulfurized Olefins

Purchased Standards (purity >95%)

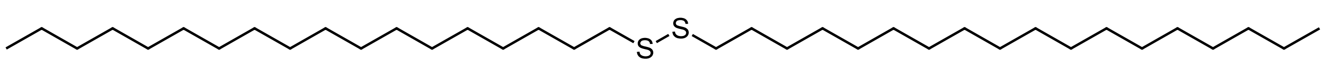
1) 1-Octadecanethiol (MW 286.6)



1) Di-(n-Octadecyl) Sulfide (MW 539.0)

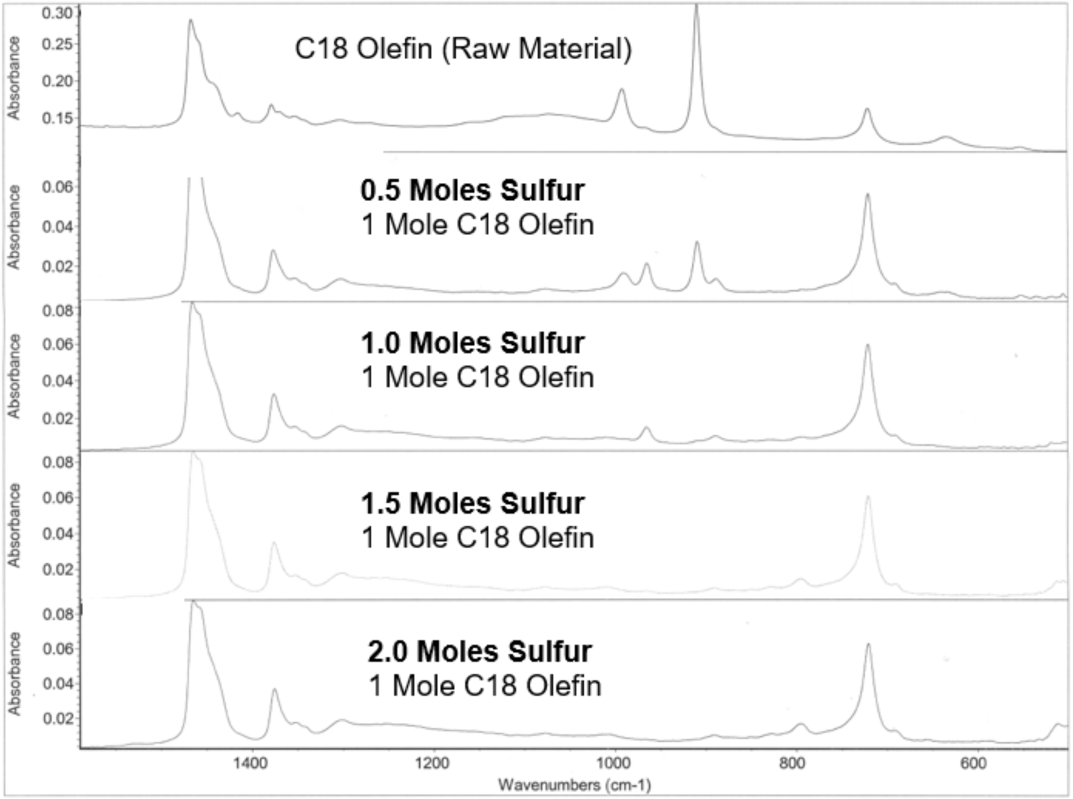


1) Di-(n-octadecyl) Di-Sulfide (MW 571.1)



C18 Olefin Sulfurizations Samples- FTIR

Significant amount of residual C18 Olefin in 0.5 mole sample
But eventually consumed as more sulfur is added. This is seen
As the gradual disappearance of peaks around 890cm^{-1} and 980cm^{-1}



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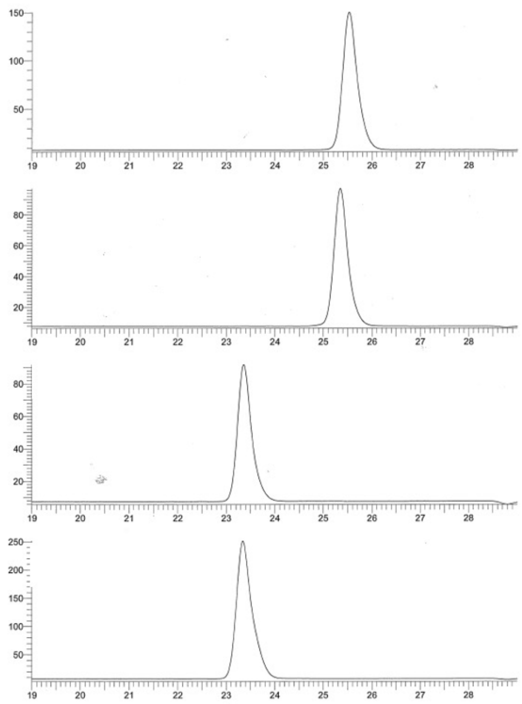
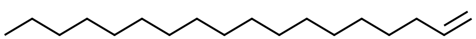
C18 Olefin Sulfurization Standards - GPC

Gel Permeation Chromatography (GPC); separation by size/MW

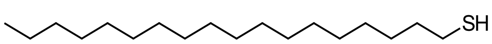
- Cannot completely separate C18 olefin from sulfurized mono-olefins
- Cannot separate molecules solely by number of sulfur atoms
- Allows complete separation of mono-, di- and tri-olefins



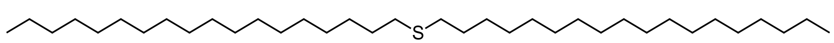
C18 Olefin (raw material) MW=252.5



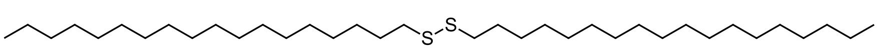
1-Octadecanethiol MW=284.6



Di-(n-Octadecyl) Mono-Sulfide MW=539.0



Di-(n-Octadecyl) Di-Sulfide MW=571.1



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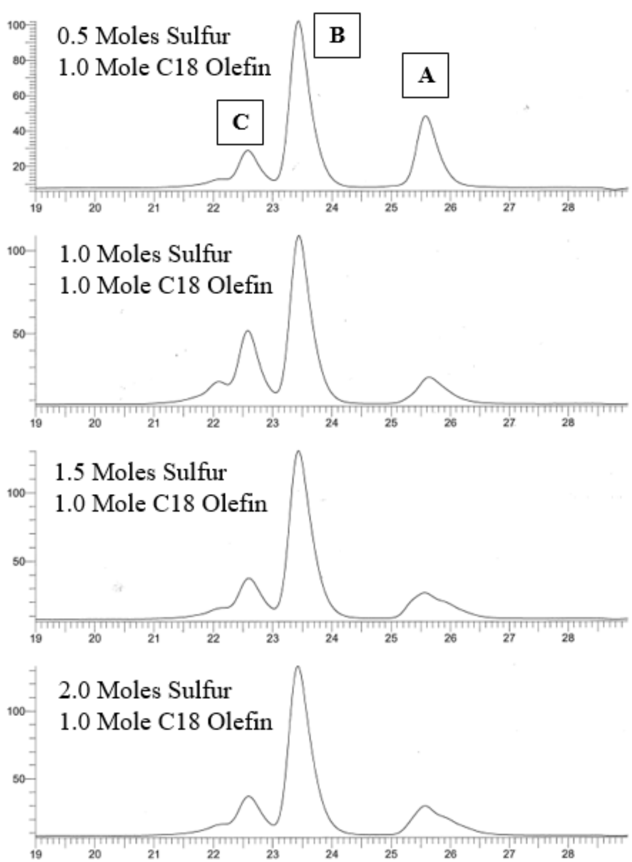
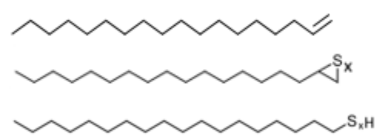
C18 Olefin Sulfurizations Samples- GPC

Sulfurized di-olefins (B) appear to be the preferred species at all sulfur ratios

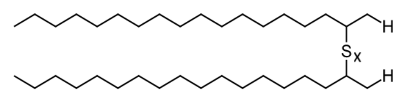


A Sulfurized Mono-olefins

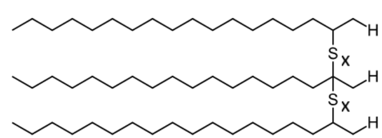


(Residual C18 AO in 0.5 mole sample)

B Sulfurized Di-olefins



C Sulfurized Tri-Olefins (and higher)



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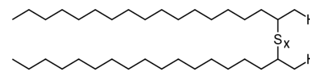

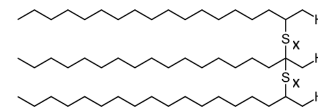

	% Sulfurized Mono-Olefins	% Sulfurized DI-Olefins	% Sulfurized Poly-Olefins
0.5 Moles Sulfur*	26	57	17
1.0 Moles Sulfur	12	55	33
1.5 Moles Sulfur	16	63	21
2.0 Moles Sulfur	17	63	20

*Residual C18AO in 0.5 mole sample co-eluted with sulfurized mono-olefin

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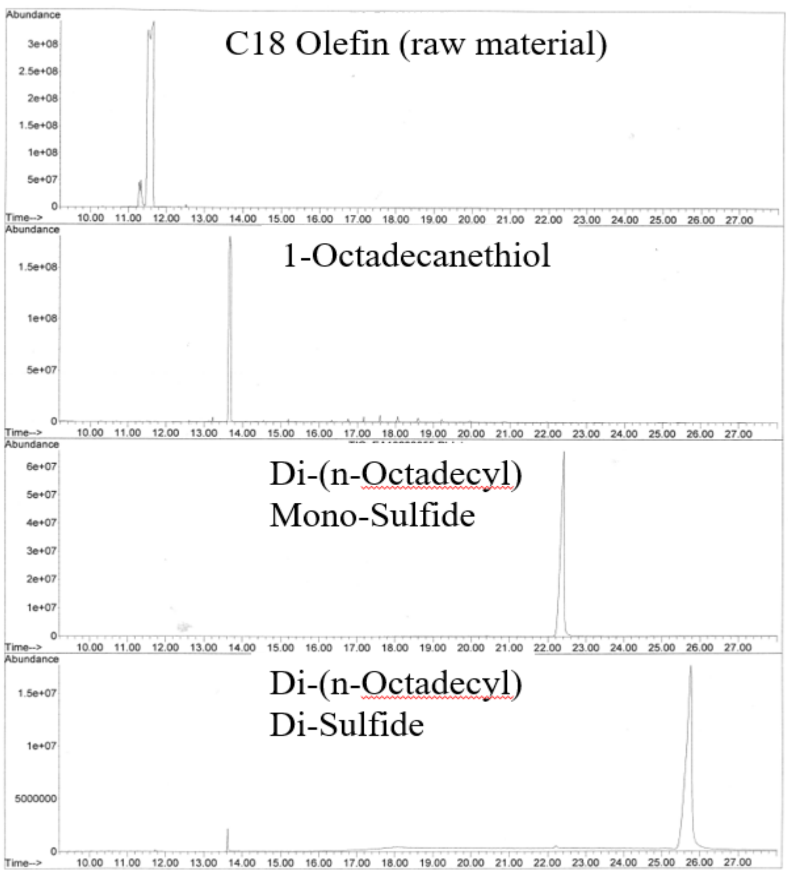
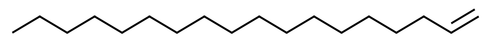
C18 Olefin Sulfurizations Standards – GC-MS

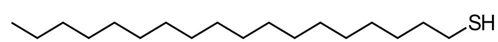
- GC-MS can resolve molecules with different numbers of sulfur atoms
- Only semi-quantitative: response factors decrease as MW and retention times increase
- Sulfurized di-olefins with > 2 sulfur atoms, and sulfurized tri-olefins are **not** observed in GC-MS



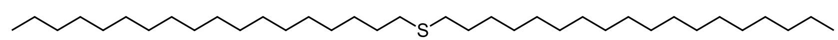
C18 Olefin (raw material) MW=252.5



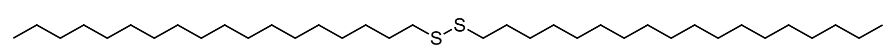
1-Octadecanethiol MW=286.6



Di-(n-Octadecyl) Mono-Sulfide MW=539.0



Di-(n-Octadecyl) Di-Sulfide MW=571.1



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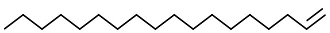
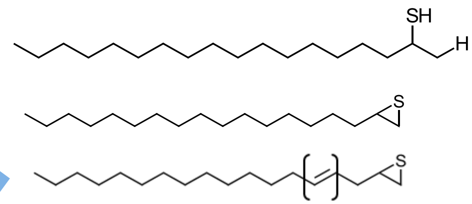
GC-MS (0.5 and 1.0 Mole Sulfur Samples)

- Mainly **Mono-Sulfur** species (with 1 and 2 olefin backbones)
- Presence of thiols and sulfides, also peaks due to branching or unsaturation, and residual C18 Olefin

Residual C18 olefin

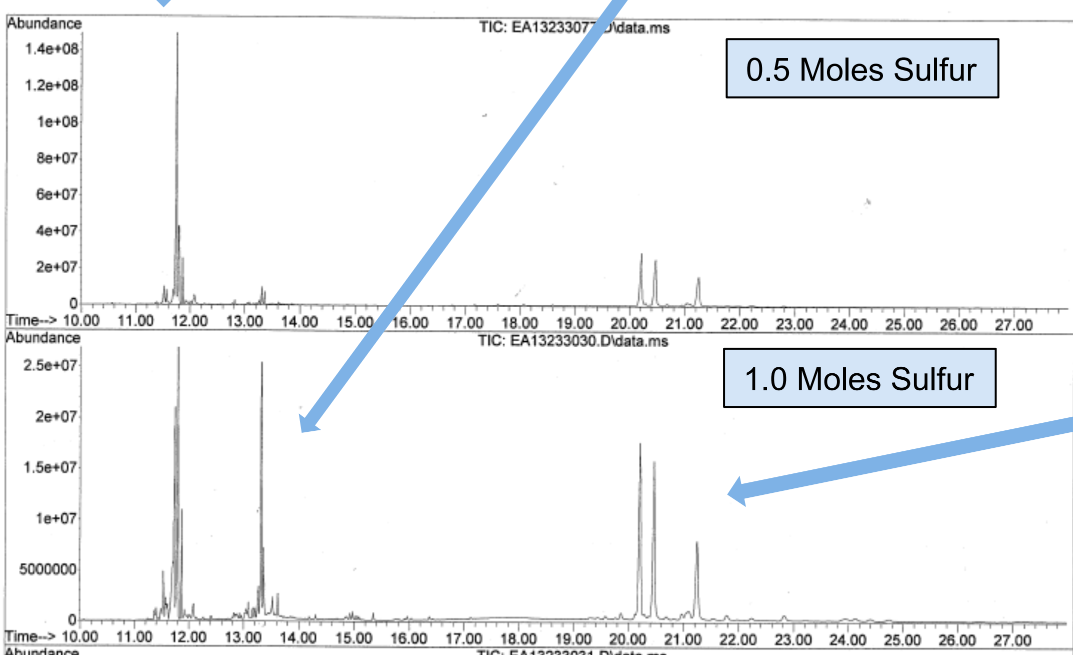


Mono-sulfur Mono-C18

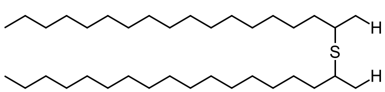


Largest Peak MW=286

Others MW=280-284



Mono-sulfur Di-C18



Majority of Peaks MW=316

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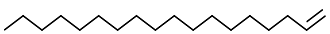
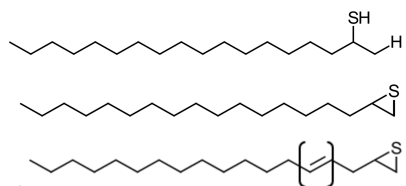
GC-MS (1.5 and 2.0 Mole Sulfur Samples)

- **Mono-sulfur, di-sulfur and tri-sulfur species**
- Presence of thiols and sulfides, also peaks due to branching or unsaturation, and residual C18 Olefin

Residual C18 olefin



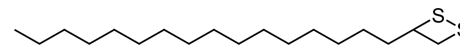
Mono-sulfur Mono-C18



Largest Peak MW=286

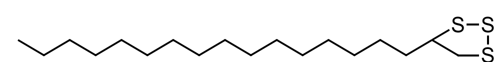
Others MW=280-284

Di-sulfur Mono-C18

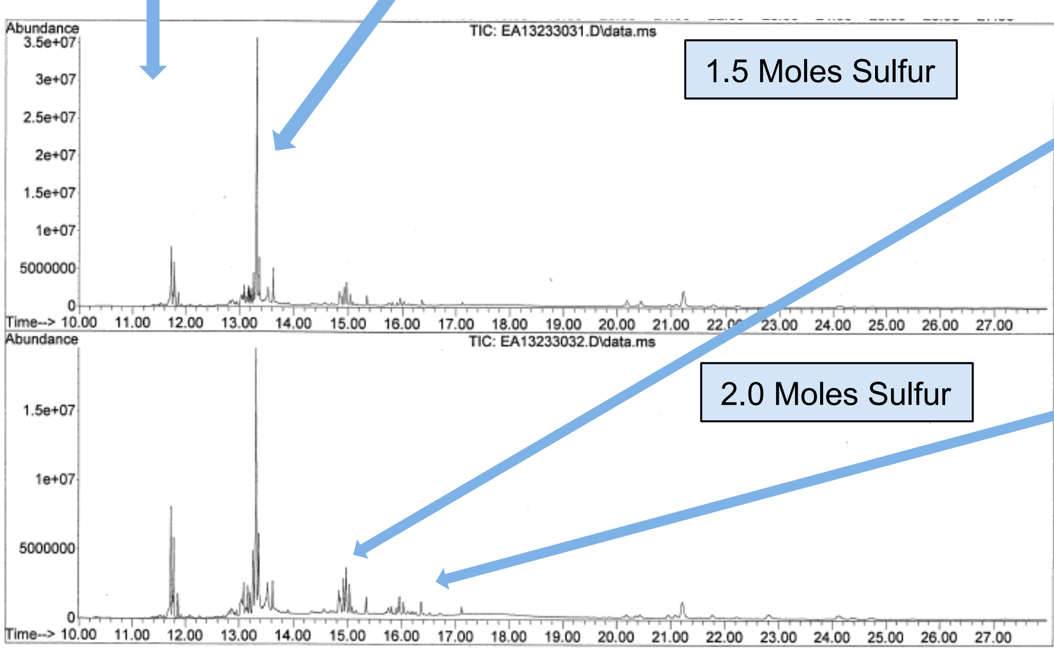


Majority of Peaks MW=316

Tri-sulfur Mono-C18



Majority of Peaks MW=348



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GC-MS Sulfurized Olefins

GC-MS indicates presence of thiol and sulfides, also peaks due to branching or unsaturation

0.5 and 1.0 mole samples
Mainly **mono-sulfur** species (mono- and di-olefin), also residual C18 AO

1.5 mole sample
Majority **mono-sulfur** species, also present were smaller amounts of **di-** and **tri-sulfur** species

2.0 mole sample
Mono-, di- and tri-sulfur species, di- and tri- present at higher levels than 1.5 mole sample

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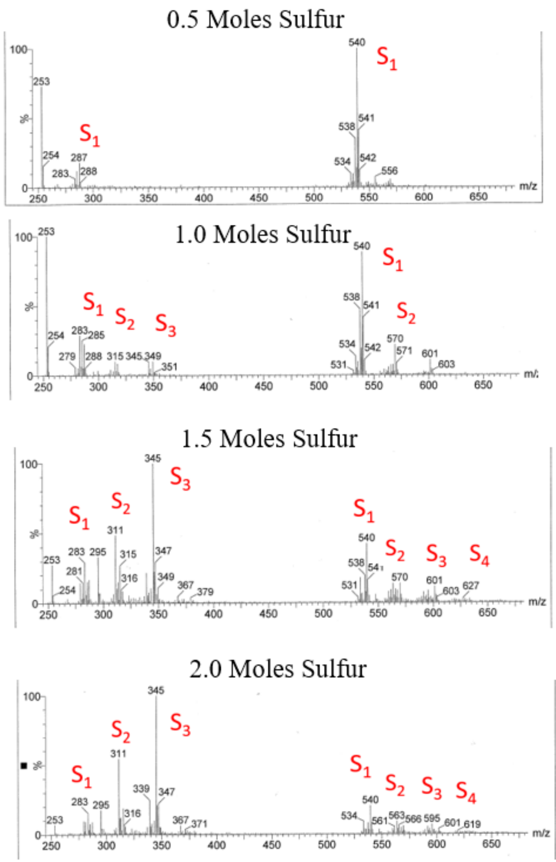
C18 Olefin Sulfurization Samples – Direct APCI Mass Spec.

- Ionization efficiency decreases with increasing molecular weight. Poor response at m/z greater than 800. m/z peaks may also arise from fragmentation of larger/parent ions

- 0.5 moles: Mono-sulfurized species (S1)
- 1.0 mole: Mostly mono-sulfur (S1) but di- (S2) and tri- (S3) are observed
- 1.5 and 2.0 moles: Increased level of multi-sulfur species (S1-S4)



m/z 252 = Residual C18 olefin

m/z 280-380 = Sulfurized Mono-Olefins

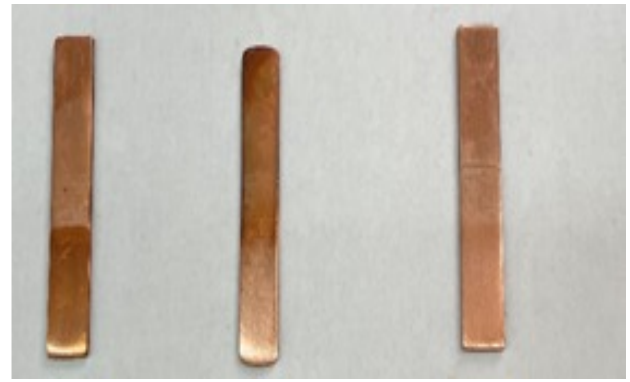
m/z 530-630 = Sulfurized Di-Olefins

(Sulfurized Tri-Olefins not shown, signal too weak)

Copper Staining: Standards

Sulfur carriers that contain sulfur as either a monosulfide or disulfide compounds do not stain copper strips and are inactive

Monothiols also do not show evidence of staining nor evidence of activity



A B C Standard

A: Monosulfide Standard

B DiSulfude Standard

C Monothiol Standard

Standard : Freshly Polished Copper Strip

Copper Staining: Synthesized Samples

As the sulfur amount is increased over 1.0 Mol, staining is increasingly observed

At the mol ratio of 1.5 and above, copper staining is observed; with stronger effects at the 2.0 mol ratio

A B C Standard

A: 1.0 Mol Sulfur Ratio to C18 Alpha Olefin

B 1.5 Mol Sulfur Ratio to C18 Alpha Olefin

C 2.0 Mol Sulfur Ratio to C18 Alpha Olefin

Standard : Freshly Polished Copper Strip

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CONCLUSIONS

Conclusions From Experimental Results

- Elemental sulfurization is a complex process resulting in many different structures, with differing unsaturation and branching amounts
- At low sulfur to olefin ratios the predominant molecules formed are monosulfide compounds
- Predominant structures formed at higher addition rates are di-olefin sulfides
- Higher sulfur to olefin ratio sulfurization reactions produce more molecules that are multisulfide
- Direct sulfur contact with copper will stain
- R-S-S-R’ sulfides are non staining
- R-S-S-S-R’ and greater show evidence of causing staining or are “active”

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Further Work

Investigate copper staining on trisulfides and tetrasulfide standards to have hard evidence on when staining starts

Isolate the specific molecules generated

Perform triblogical testing to identify possible performance differences between the differing sulfides

Perform analytical testing at lower temperatures of reaction to check for unsaturation

Acknowledgements

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