## New Antifoam Reduces Silicone Carryover

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More Production - Less Risk

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## Agenda

- **Delayed coker foam control**
- **Silicone decomposition**
- **New coker antifoam**
- **Case histories**




## Delayed Coker Foaming

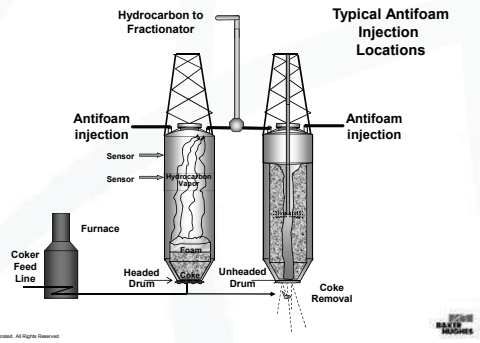
- Operation of the delayed coker drum makes it an ideal place for foam to form
  - Gas (steam and hydrocarbon) flowing through hot, viscous, and polar liquid
  - Cracking of molecules creating additional polarity
  - Pressure not too high so that the gases can be pulled off the drum and sent to the main fractionator
- Excessive or uncontrolled foaming causes “foam-over” from the drum into the main fractionator
  - Will carry coke fines into the main fractionator and up the tower fouling the trays, downcomers, and lines
  - Will force the unit to shut down

## Antifoams for Delayed Cokers

- Polydimethylsiloxanes (PDMS) are currently the most cost-effective coker foam control agents available
- PDMS:
  - Reduces foaming while filling drum
  - Minimizes foam-over potential in coke drum
  - Allows smaller outages; more coke production
- Silicon poisons downstream HDS catalyst
  - Mechanical entrainment
  - Distillation of small silicone molecules
- Higher MW PDMS = increased stability / slower decomposition




## Coker Antifoam Technology





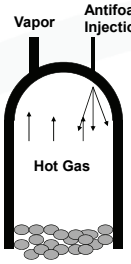


## Factors Affecting Antifoam Performance

- Dilution of antifoam in carrier stream
- Type of diluent can make a difference
- Inject so antifoam is spread on foam front
- Injection should be opposite overhead vapor line
- Less foaming with higher drum temperatures
- Thermal decomposition rate of PDMS

## How Does Silicon End Up in Liquid Products?

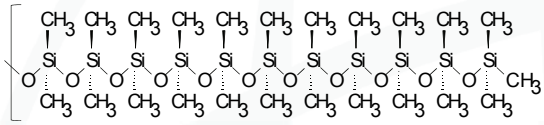
- Entrainment controlled by:
  - Injection away from OH
  - Use carrier to blow antifoam to foam front
  - High boiling carrier to minimize flashing
- Decomposition rate controlled by:
  - Drum temperature
  - PDMS molecular weight







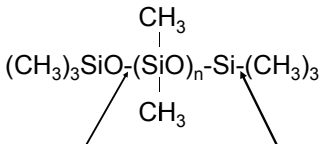
## Poly-DimethylSiloxane (PDMS)



- Relatively thermally stable
- Effectively reduces foam in oil based systems




## Poly-DimethylSiloxane (PDMS)




**Very strong; 'protects' adjacent Si-C linkage**

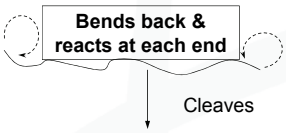
**Most susceptible to degradation; forms active site**

## Thermal Degradation of Silicone

- PDMS begins to decompose at 350˚C (662˚F)
- Higher temperature = faster decomposition
- Forms cyclic methysiloxane trimers and larger
- Defoaming ability is reduced
- Breakdown products go overhead and contaminate cracked products – leads to HDS poisoning




## PDMS Degradation Mechanism

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**Degradation products include:**

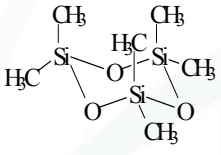
- **Hexamethylcyclotrisiloxane**
- **Octamethylcyclotetrasiloxane, etc.**

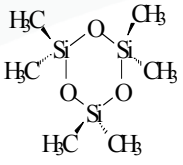
**Volatile species; B.P. ~ 350°F (~177°C)**

**Seven or less monomers – volatile at coker temperatures**




## Cyclic Trimer Breakdown Products



## Decomposition Products of Silicone Oil

| Product | B.P. °C | B.P. °F |
|---|---|---|
| Cyclic Trimer | 134 | 273 |
| Cyclic Tetramer | 175.8 | 348 |
| Cyclic Pentamer | 210 | 410 |
| Cyclic Hexamer | 245 | 473 |




## Higher Viscosity Silicone

- Higher viscosity = larger molecule
- Larger molecule takes longer to degrade
  - Defoams longer
  - Lower dosage required
  - Less Si in products
  - Less catalyst contamination
- Even ultra-high viscosity silicone oil will thermally decompose

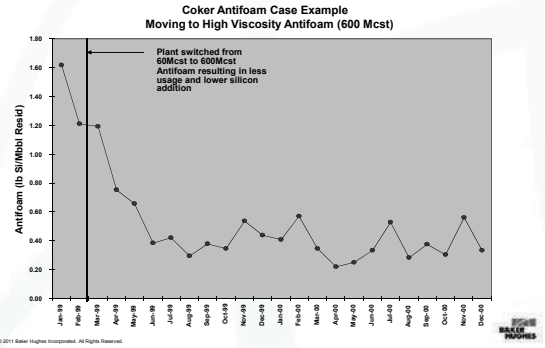



## MW of Stressed Silicone

**PDMS Stressed for 5 Hours at 375°C (700°F)**

| Silicone Viscosity(cSt) | MW Initial | MW Stressed | % Reduction |
|---|---|---|---|
| 60,000 | 95,348 | 82,646 | 13.3% |
| 100,000 | 105,204 | 98,802 | 6.1% |

## Higher MW Results in Less Si to Coke Drum







## Silicon Reduction in Products

| | 60,000 cSt ppm Si | 600,000 cSt ppm Si | ppm Si reduction | %Si reduction |
|---|---|---|---|---|
| **Naphtha** | 34 | 12.3 | 21.7 | 63% |
| **LCGO** | 7.9 | 3.2 | 4.7 | 59% |
| **HCGO** | 7.3 | 2.7 | 4.6 | 63% |




## How Can We Overcome Si Poisoning?

- Find a cost-effective non-silicon antifoam / defoaming agent
- Identify alternate structures of siloxane antifoams
- Trap silicon compounds in the cracked gases

## Introducing Baker Petrolite FOAMSTOP™ 5000 Low Catalyst Impact (LCI) Antifoam

- Limit to higher molecular weight PDMS
  - High viscosity difficult to handle
  - Higher molecular weight costs more
- New type of antifoam developed
  - Alternate structure PDMS
  - Effective at lower dosages
  - Significantly lower rate of thermal decomposition
  - Prevents foam build-up
  - Patents granted

Baker Petrolite FOAMSTOP is a trademark of Baker Hughes Incorporated




## Field Trial #1

- Coker makes fuel grade coke
- Base case 600,000 cSt silicone antifoam
- Measured foam knock down
- Re-foam after drum switch
- Plant wanted to reduce Si contamination of coker products




## Field Trial #1

| Sample | 600,000 cSt (ppm Si) | FOAMSTOP 5000 LCI (ppm Si) | % Reduction |
|---|---|---|---|
| **Coker Naphtha** | 3.29 | 1.29 | 62.5% |
| **Coker Kerosene** | 4.41 | 1.92 | 56.5% |

- All samples taken at the same timing before drum switch

## Field Trial #1

- Results with Baker Petrolite FOAMSTOP LCI antifoam
  - Knocked down foam better
  - Prevented re-foam after switch better
  - Could allow reduced outages
  - Reduced silicon contamination of products by over 50%




## Field Trial #2

- Anode grade coke production
- Si in product poisoning catalyst
- Excessive defoamer usage
- Used 600,000 cSt silicone antifoam for four years




## Field Trial #2

**PPM Silicon In Cracked Products**

| Coker Product | 600,000 cSt | FOAMSTOP 5000 LCI | % Reduction |
|---|---|---|---|
| | Drum 1 | | |
| **Naphtha** | 58.0 | 35.9 | 38 |
| **LCGO** | 38.8 | 10.3 | 73 |
| **HCGO** | 5.5 | 2.2 | 60 |
| | Drum 2 | | |
| **Naphtha** | 33.8 | 8.2 | 75 |
| **LCGO** | 28.7 | 3.2 | 88 |
| **HCGO** | 1.8 | 0.9 | 50 |

**Samples taken one hour before drum switch**

## Field Trial #2

- Baker Petrolite FOAMSTOP 5000 LCI antifoam reduced Si in product
- More efficient to add antifoam early
  - Foam easier to prevent than knock down
  - Use less antifoam
- Kept foam down after drum switch
- New material easy to handle




## Summary

- Baker Petrolite FOAMSTOP 5000 low catalyst impact antifoam is more stable than traditional coker antifoams
- Controls foam better
- More persistent in the coke drum
- Reduces silicon contamination of coker products which slows deactivation rates of downstream hydrotreater catalysts
- Improves refinery profitability by minimizing costs of HDS catalyst replacement




## Closing

Thank you for your attention!

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