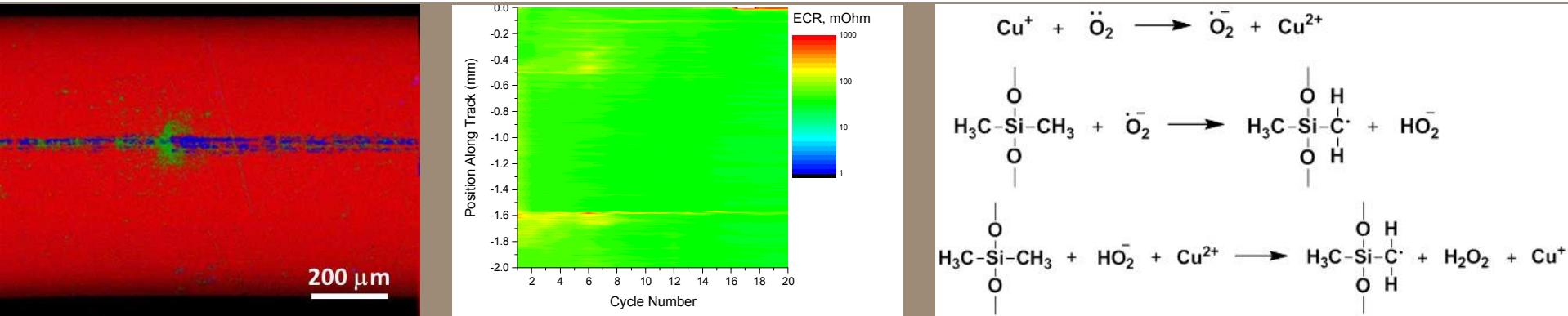


*Exceptional service in the national interest*



# Mechanically-Induced Degradation of Metallic Sliding Electrical Contacts in Silicone Fluid at Room Temperature

M.T. Dugger, D. Groysman, M.C. Celina, T.M. Alam, N. Argibay, B.L. Nation and S.V. Prasad

2014 IEEE Holm Conference, 13-15 October 2014, New Orleans, LA

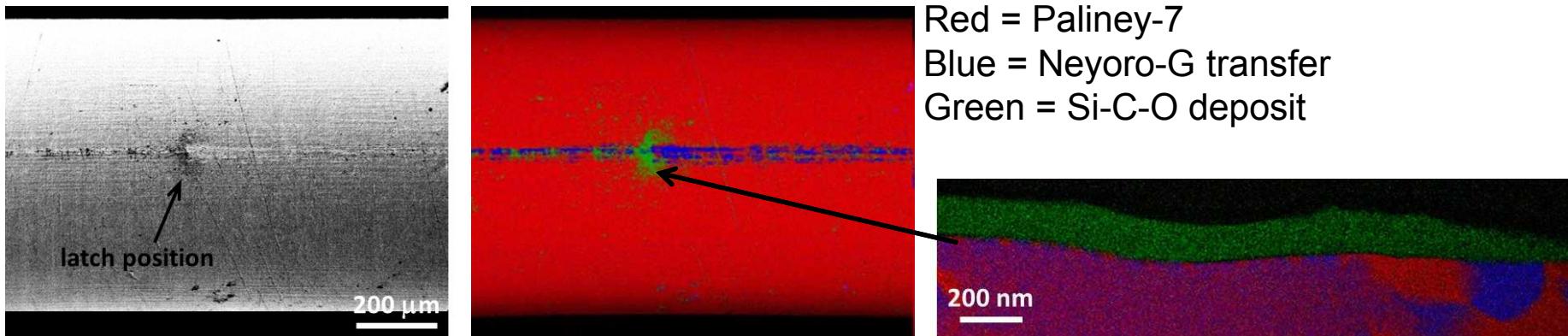


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# Background

A fluid-damped accelerometer exhibits increased electrical contact resistance (ECR) after storage

- contacts are precipitation hardened electrical contact alloys; a Pchiney-6 or -7 pin (Deringer-Ney Company)
- the device is filled with PDMS-200 silicone fluid (Dow Chemical Company)



	atomic %						
	Pd	Ag	Cu	Pt	Ni	Zn	Au
Pchiney-6	39.8	33.9	24.2	0.5	1.6	0.01	NA
Pchiney-7	34.8	29.4	23.3	5.4	NA	1.6	5.4
Neyoro-G	NA	6.0	33	6.3	NA	2.2	52.5

EDS/AXSIA image of a focused Ion Beam (FIB) cross section through deposit

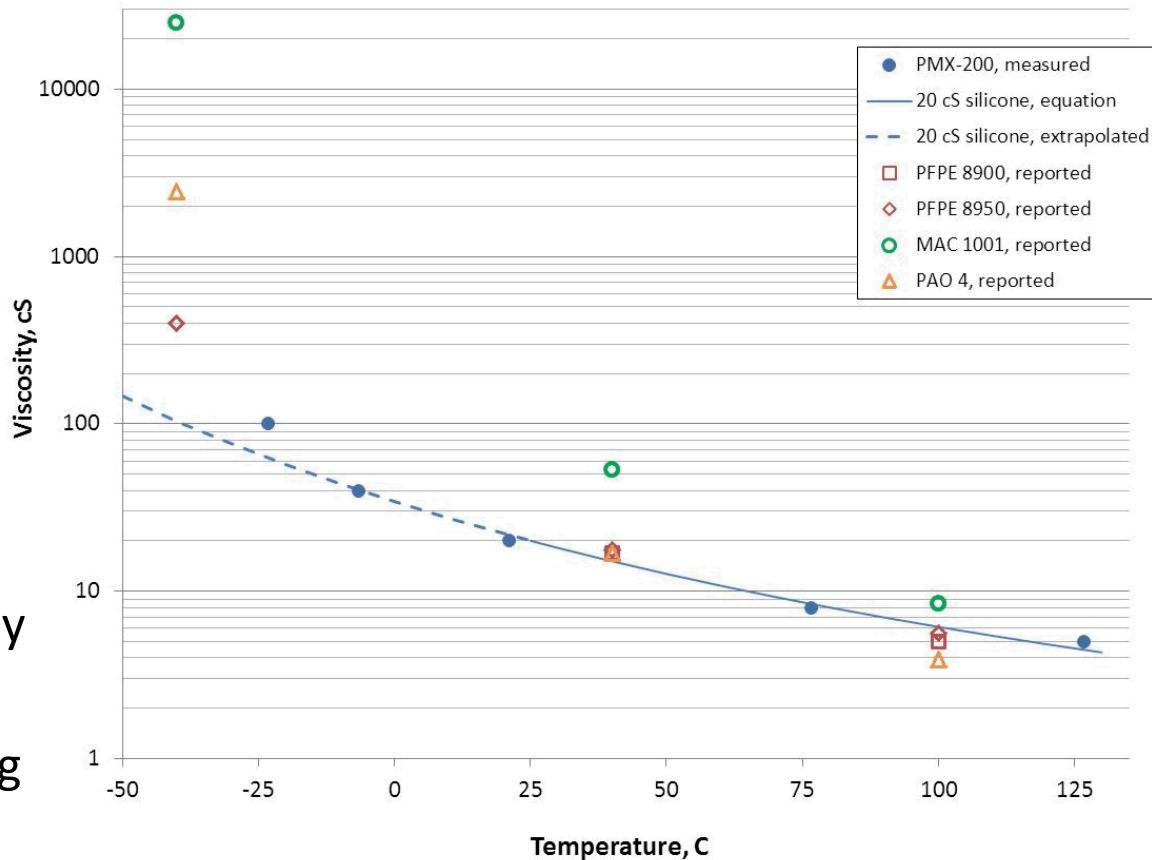
# Silicone Fluids

## Desirable Properties

- low freezing point (-65°C)
- low temperature-viscosity coefficient
- high thermal and chemical stability

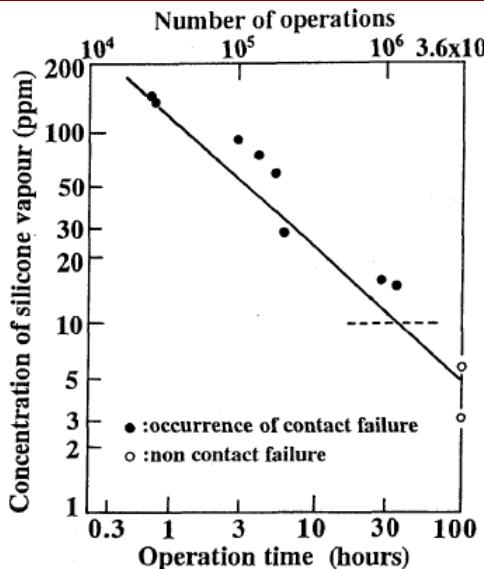
## Deficiencies as Lubricants

- poor elastohydrodynamic film formers (low pressure viscosity coefficient)
- attempt to improve lubricating properties by inducing polymerization at metal surfaces
- film forms on copper surfaces at 100°C and higher

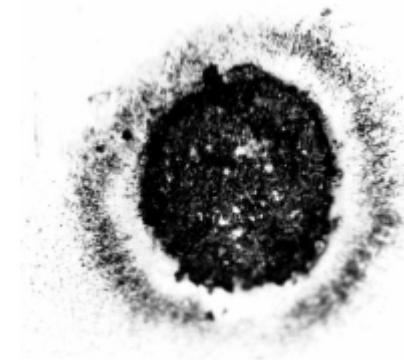
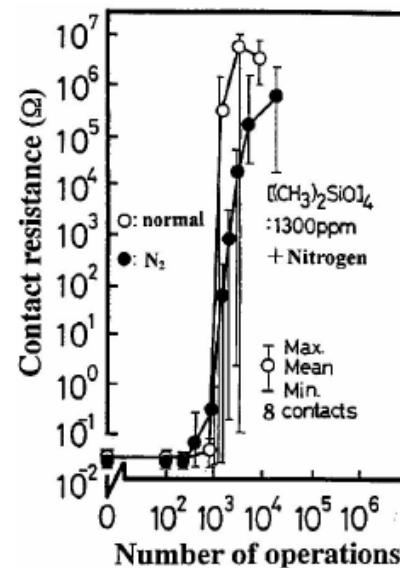


D. Tabor and R.F. Willis, Wear **13**  
(1969) p. 413-442

# Electrical Contact Degradation by Silicones



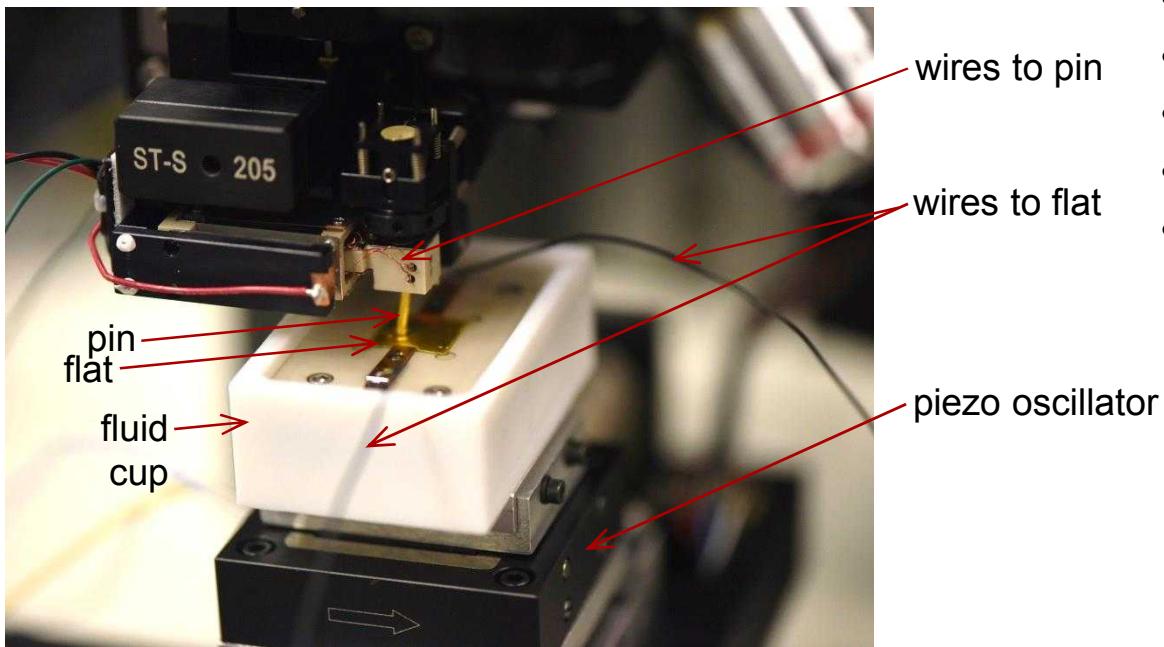
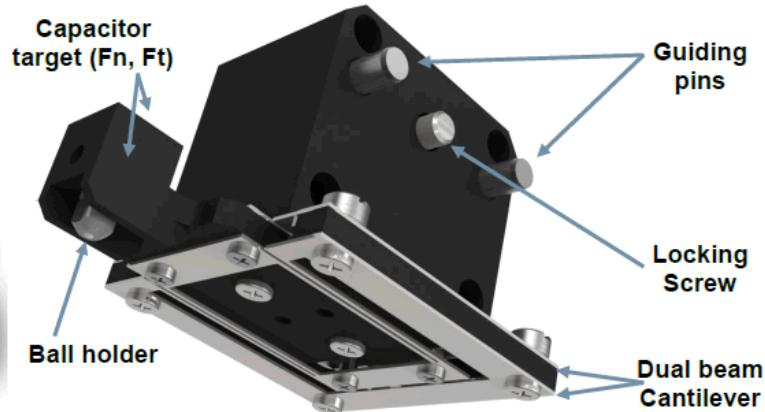
T. Tamai and M. Aramata, "Safe levels of silicone contamination for electrical contact," Proc. IEEE Holm Conference on Electrical Contacts, Pittsburgh, PA, 27-29 Sept. 1993



T. Tamai, "Acceleration and suppression factors for contact failure due to silicone contamination," Proc. IEEE Holm Conference on Electrical Contacts, Montreal, QC, Canada, 25-27 Sept. 2006, pp. 26-31

- Adsorbed silicone vapors thermally decompose during make-break arcs and result in ECR increase in micro-relays
- Operating in nitrogen had no effect on this degradation mechanism
  - water vapor, ozone and amines suppressed deposit formation by competing with silicone for surface adsorption sites

# Electrical Contact Nanotribometer

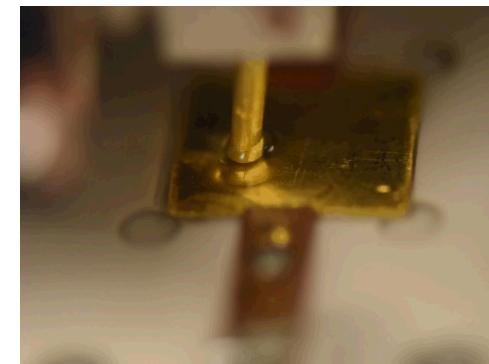


CSM nanotribometer modified for 4-wire ECR measurement

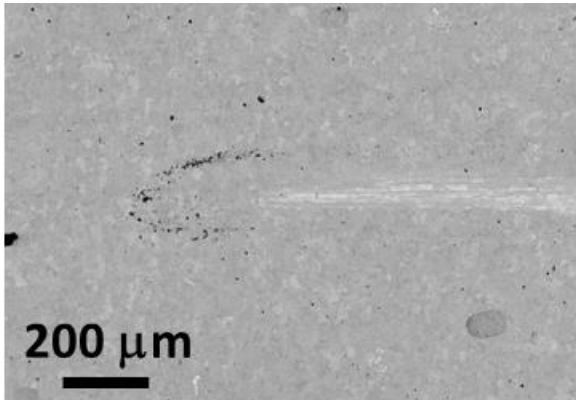
- DC power supply
- nano-ohm meter

Test parameters:

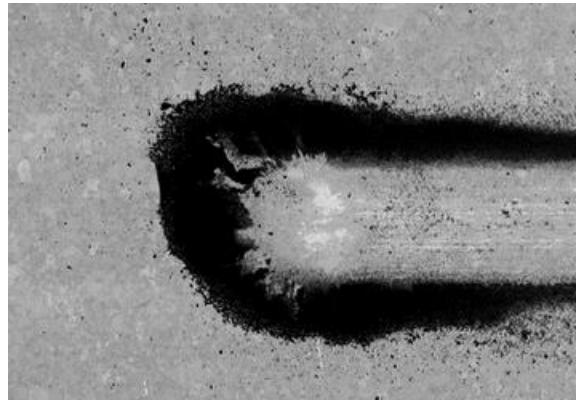
- $N = 88 \text{ mN}$
- pin radius = 1.6 mm
- track length = 1 to 2 mm
- fluid volume = 5 mL
- $i = 20 \text{ mA}, 1.1 \text{ V open circuit}$
- vibe = 50  $\mu\text{m}$  at 100 Hz



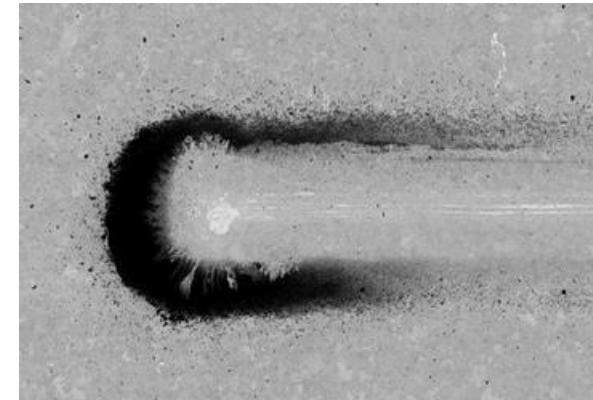
# Pin-on-Flat Tests



current + no vibration



current + vibration



no current + vibration

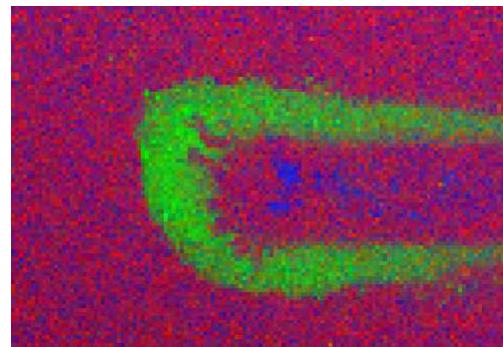
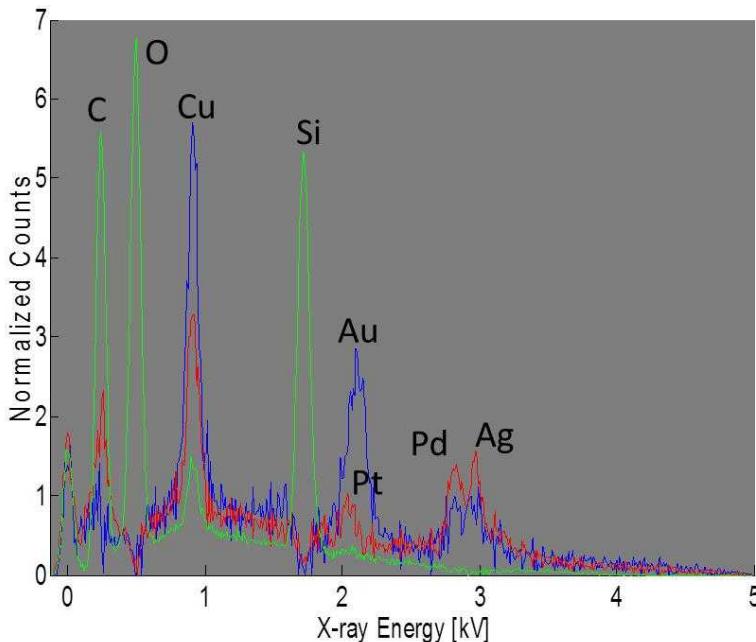
Initial experiments focused on the role of contact parameters in deposit formation

- current alone produced gold transfer, but very little deposit
- suspected make-break arcs during movement, leading to thermal decomposition of silicone

Deposit is created during mechanical contact of the metals, with little or no influence of current

- related to the creation of freshly-exposed metal surface by sliding

# Deposit Characterization



Red = Paliney-7 coupon  
 Blue = Neyoro-G transfer  
 Green = Si-C-O deposit

## Automated eXpert Spectral Image Analysis (AXSIA)

- uses full EDS spectrum from each pixel
- principal component analysis technique to identify major spectral components

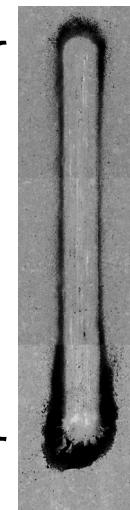
- Deposit contains constituents of the silicone fluid
- Composition identical to that on accelerometer pins
- Surface analytical methods (Auger, XPS, ToF-SIMS) provided no insight into deposit formation mechanism

# Relating Deposit to ECR Change

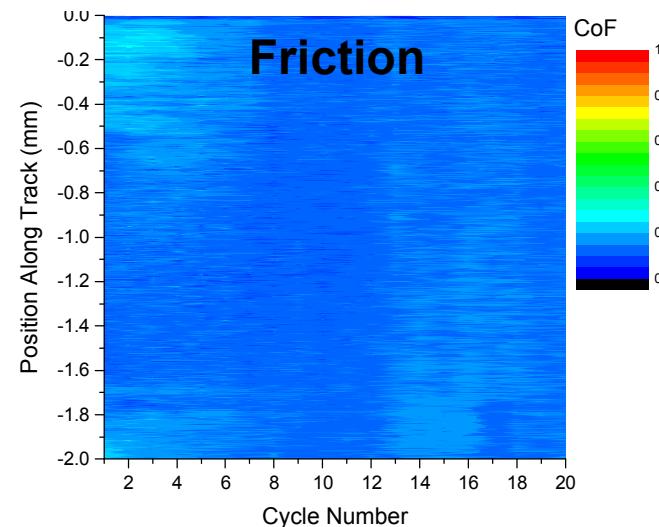
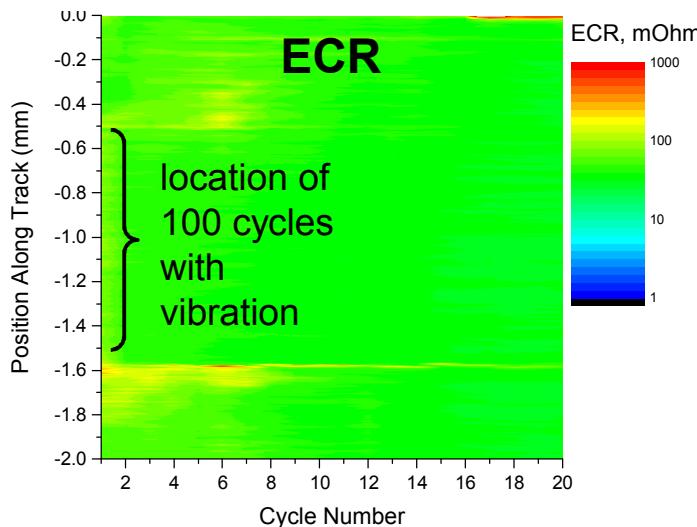
## Procedure:

1. Measure CoF and ECR along 2 mm track for 3 cycles with no vibration
  - a. 88 mN (9 gf) contact force
  - b. 20 mA DC current, with 1.1 V open circuit limit
2. Perform 100 cycles sliding with vibration on central 1 mm
  - a. 50  $\mu\text{m}$  displacement amplitude orthogonal to sliding direction, 100 Hz
3. Measure CoF and ECR along 2 mm track for 20 cycles with no vibration

initial wear track  
with vibration



1 mm

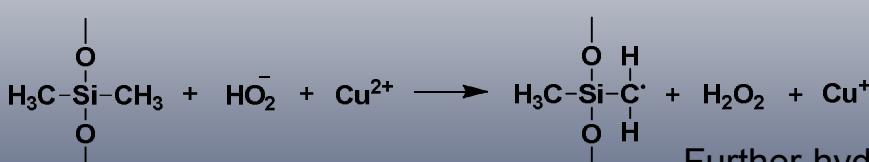
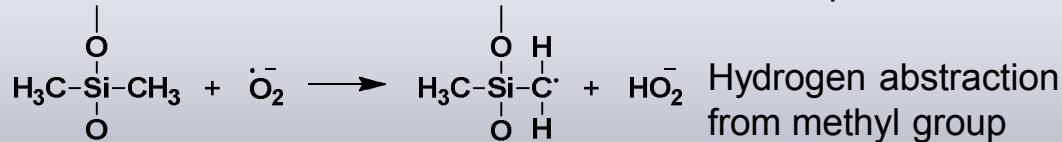


***Increased ECR is observed when pin slides over deposit***

# Silicone Polymer Degradation



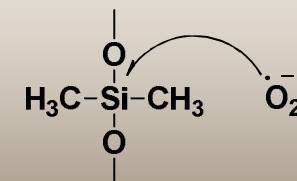
$\text{Cu}^+$  with  $\text{O}_2$  catalyzes the formation of superoxide anion



## Pathway I Side Group Oxidation

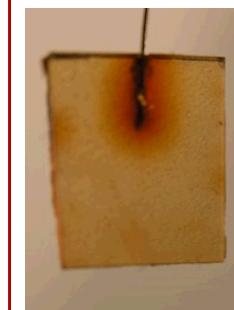
Further hydrogen abstraction, hydroperoxide formation and  $\text{Cu}^+$  regeneration

- Direct attack of superoxide anion
- Suggested in limited literature

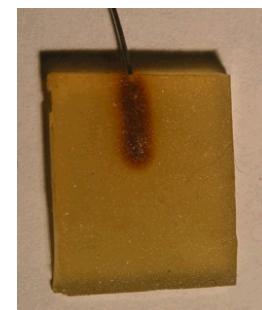


## Pathway II Direct Silicone Oxidation

- Both pathways result in localized crosslinking
- Reactions are controlled by diffusion of metal ions, hydroperoxide, and hydroxyl radicals for propagation
- Surface catalyzed degradation
- A larger sample of deposit is needed to gain insights on chemical pathway active during sliding of electrical contacts in silicone



HTPB polymer  
1.3 y at 50°C



PBAN polymer  
1.4 y at RT

**Degradation facilitated by Cu ions despite tin coating**

# The “Tumble Test”

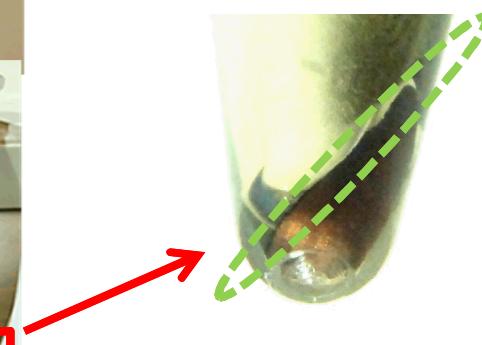


rock tumbler



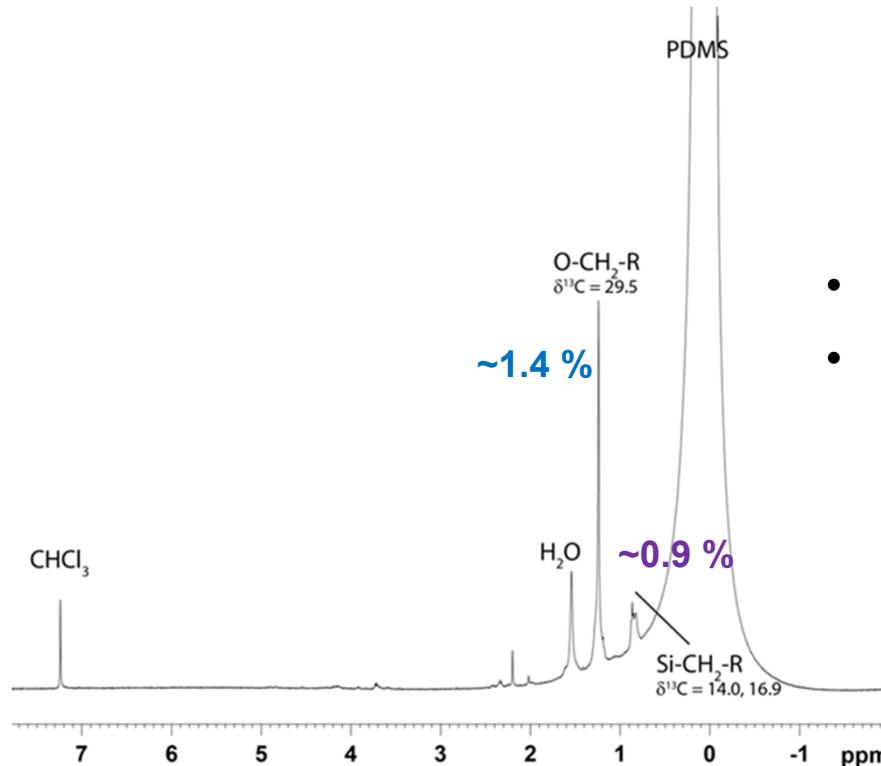
bottles filled with 3.2 mm dia. balls, covered with silicone fluid, tumbled 12 hrs.

fluid centrifuged  
thin black film isolated



- degradation is not due to fluid shear, since the squeeze film shear rate would be greater with SS balls (greater mass)
- not thermal decomposition since interfacial flash temperature during contact would be higher for steel balls (greater impact energy and lower thermal conductivity)

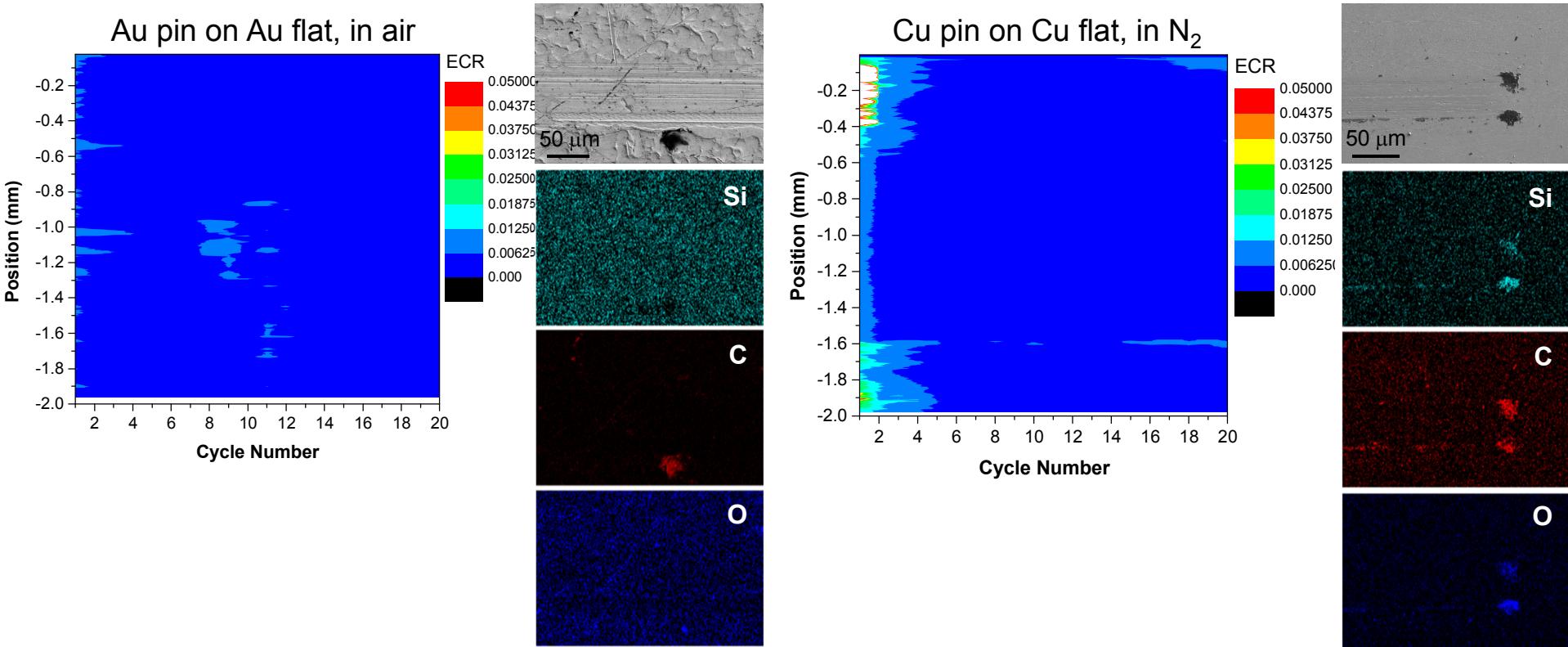
# $^1\text{H}/^{13}\text{C}$ NMR Analysis of the Black Film



- $^{13}\text{C}$  NMR reveals these are  $\text{CH}_2$  species
- Data bases suggest a  $\text{O}-\text{CH}_2-\text{R}$  linkage

- Product is consistent with alkyl radical formation by oxidative metal catalysis
- Methyl side group oxidation, free radical hydrocarbon oxidation

# Testing the Reaction Hypothesis



- Sliding of gold surfaces in silicone produced no deposit nor changes in ECR
- Self-mated sliding of copper surfaces produced a change in ECR and deposit formation
  - qualitatively much less deposit than observed for contact of reactive metals in air
  - fluid may have contained some dissolved oxygen

# Conclusions

- Silicone fluid can degrade at room temperature when exposed to oxygen and fresh metal oxide surfaces
  - deposit on Cu-containing alloys requires only mechanical agitation to continually displace passivating surface films and expose surface oxide
  - deposit increases electrical contact resistance by orders of magnitude
- NMR suggests that the deposit is formed through surface-catalyzed radical formation and crosslinking
  - methyl radical formation produced the highest concentration of degradation species
- Mitigation should be possible by eliminating reactants that facilitate radical formation
  - gold plating to eliminate metal oxide as catalyst
  - de-oxygenate fluid; may be impractical in a production setting
  - change fluid chemistry

# Acknowledgments

Bonnie McKenzie and Amy Allen for SEM and EDS

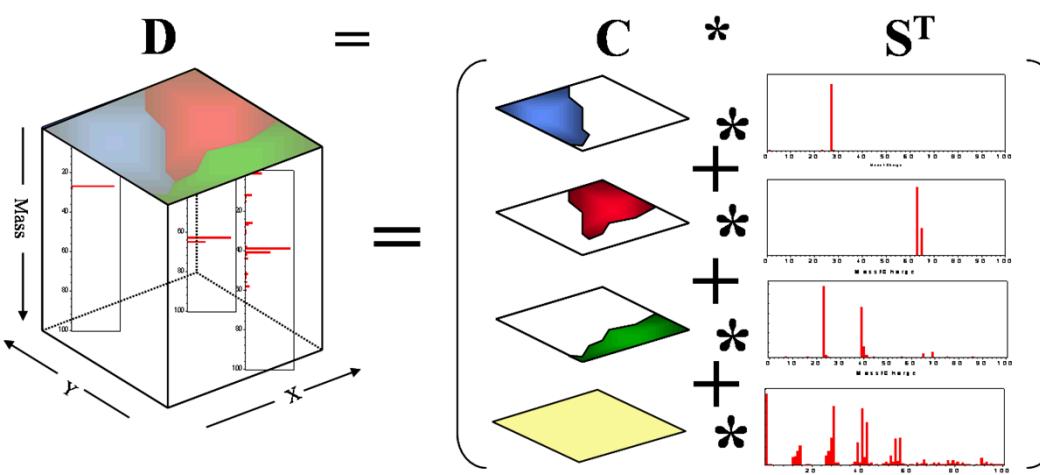
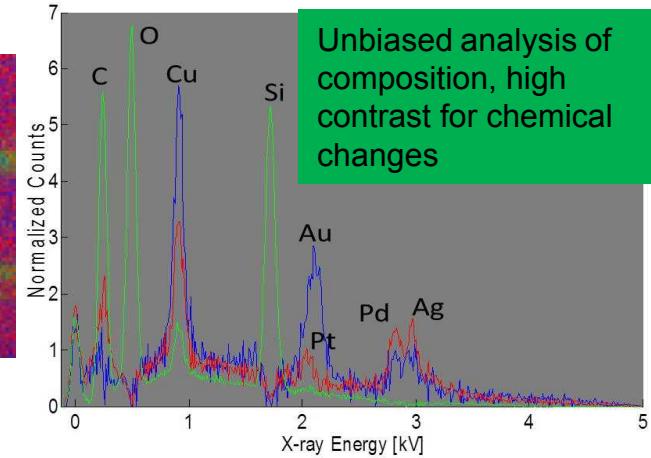
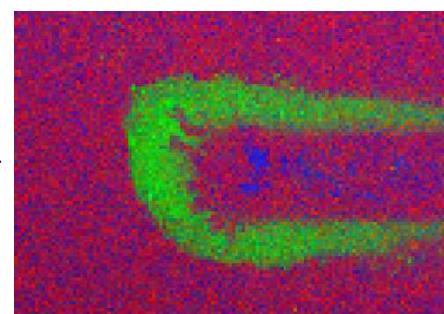
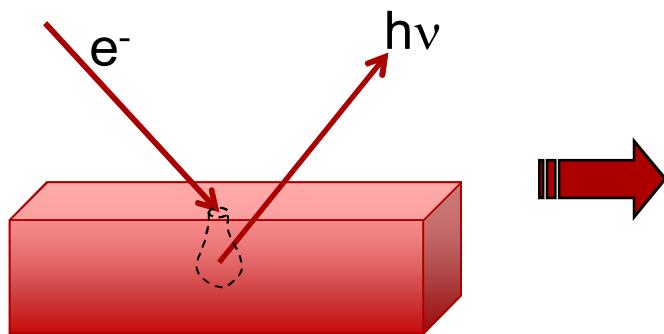
Paul Kotula for TEM and AXSIA

Rand Garfield for friction tester development

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# Multivariate Analysis Of EDS Data Allows Unbiased Detection of Composition Changes

Energy Dispersive x-ray Spectroscopy (EDS)  
+ Automated eXpert Spectral Image Analysis (AXSIA)



- solve  $D = C * S^T$  using constrained alternating least squares
- constrain to physically realistic solutions
- number of components  $C$  is the minimum needed to reconstruct the original data, minus noise
- no bias or assumptions; rapidly identifies subtle changes

M. Keenan and P. Kotula, *Surf. Interface Analysis* **36** (2004) p. 2433