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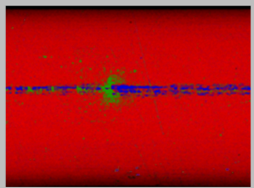

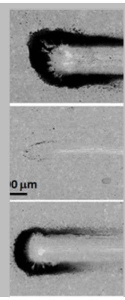

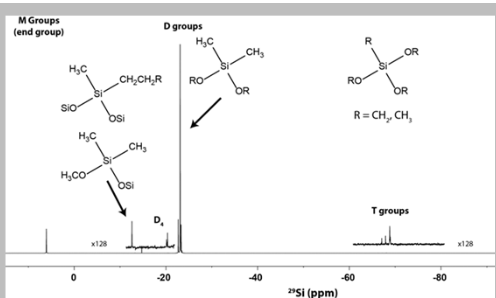

Heterogeneous Oxidation of PDMS Fluids at Metal Surfaces

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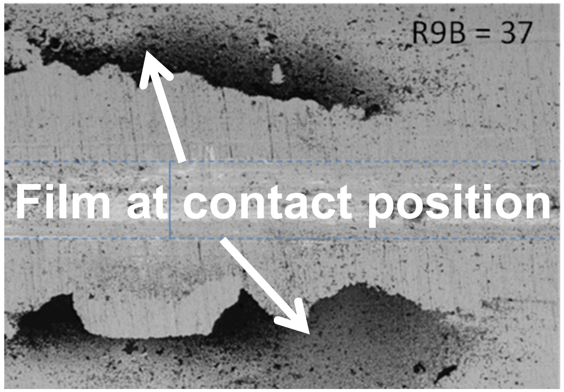
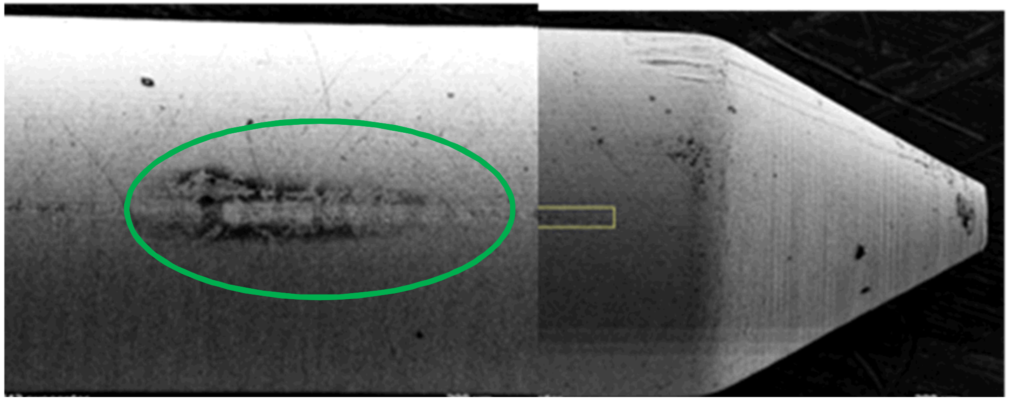
A Story:
"Polymer Aging in Unexpected Places and Conditions"

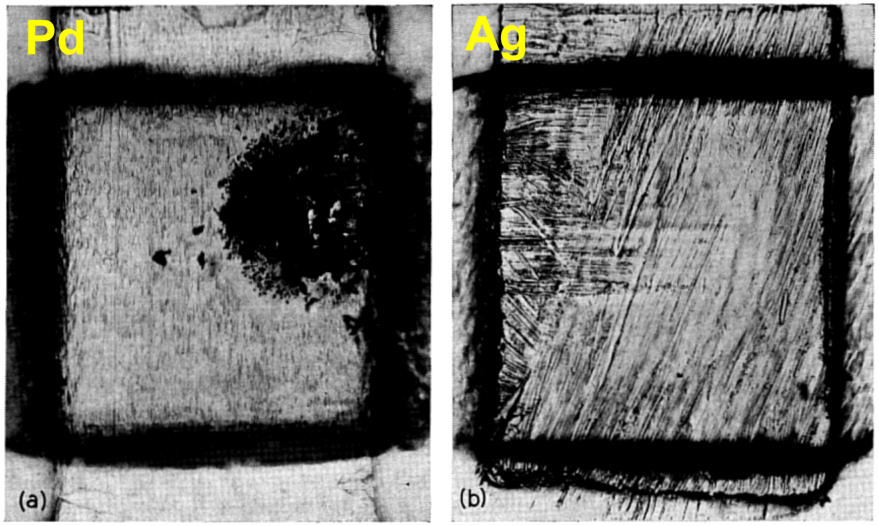
- Environmental sensing devices (ESD).
- Contain poly(dimethyl siloxane) PDMS fluids for viscosity/density control.
  - Vibration/shock damping.
  - Insulative properties.
- Used in components since 1980's.
- PDMS is considered very chemically inert, and has shown very little issues concerning degradation!
- Has systems are miniturized and electronic circutry changes lower voltages and currents are utilized.
- This example invovled thin film formation ("Halos") leading to increased resistivity of these electrical contacts.





Known Issue!
Polymer Aging at Metal Surfaces

- Friction polymerization to form thin films known for many decades.
- Polymer films are know to increase electrical resistivity.
- Frictional motion can arise from switch motion, vibrations and thermal expanion.
- Metal catalysis or electrical arching can lead to the degradation of organic vapors and fluids.
- In the current study it is proposed that newly exposed metal surfaces (and metal oxides) act as the catalytic agent.



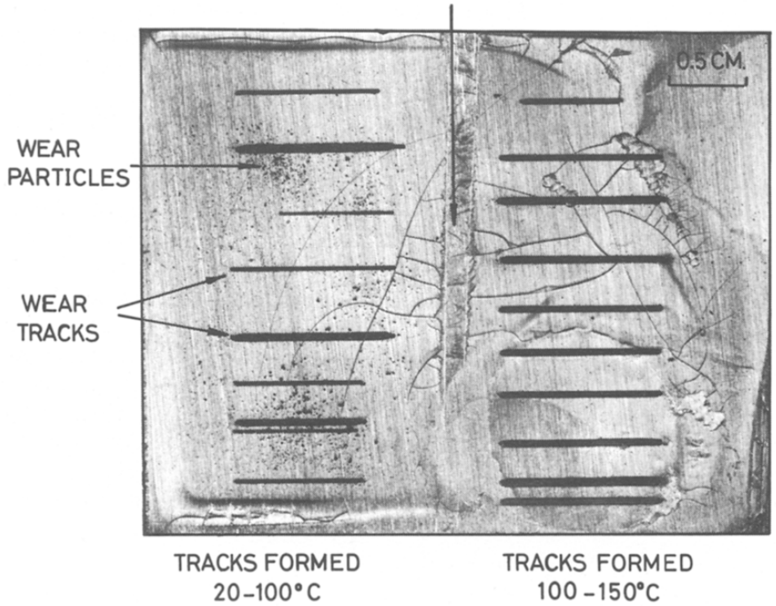
- 10^6 closures – organic vapor (Hermance, 1958)

[1] H. W. Hermance, T. F. Egan, *Bell Systems Technical Journa*l, May (1958), 739-776.
[2] M. Antler, *ASLE Transactions, 26, 376-380.*
[3] M. Antler, *IEICE Trans. Electron.*, E82-C (1999), 3-12.
[4] D. Tabor, R. F. Willis, *Wear*, II (1968) 145-162.

PDMS Film Formation at Metal Surfaces

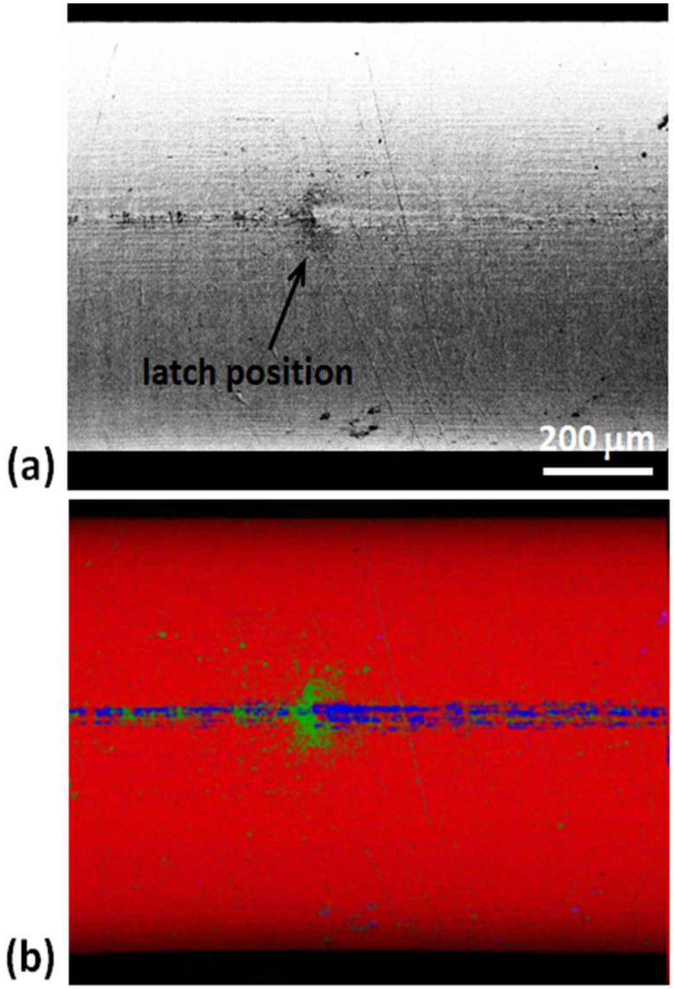
- PDMS has typically been considered chemically inert below ~ 200°C.
- Films formation due to heat has been reported.
- Frictional polymerization not typically considered an issue.
- In fact – PDMS has been added as a "lubricant" to *reduce* fretting and frictional polymerization.

Polysiloxane films over steel

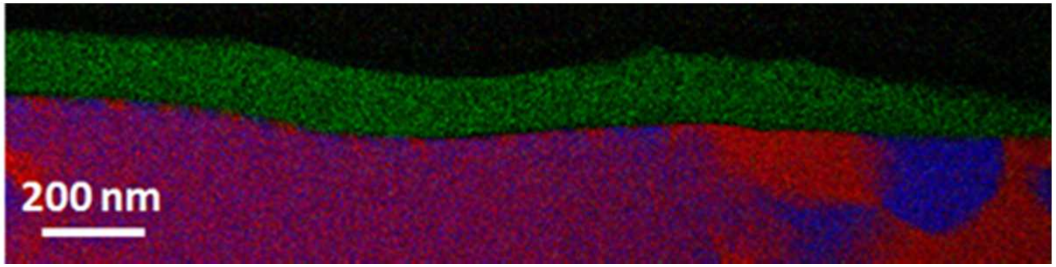


D. Tabor, R. F. Willis, *Wear*, II (1968) 145-162.

Characterization of Degraded Films



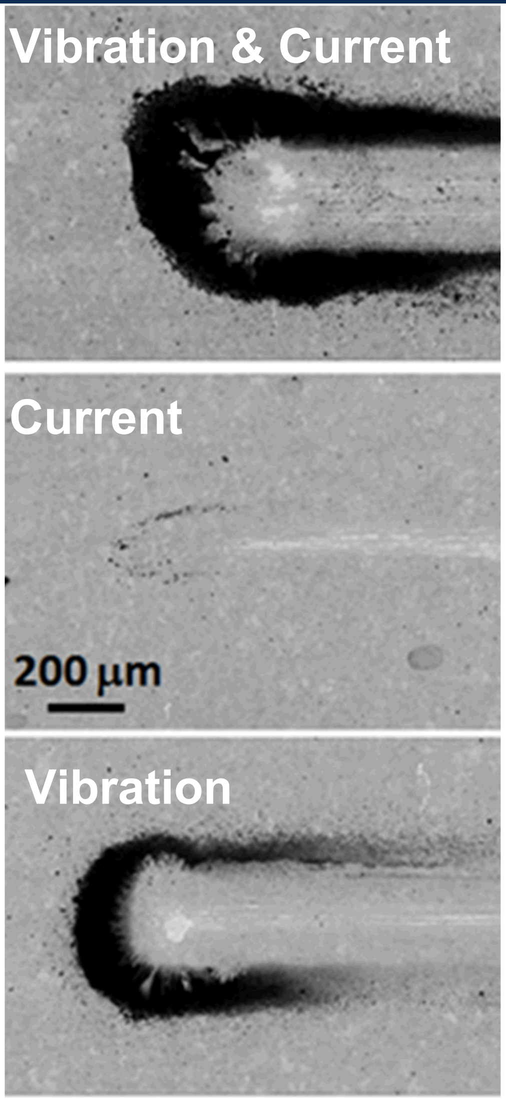
a) Backscattered SEM image (a) and AXSIA image of the EDS (energy dispersice spectroscopy) maps. In the AXSIA (Automated eXpert Spectral Image Analysis) image: Paliney-7 matrix, transferred Au and Cu from the Neyoro-G, and Si, C, O deposit.



AXSIA-processed EDS image from the TEM, of a FIB (focused ion beam) section through the deposit in a halo. Deposit ~ 100 nm thick.

Note the film is only formed at the metal-metal contact – not on the entire metal surface!

Characterization of Degradation Films

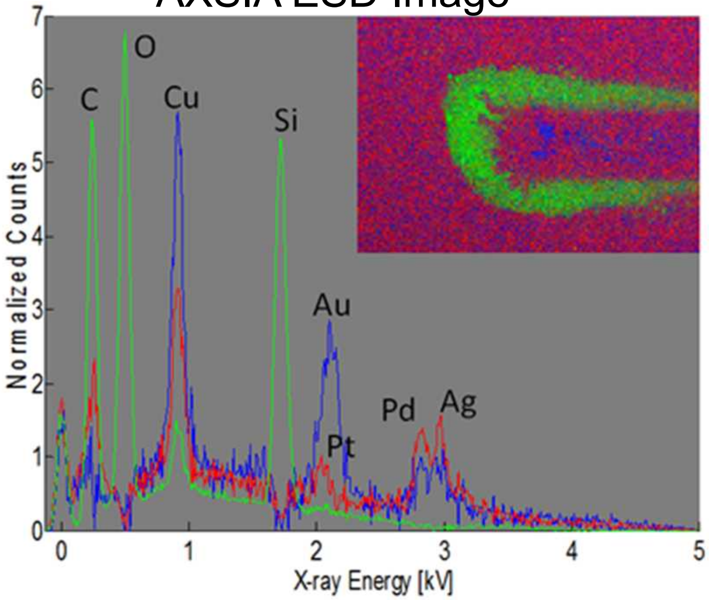


The role of electrical currents and vibrations explored in sliding contact experiment.

Paliney-7 and Neyoro-G contact.

Dominante mechanism originated from vibration in contact.

AXSIA ESD Image

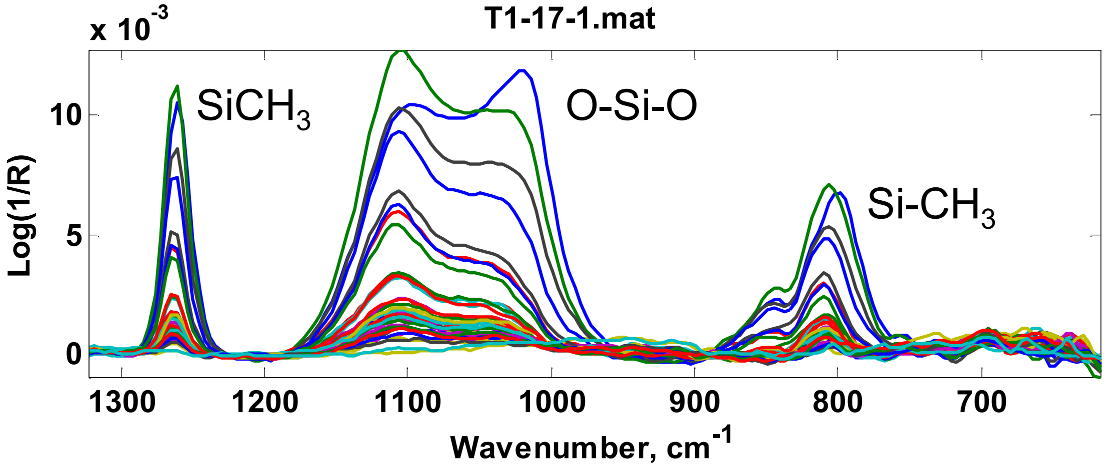


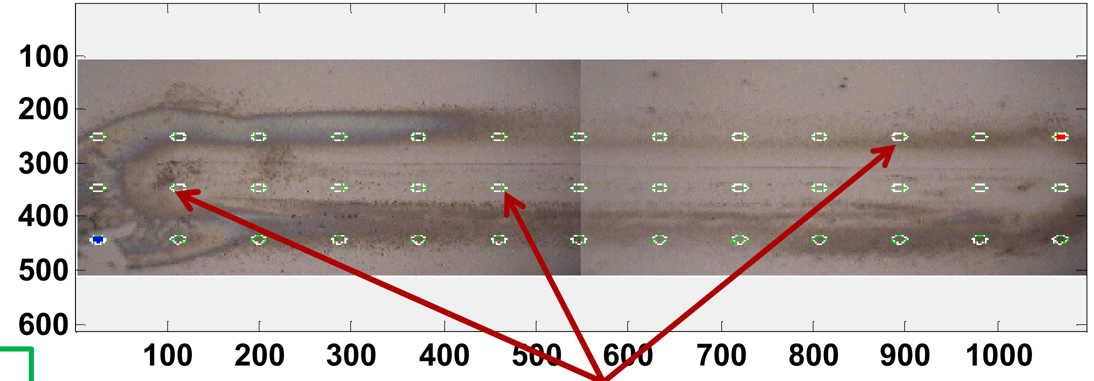
Si, C, O deposit.

IR Reflectance Characterization

IR Reflectance

- Bruker Vertex 70v, with Hyperion IR microscope
- 8cm^{-1} resolution
- 256 scans averages
- Referenced to clean Paliney 7
- ~39 spectra per track
- 120 µm rows with 110 µm separation





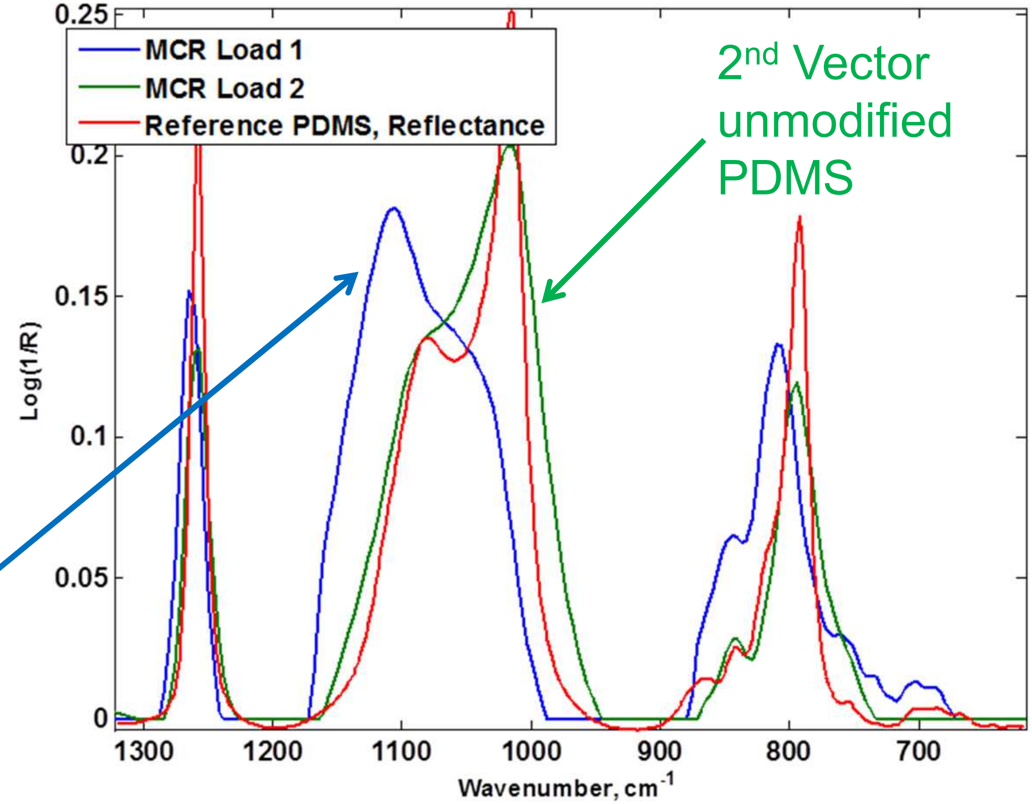
Dots signify location of data collection

IR signature arises entirely from deposition and is consistent with PDMS

IR Analysis

MCR (Multivariate Curve Resolution)

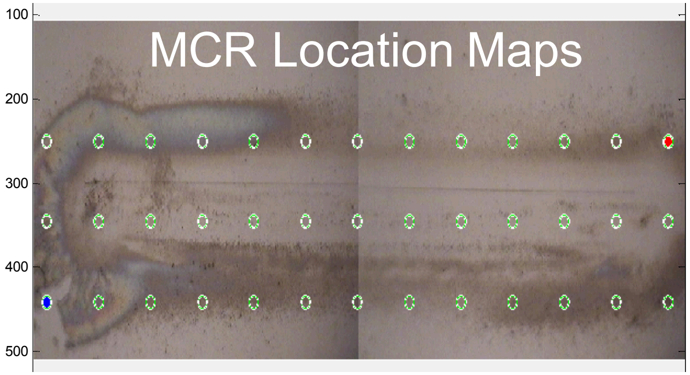
- Used to identify sources of variation in infrared data.
- Applied to each image set collected to look for common spectra.
- Two spectra found consistently.



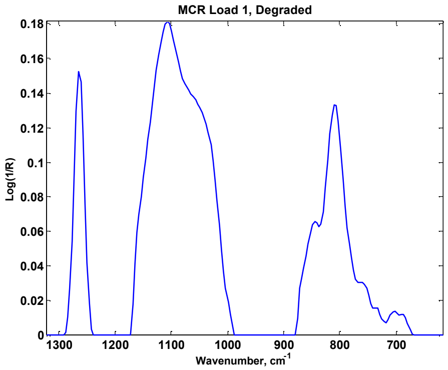
1st Vector, shift and reduction of split indicates shorter chain length and/or increased cross-linking.

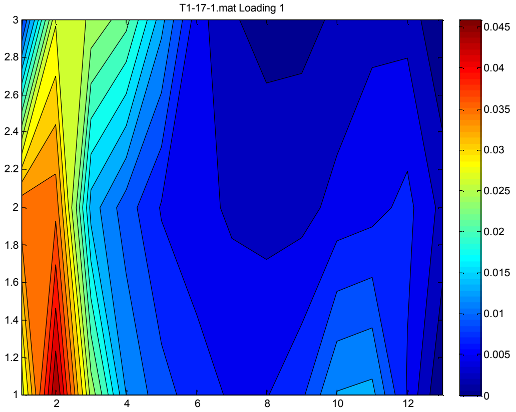
[1] Smith, A. Lee; "Infrared Spectra-Structure Correlation for Organosilicone Compound", Spectrochimica Acta, (1960) Vol. 16, p 87-105.

IR Analysis – MCR Maps

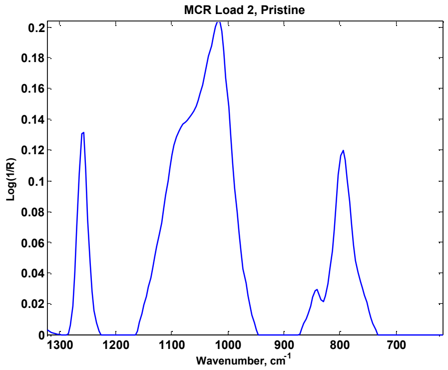


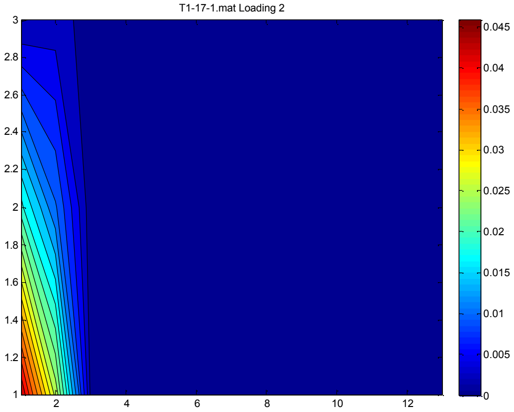
Degraded PDMS





Unmodified PDMS



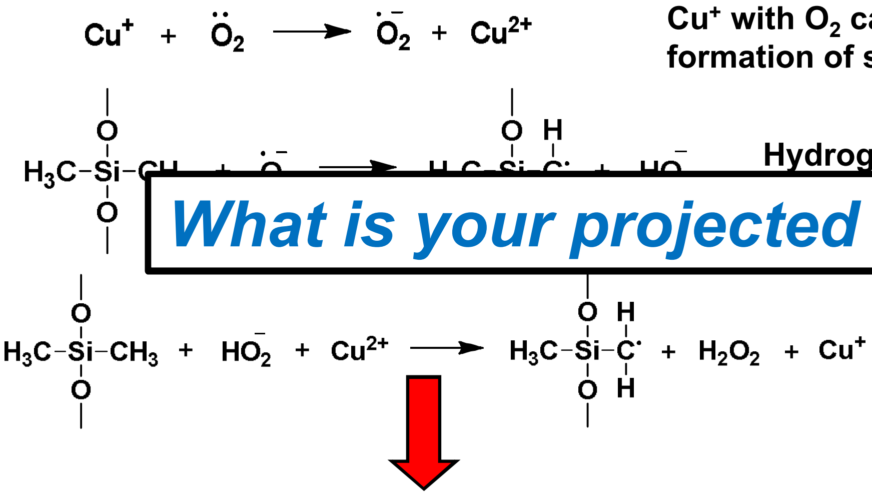


- Deposits composed of degraded PDMS.
- What is the mechanism for film formation?

Polymers with Oxygen and Certain Metal Catalysts are a Bad Combination

Polymer degradation can be facilitated by metal catalysts both under oxidative and inert conditions when hydroperoxides are present

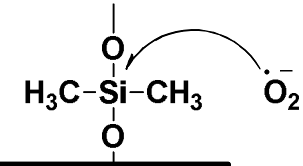
- Redox catalysts like Cu^{+} or Fe^{2+} make oxygen more aggressive
- They also encourage hydroperoxide decomposition (classic Fenton chemistry)



Cu^{+} with O_2 catalyzes the formation of superoxide anion

Hydrogen abstraction

Further hydrogen abstraction, hydroperoxide formation and Cu^{+} regeneration

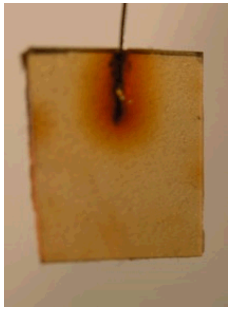


superoxide anion has been suggested but is likely less important

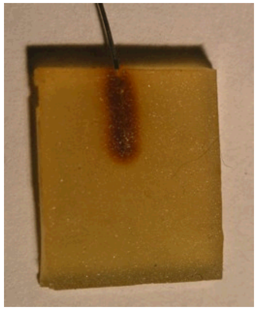
What is your projected degradation mechanism??

- **DEGRADATION OF SILICONE (PDMS)**
- **Alkyl radicals form further hydroperoxides with O_2**
- **Follow-up free radical oxidative chemistry**
- **Crosslinking via silicone methyl side group**
- **Polymer degrades with higher M_w being encouraged**

Reactions likely diffusion controlled by metals ions, hydroperoxide, and hydroxyl radicals for propagation



HTPB polymer
1.3 y at 50°C

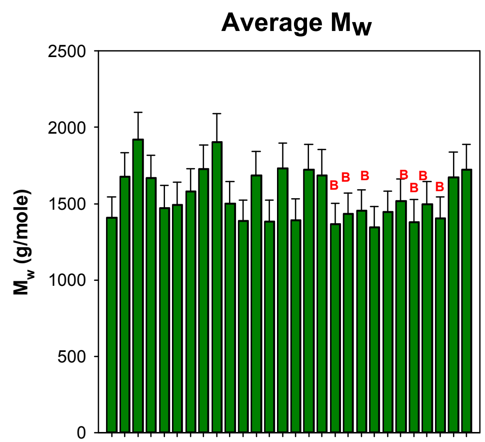


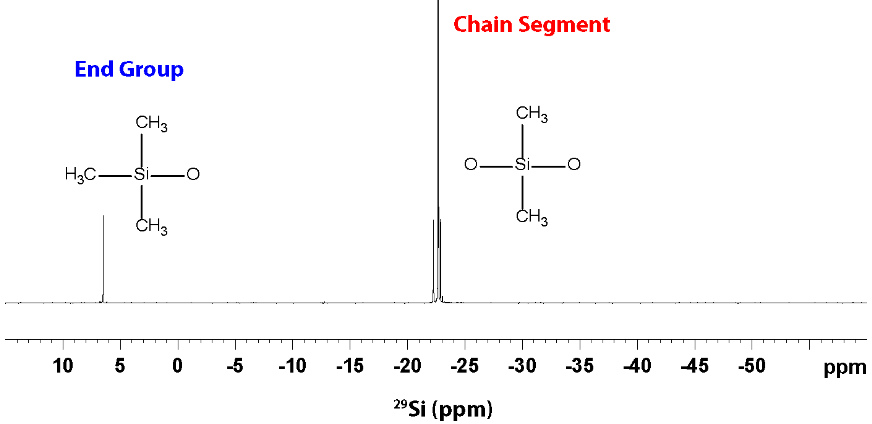
PBAN polymer
1.4 y at RT

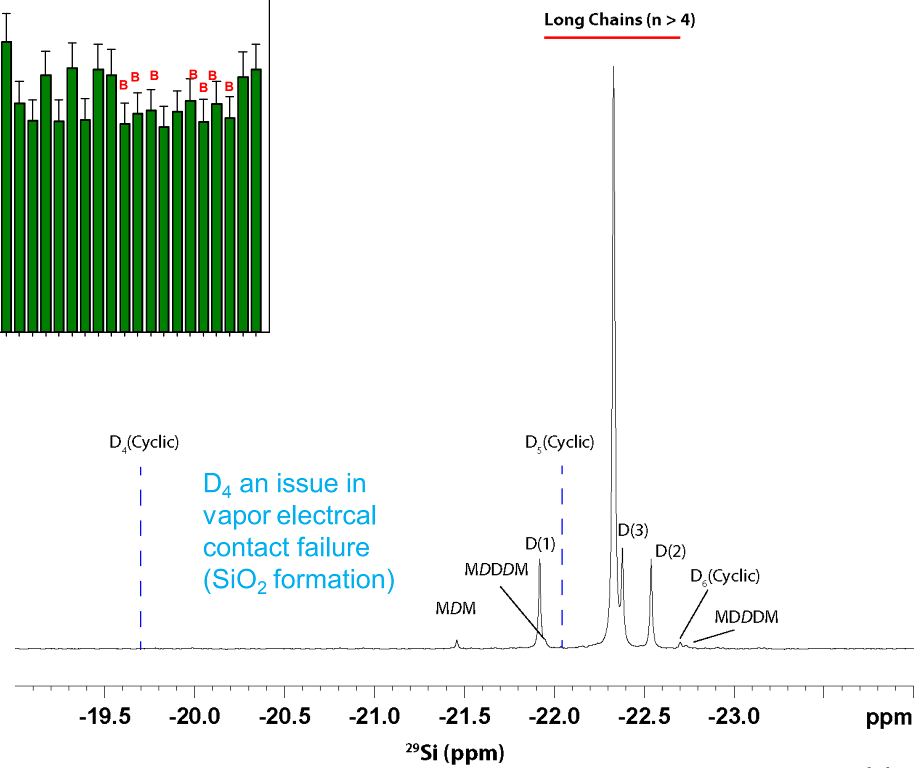
Polymer degradation facilitated by Cu ions despite tin coating on copper wire

Bulk PDMS Fluid – ^{29}Si NMR

Tried to identify correlation between M_w, presence of impurities, cyclics, etc …. and degradation film formation.

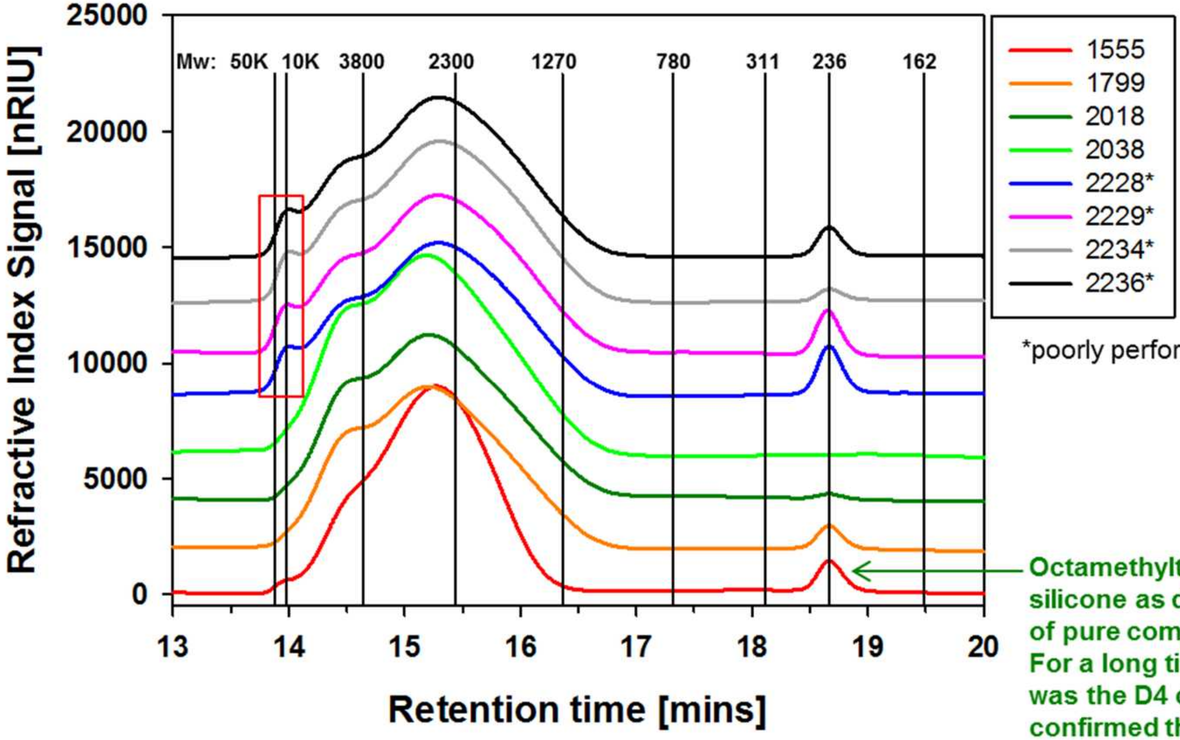






GPC Analysis

M_w variability if PDMS Fluids



*poorly performing Si oil samples

Octamethyltrisiloxane, the linear silicone as determined from timing of pure compound.
For a long time we assumed this was the D4 cyclic, but NMR never confirmed the presence of a larger amount of the cyclic in these oils, plus the GPC peak of the cyclic was at a slightly earlier time.

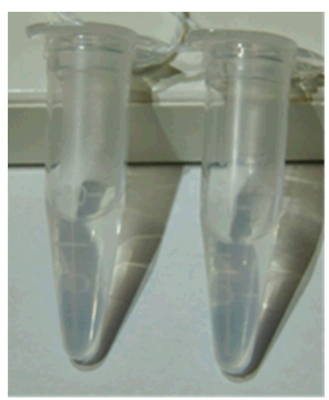
Bulk PDMS fluid does not reveal degradation species or changes!!

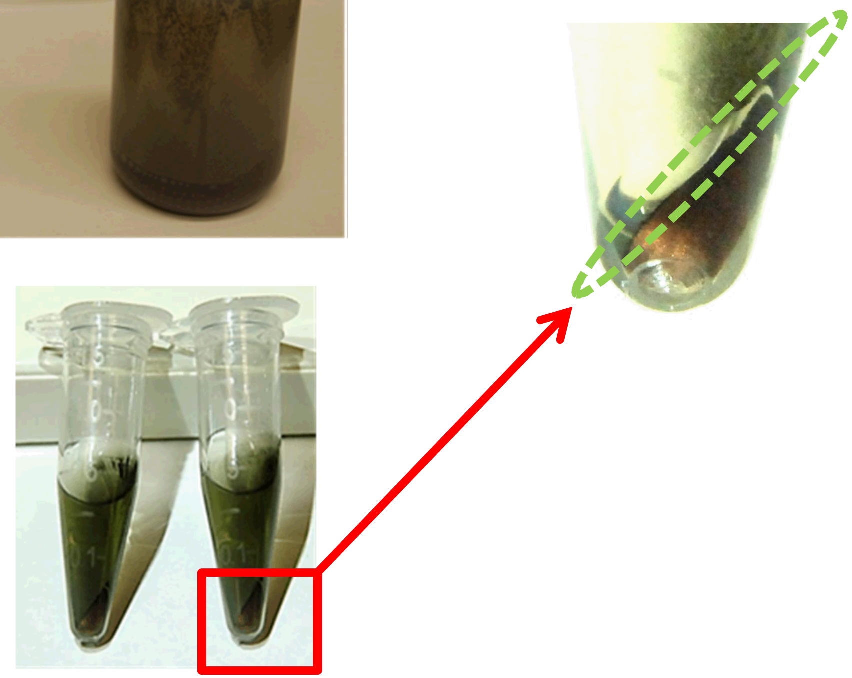
Cu catalyzed PDMS Decomposition
“Tumble Test”

	wt. %, min-max						
	Pd	**Ag**	**Cu**	**Pt**	**Ni**	**Zn**	**Au**
Paliney-6	43-45	37-39	15.5-16.5	0.8-1.2	0.8-1.2	0-0.01	NA
Paliney-7	34-36	29-31	13-15	9-11	NA	0.5-1.5	9-11
Neyoro-G	NA	4.0-5.0	13.5-15.5	8.0-9.0	NA	0.7-1.3	70.5-72.5

- PDMS Fluid shaken with stainless stell or copper balls
  - 12 hrs tumbling
  - Fluid collected
  - Analyzed
  - Centrigued

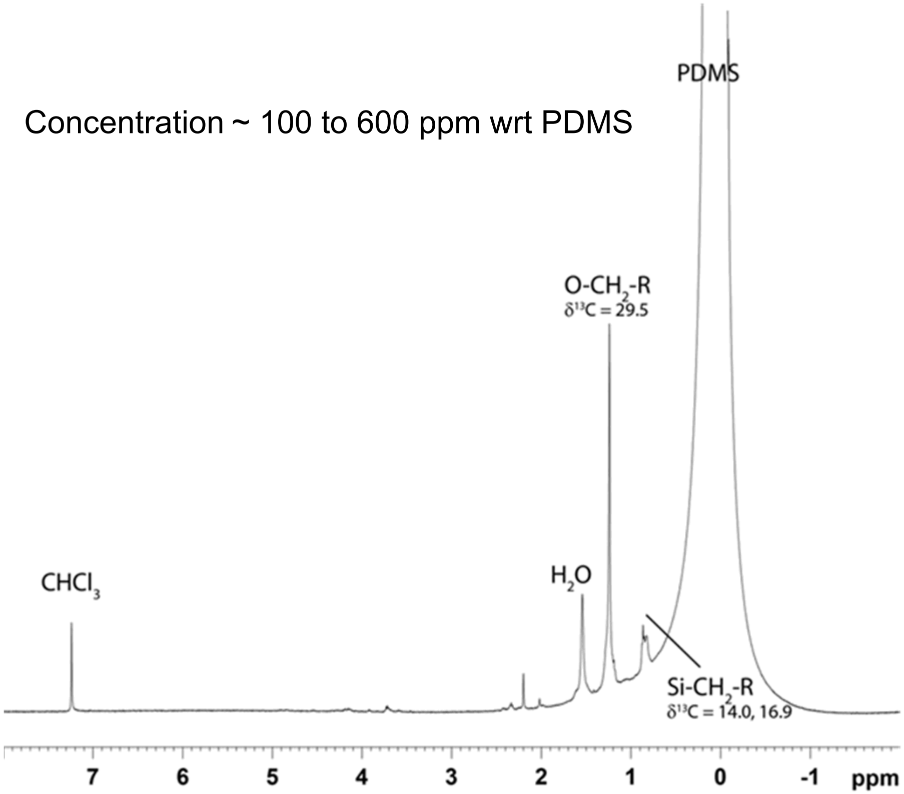
Thin Black Film Isolated

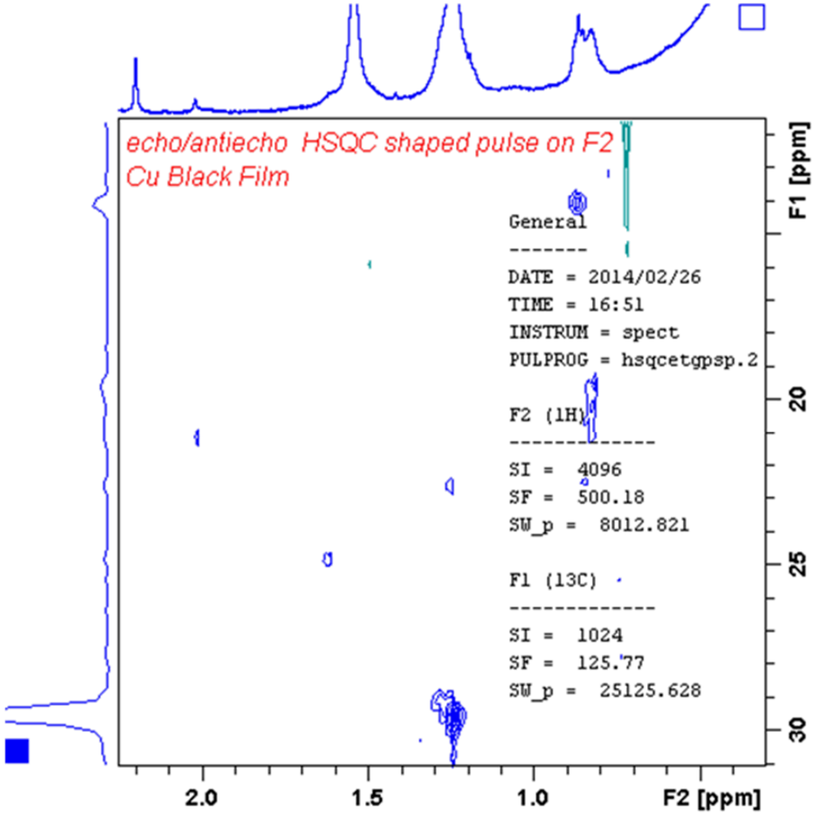




$^{1}H/^{13}C$ NMR Analysis

Concentration ~ 100 to 600 ppm wrt PDMS

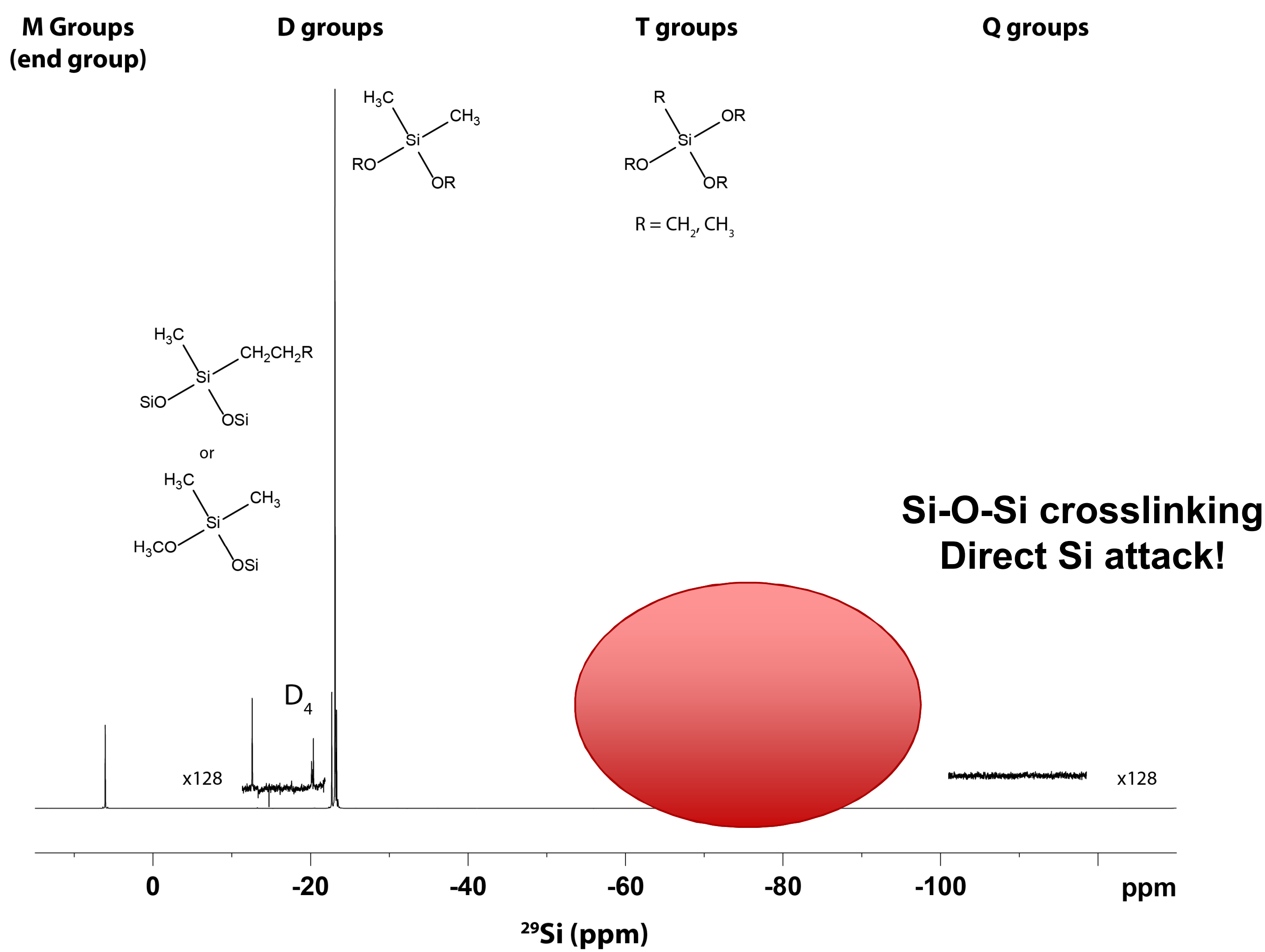




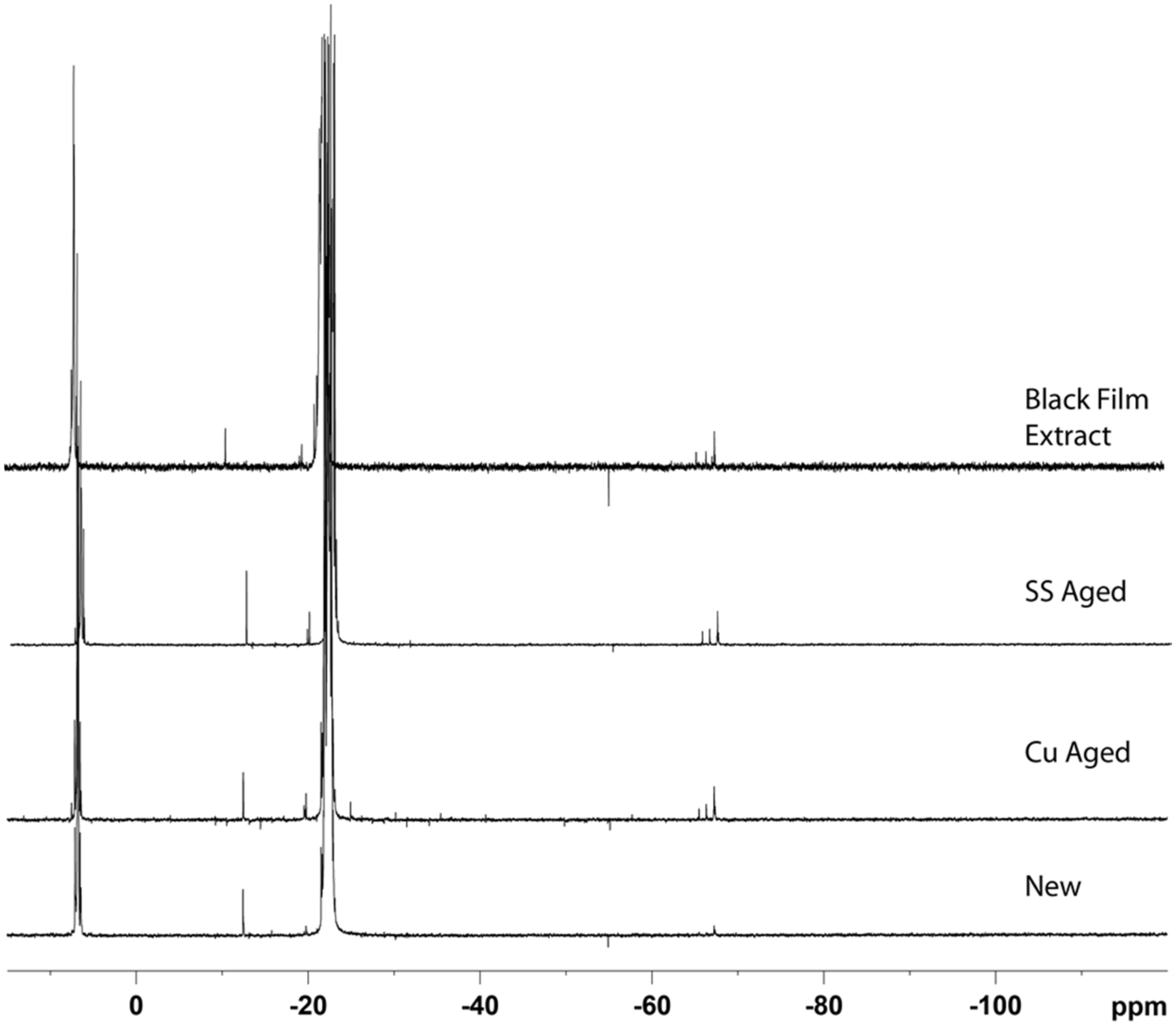
Consistent with Alkyl radical formation of oxidative metal catalysis!

Mechanism here….

Cu Tumble PDMS Fluid – ^{29}Si NMR



Cu Tumble PDMS Fluid – ^{29}Si NMR



Conclusions

- Frictional polymerization occur at electrical contact metal surfaces submersed in PDMS fluids.
- Occurs at room temperature and is an oxidative mechanism.
- Involves both alkyl radiacal cross-linking and Si condensation.
- Very heterogeneous in nature and is isolated to the metal surface of the contact, not the entire metal surface.

Acknowledgments:

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