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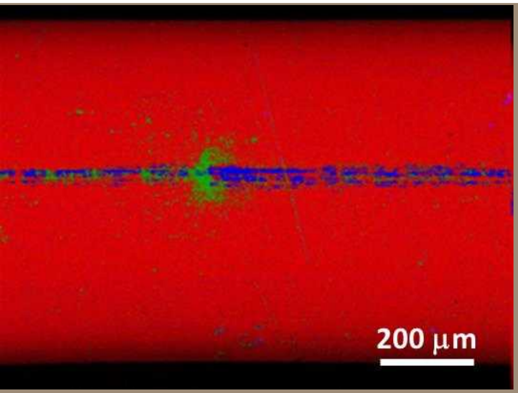
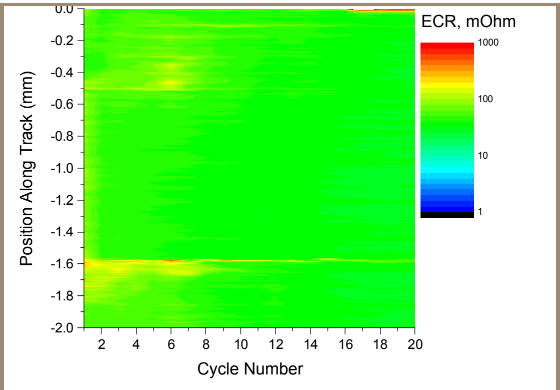
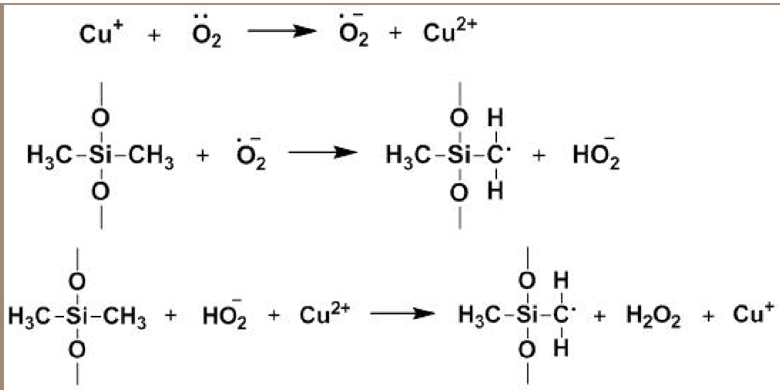
SAND2014-19029C







Degradation of Sliding Electrical Contacts Submerged in Silicone Fluid

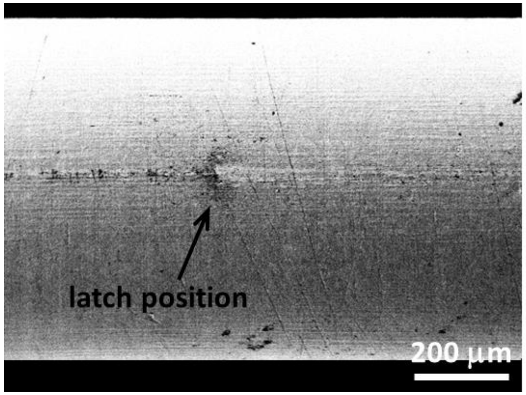
M.T. Dugger, D. Groysman, M.C. Celina, T.M. Alam, M.K. Alam, N. Argibay, B.L. Nation and S.V. Prasad

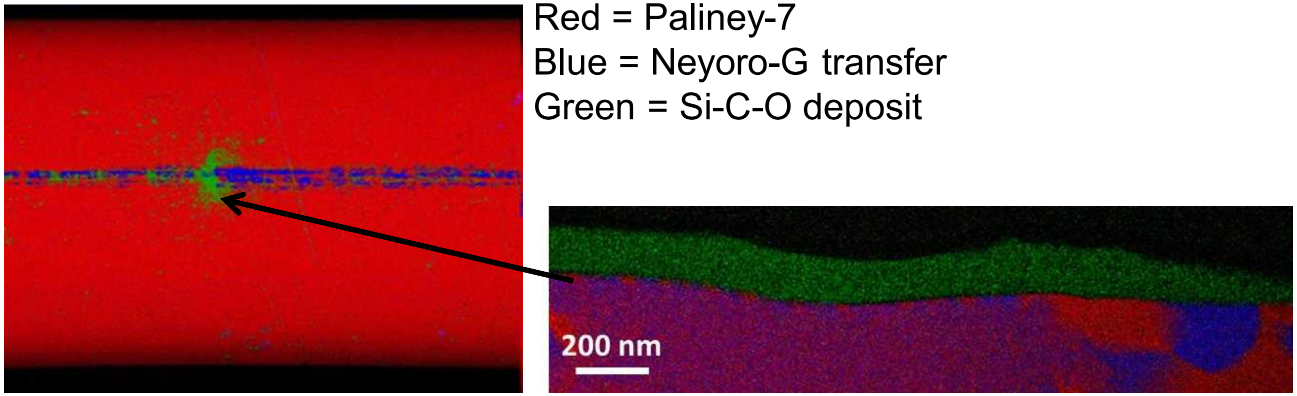
2014 Tribology Frontiers Conference, 26-28 October 2014, Rosemont, IL

Background

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

- contacts are precipitation hardened electrical contact alloys; a Neyoro-G spring slides on the side of a Paliney-6 or -7 pin (Deringer-Ney Company)
- the device is filled with PDMS-200 silicone fluid (Dow Chemical Company)





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

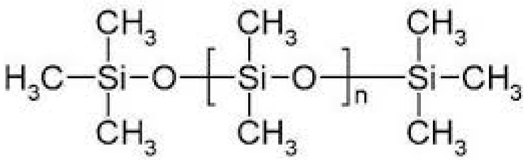
EDS/AXSIA image of a focused Ion Beam (FIB) cross section through deposit

atomic %

	Pd	Ag	Cu	Pt	Ni	Zn	Au
Paliney-6	39.8	33.9	24.2	0.5	1.6	0.01	NA
Paliney-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

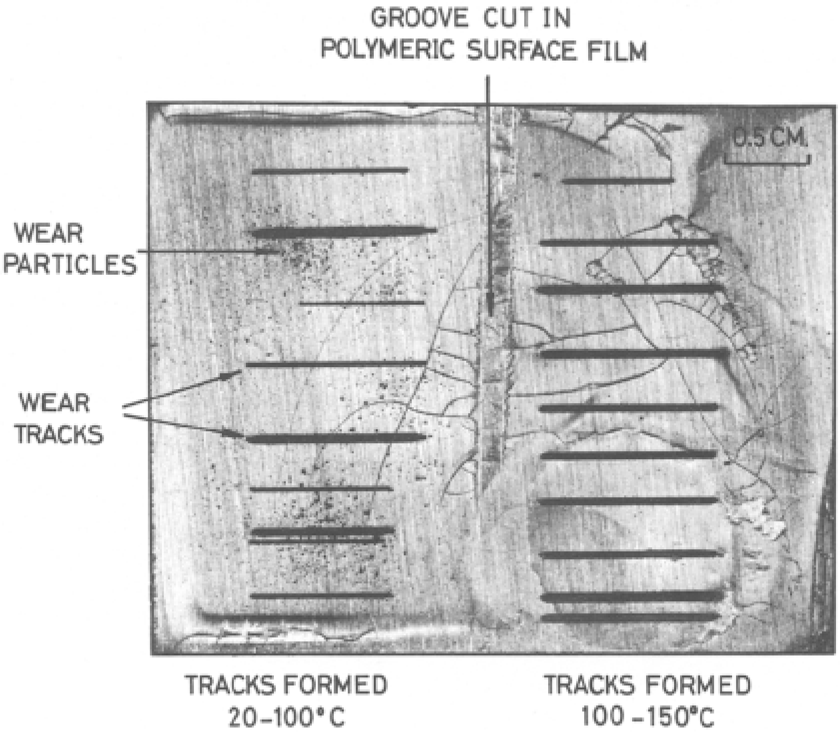
Interaction of Silicone Fluids with Metals

polydimethylsiloxane (PDMS)



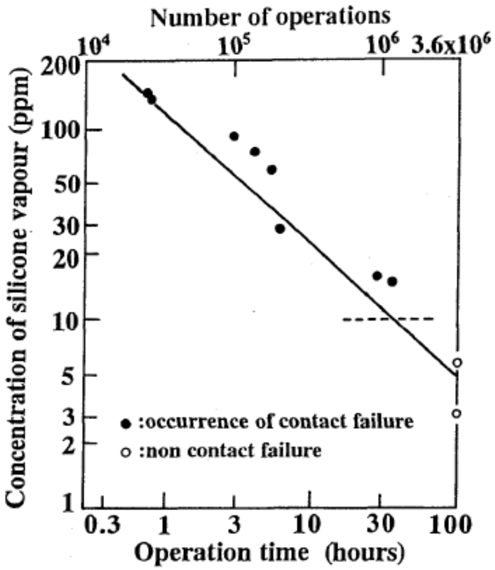
$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

- many organic species form “friction polymer;” PDMS inert below 200^{o}C
  - H.W. Hermance and T.F. Egan, Bell System Tech. J. **37** (1958) pp. 739-776
- heated surfaces improve elastohydrodynamic lubrication
- film forms on copper at > 100^{o}C
  - D. Tabor and R.F. Willis, Wear **13** (1969) p. 413-442
- added as a lubricant to resist contact fretting and polymer formation
  - M. Antler, ASLE Trans. **26** (1983) pp. 376-380

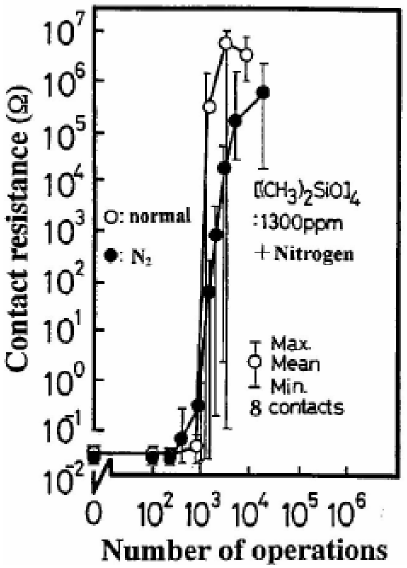


D. Tabor and R.F. Willis, Wear 11 (1968) pp. 145-162

Electrical Contact Degradation by Silicones



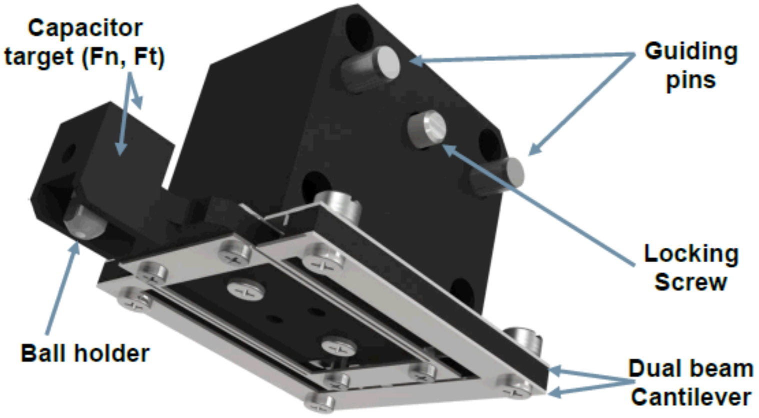
T. Tamai and M. Aramata, Proc. IEEE Holm Conference on Electrical Contacts, Pittsburgh, PA, 27-29 Sept. 1993



T. Tamai, 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

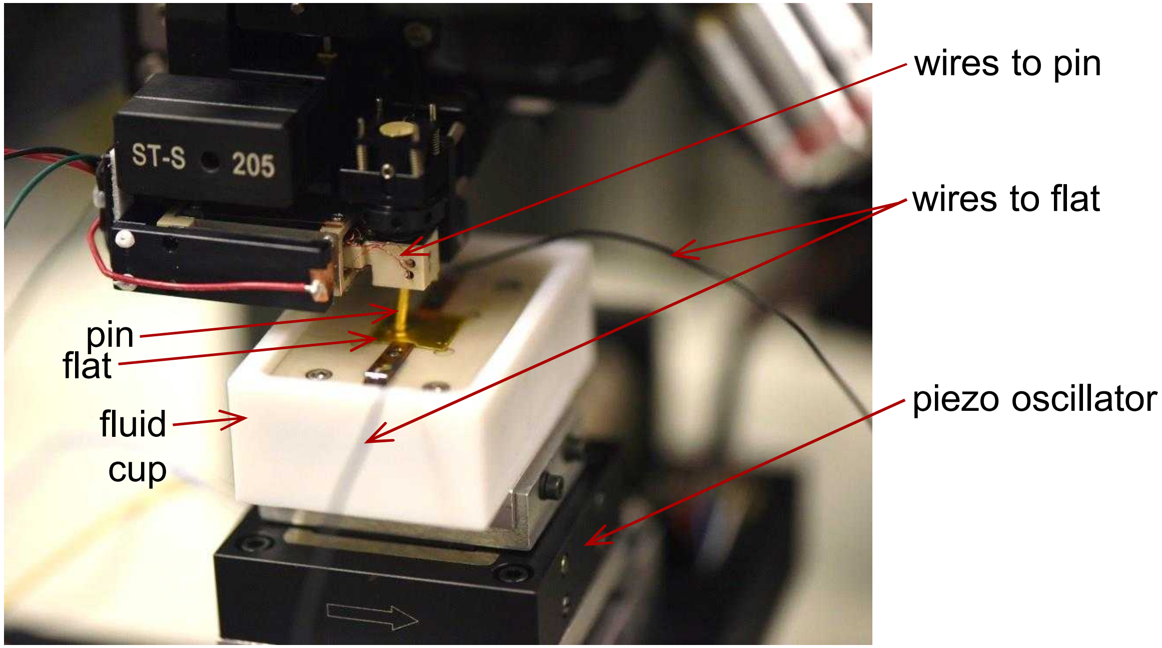


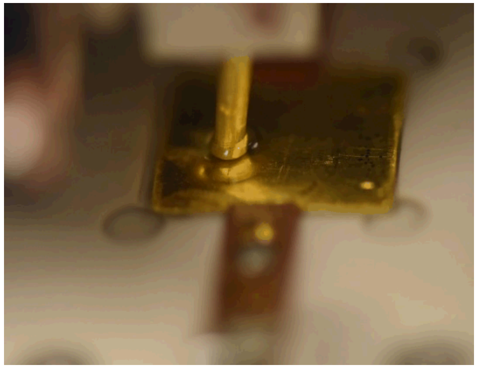
CSM nanotribometer modified for 4-wire ECR measurement

- DC power supply
- micro-ohm meter

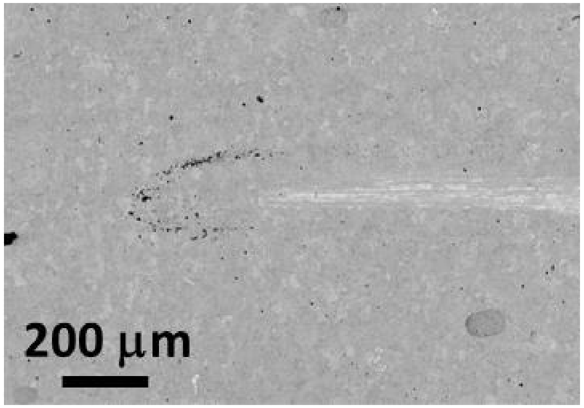
Test parameters:

- N = 88 mN
- pin radius = 1.6 mm
- track length = 1 to 2 mm
- fluid volume = 5 mL
- i = 20 mA, 1.1 V open circuit
- vibe = 50 μm at 100 Hz

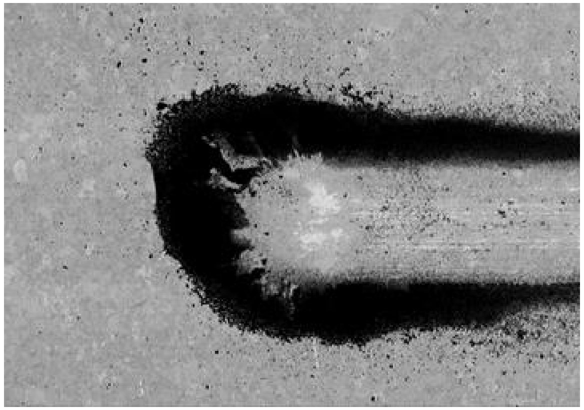




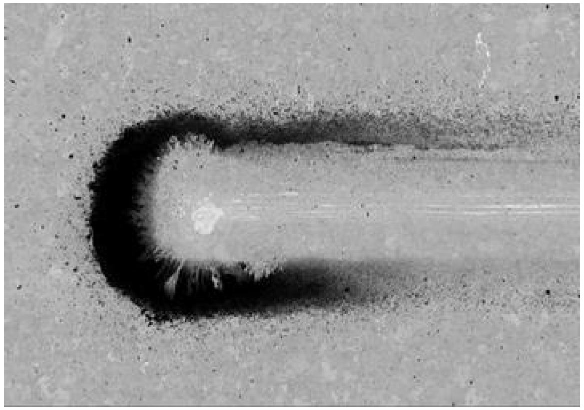
Pin-on-Flat Tests



current + no vibration



current + vibration



no current + vibration

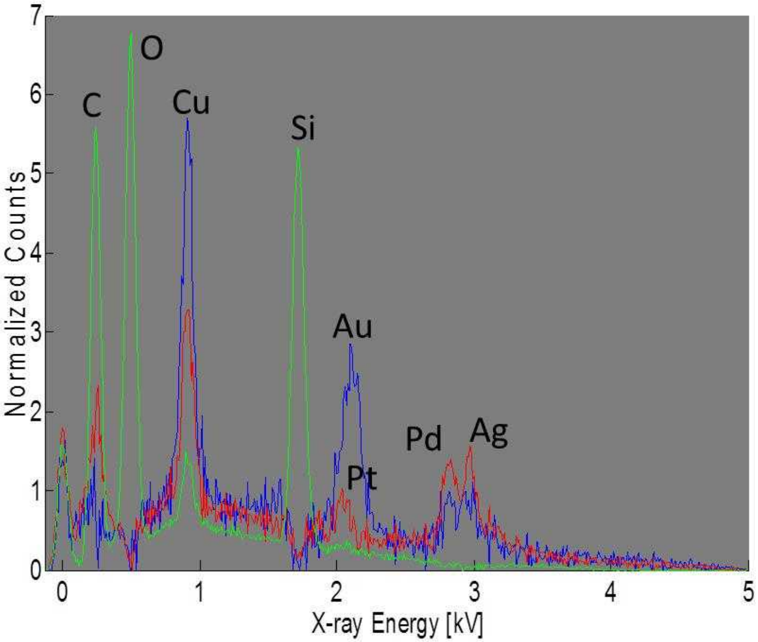
Initial experiments focused on the role of contact parameters in deposit formation

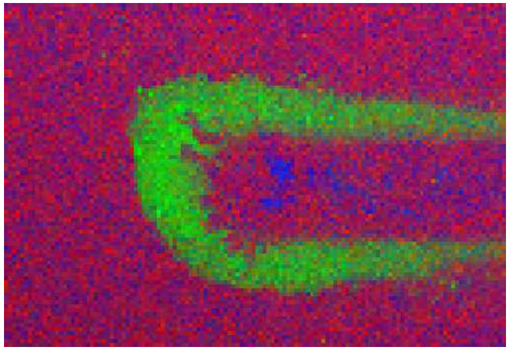
- current alone produced gold transfer, but very little deposit
- suspected make-break arcs during movement, leading to thermal decomposition of silicone

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

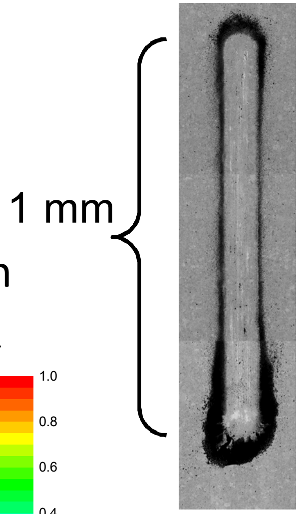
- Deposit contains constituents of the silicone fluid
- Composition identical to that on accelerometer pins
- Surface analytical methods (Auger, XPS, ToF-SIMS) provided no insight into deposit formation mechanism

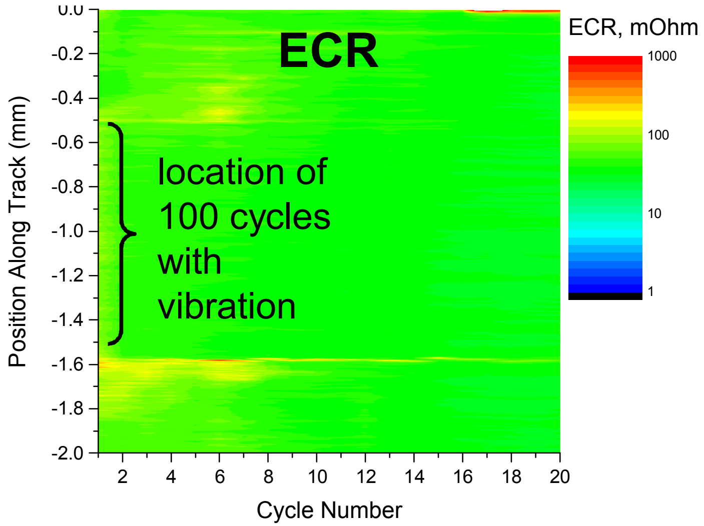
Relating Deposit to ECR Change

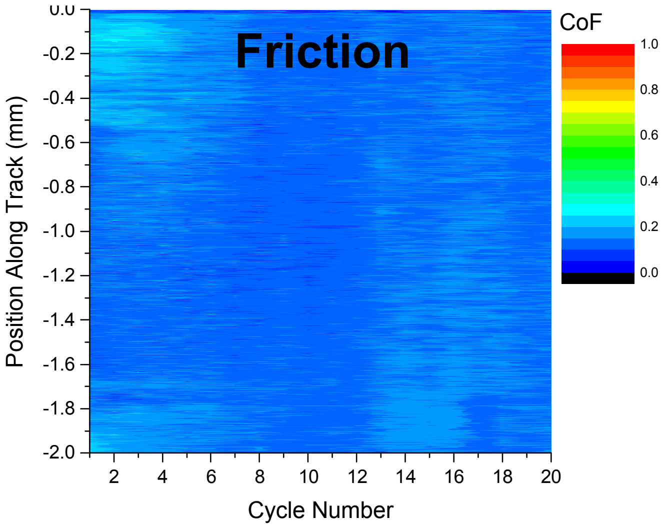
Procedure:

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 μm 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

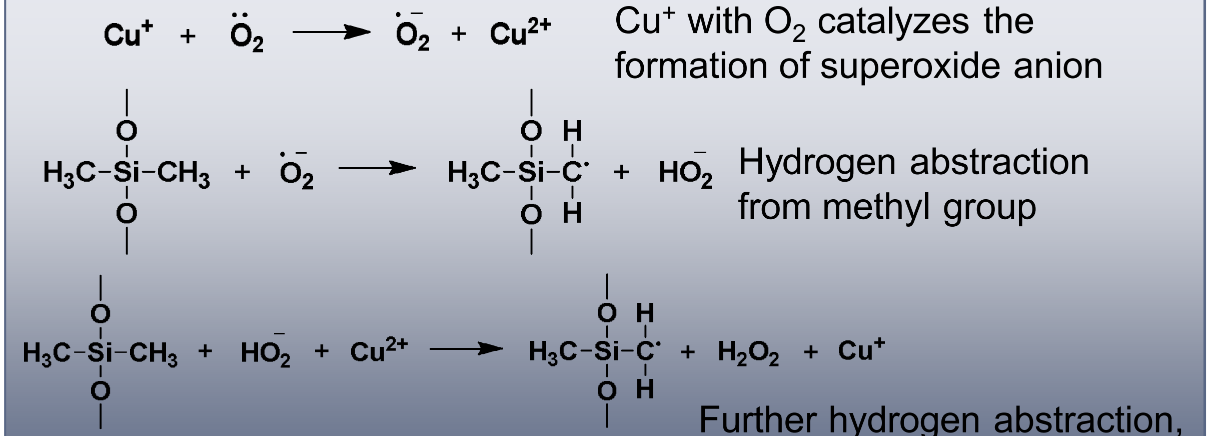






Increased ECR is observed when pin slides over deposit

Silicone Polymer Degradation



$$Cu^{+} + \ddot{O}_2 \longrightarrow \dot{O}_2^{-} + Cu^{2+}$$

Cu+ with O_2 catalyzes the formation of superoxide anion

$$H_3C{-}Si(O)(O){-}CH_3 + \dot{O}_2^{-} \longrightarrow H_3C{-}Si(O)(O){-}\dot{C}H_2 + HO_2^{-}$$

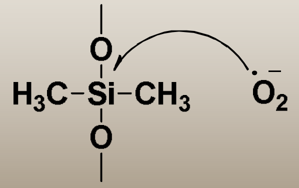
Hydrogen abstraction from methyl group

$$H_3C{-}Si(O)(O){-}CH_3 + HO_2^{-} + Cu^{2+} \longrightarrow H_3C{-}Si(O)(O){-}\dot{C}H_2 + H_2O_2 + Cu^{+}$$

Further hydrogen abstraction, hydroperoxide formation and Cu+ regeneration

Pathway I
Side Group Oxidation

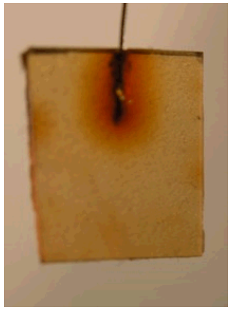
- Direct attack of superoxide anion
- Suggested in limited literature



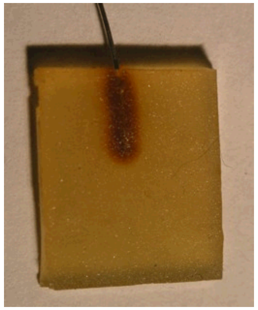
$$H_3C{-}Si(O)(O){-}CH_3 \quad \dot{O}_2^{-}$$

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

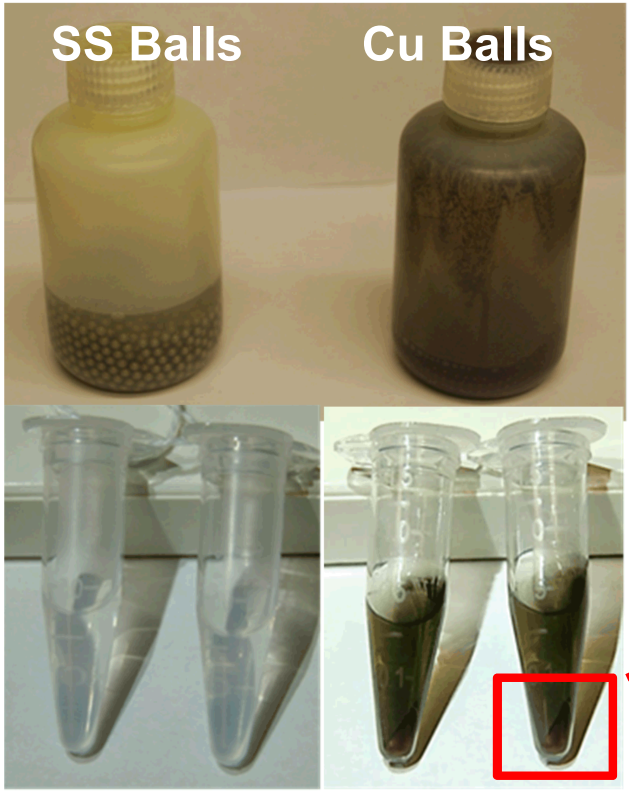


PBAN polymer
1.4 y at RT

Degradation facilitated by Cu ions despite tin coating

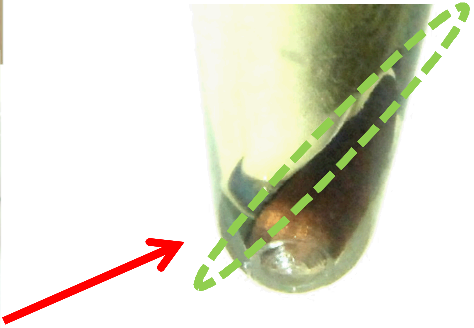
The “Tumble Test”

rock tumbler



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

fluid centrifuged
thin black film isolated

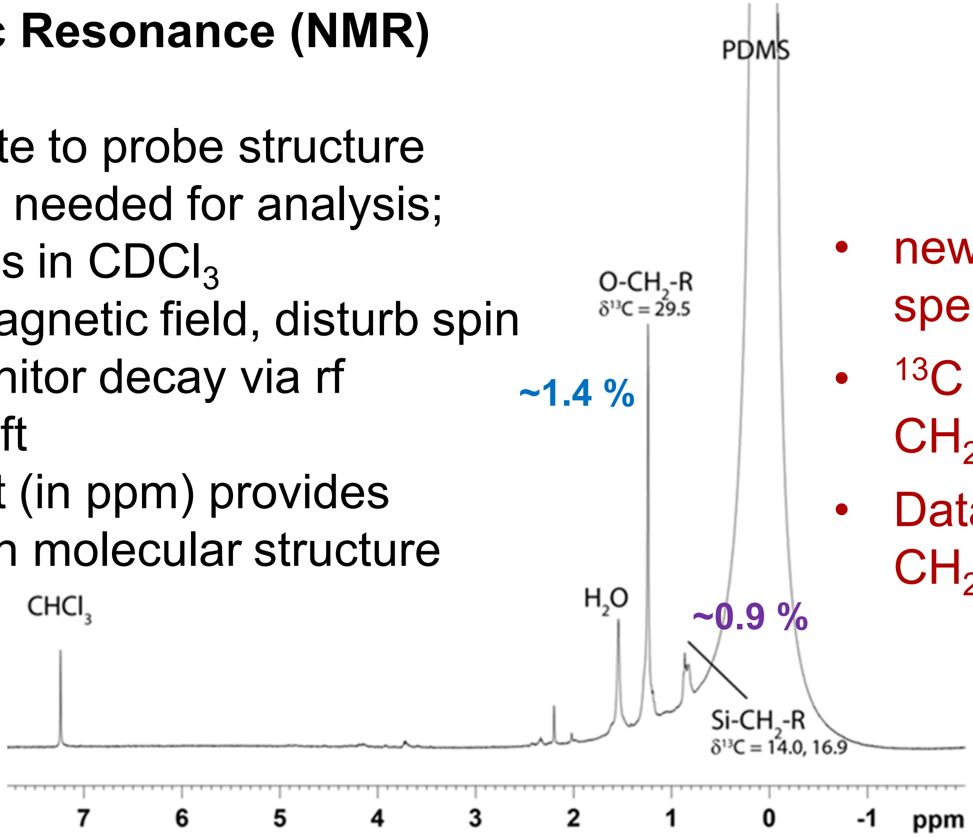


- degradation is not due to fluid shear, since the squeeze film shear rate would be greater with SS balls (greater mass)
- not thermal decomposition since interfacial flash temperature during contact would be higher for steel balls (greater impact energy and lower thermal conductivity)

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

Nuclear Magnetic Resonance (NMR) Spectroscopy

- uses spin state to probe structure
- mg quantities needed for analysis; dissolve solids in $CDCl_3$
- in a strong magnetic field, disturb spin state and monitor decay via rf frequency shift
- chemical shift (in ppm) provides information on molecular structure

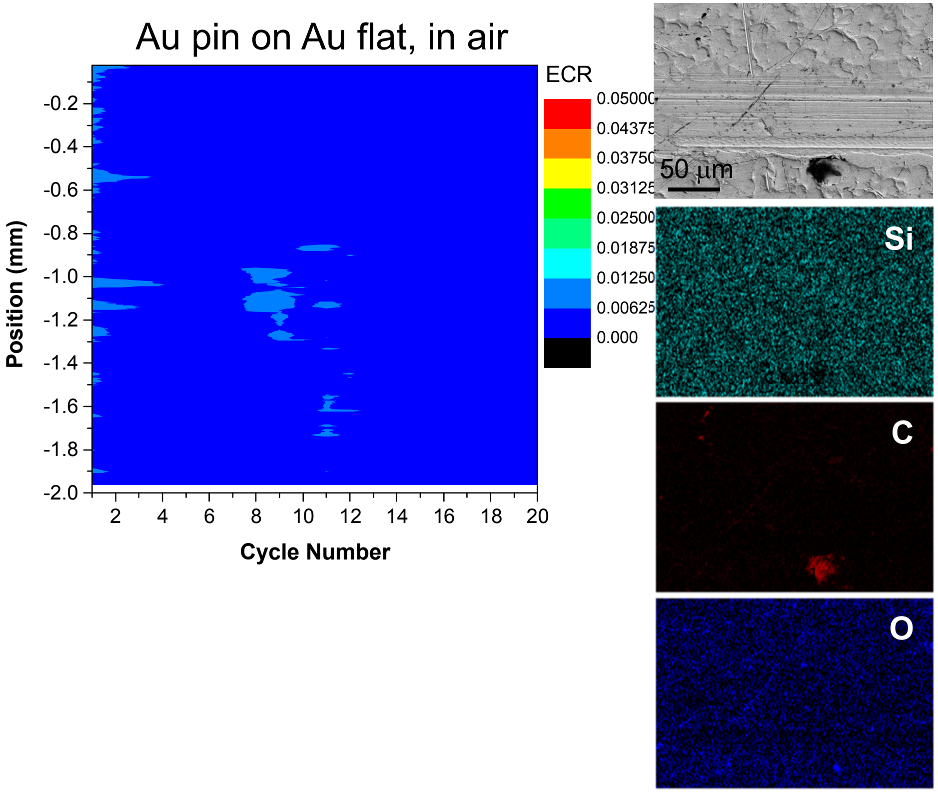


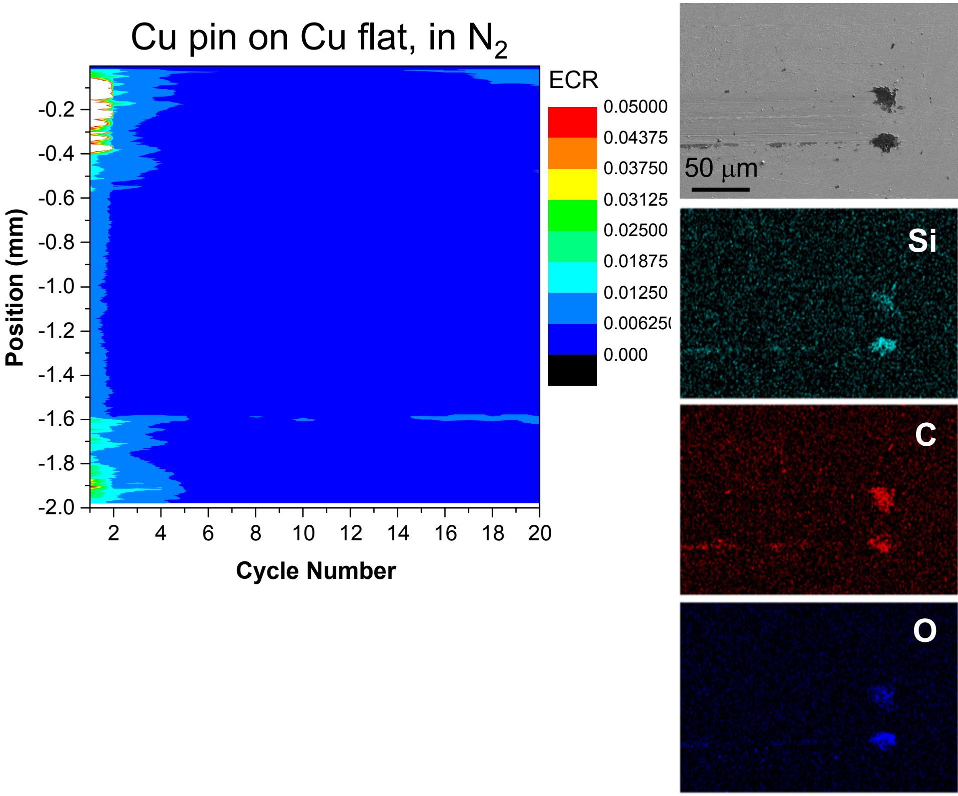
- new organic degradation species observed
- ^{13}C NMR reveals these are CH_2 species
- Data bases suggest a $O\text{-}CH_2\text{-}R$ linkage

$$\text{chemical shift} = \frac{\text{peak position relative to TMS, Hz}}{\text{spectrometer frequency, MHz}}$$

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

Testing the Reaction Hypothesis


Au pin on Au flat, in air


Cu pin on Cu flat, in N_2

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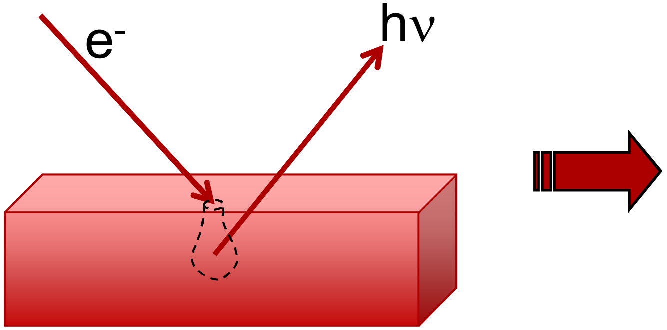
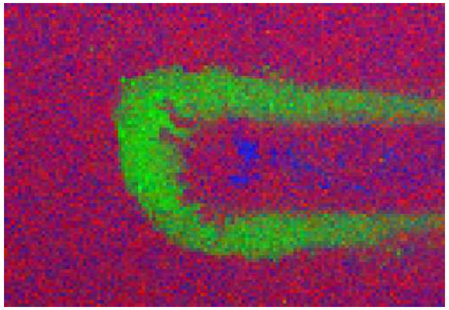
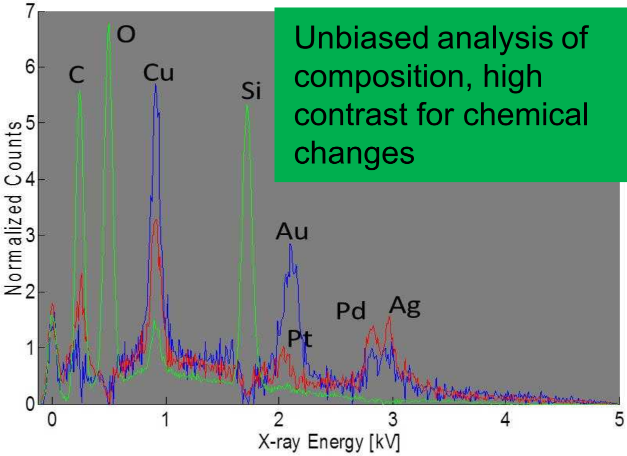
Multivariate Analysis Of EDS Data Allows Unbiased Detection of Composition Changes

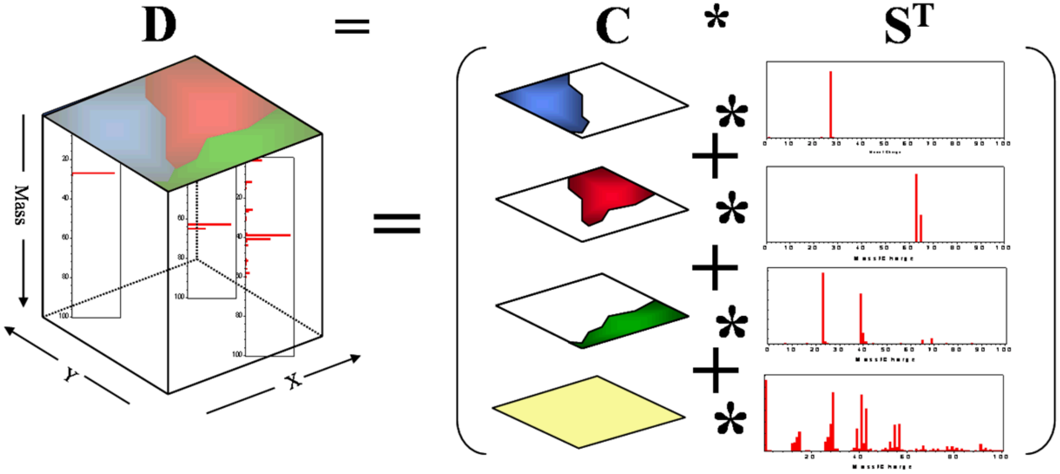
Energy Dispersive x-ray Spectroscopy (EDS)
+ Automated eXpert Spectral Image Analysis (AXSIA)







Unbiased analysis of composition, high contrast for chemical changes



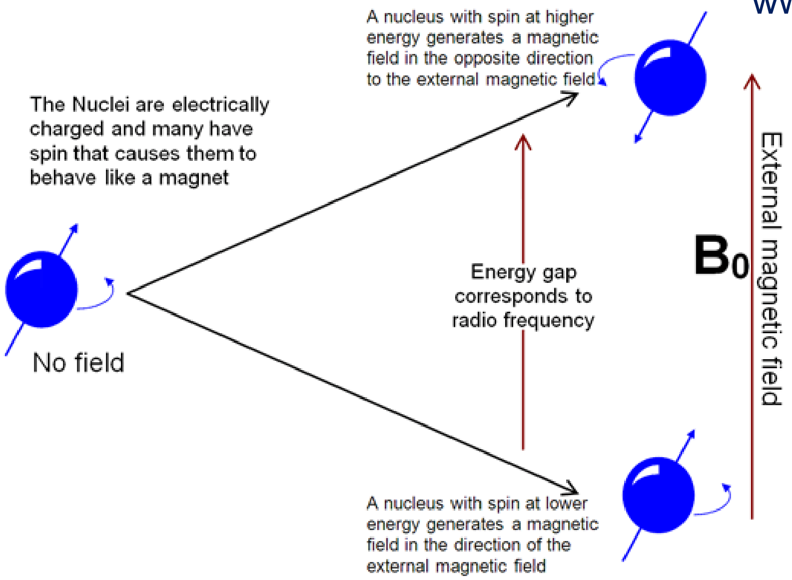
- solve $D=C*S^T$ using constrained alternating least squares
- constrain to physically realistic solutions
- number of components C is the minimum needed to reconstruct the original data, minus noise
- no bias or assumptions; rapidly identifies subtle changes

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

Nuclear Magnetic Resonance (NMR) Spectroscopy

www/sandia.gov/nmr_lab

- based on the alignment of atomic nuclei in strong magnetic fields to produce different energy levels
- alignment is disturbed with an electromagnetic field to produce rf frequencies (5 to 1000 MHz)
- most nuclei have a NMR active isotope (see periodic table) which resonates at a distinct rf frequency
- the local nuclear environment (bonding, solvent, nearest neighbor, J coupling, etc.) provide additional frequency shifts, giving high resolution spectra used to probe structural details



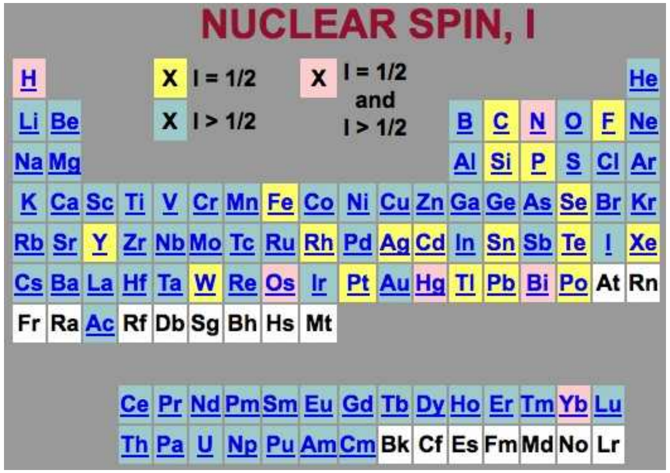
The case of the spin-½ nucleus

The Nuclei are electrically charged and many have spin that causes them to behave like a magnet

A nucleus with spin at higher energy generates a magnetic field in the opposite direction to the external magnetic field

A nucleus with spin at lower energy generates a magnetic field in the direction of the external magnetic field

Energy gap corresponds to radio frequency



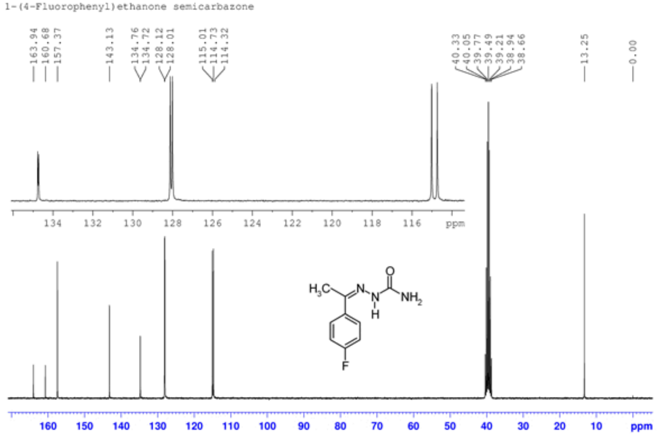
NUCLEAR SPIN, I

🟨 X I = 1/2

🟦 X I > 1/2

🟥 X I = 1/2 and I > 1/2

🟥 H																	🟦 He
🟦 Li	🟦 Be											🟦 B	🟨 C	🟥 N	🟦 O	🟨 F	🟦 Ne
🟦 Na	🟦 Mg											🟦 Al	🟨 Si	🟨 P	🟦 S	🟦 Cl	🟦 Ar
🟦 K	🟦 Ca	🟦 Sc	🟦 Ti	🟦 V	🟦 Cr	🟦 Mn	🟨 Fe	🟦 Co	🟦 Ni	🟦 Cu	🟦 Zn	🟦 Ga	🟦 Ge	🟦 As	🟨 Se	🟦 Br	🟦 Kr
🟦 Rb	🟦 Sr	🟨 Y	🟦 Zr	🟦 Nb	🟦 Mo	🟦 Tc	🟦 Ru	🟨 Rh	🟦 Pd	🟨 Ag	🟨 Cd	🟦 In	🟨 Sn	🟦 Sb	🟨 Te	🟦 I	🟨 Xe
🟦 Cs	🟦 Ba	🟦 La	🟦 Hf	🟦 Ta	🟨 W	🟦 Re	🟥 Os	🟦 Ir	🟨 Pt	🟦 Au	🟥 Hg	🟨 Tl	🟨 Pb	🟥 Bi	🟨 Po	At	Rn
Fr	Ra	🟦 Ac	Rf	Db	Sg	Bh	Hs	Mt									
			🟦 Ce	🟦 Pr	🟦 Nd	🟦 Pm	🟦 Sm	🟦 Eu	🟦 Gd	🟦 Tb	🟦 Dy	🟦 Ho	🟦 Er	🟦 Tm	🟥 Yb	🟦 Lu	
			🟦 Th	🟦 Pa	🟦 U	🟦 Np	🟦 Pu	🟦 Am	🟦 Cm	Bk	Cf	Es	Fm	Md	No	Lr	



1-(4-Fluorophenyl)ethanone semicarbazone

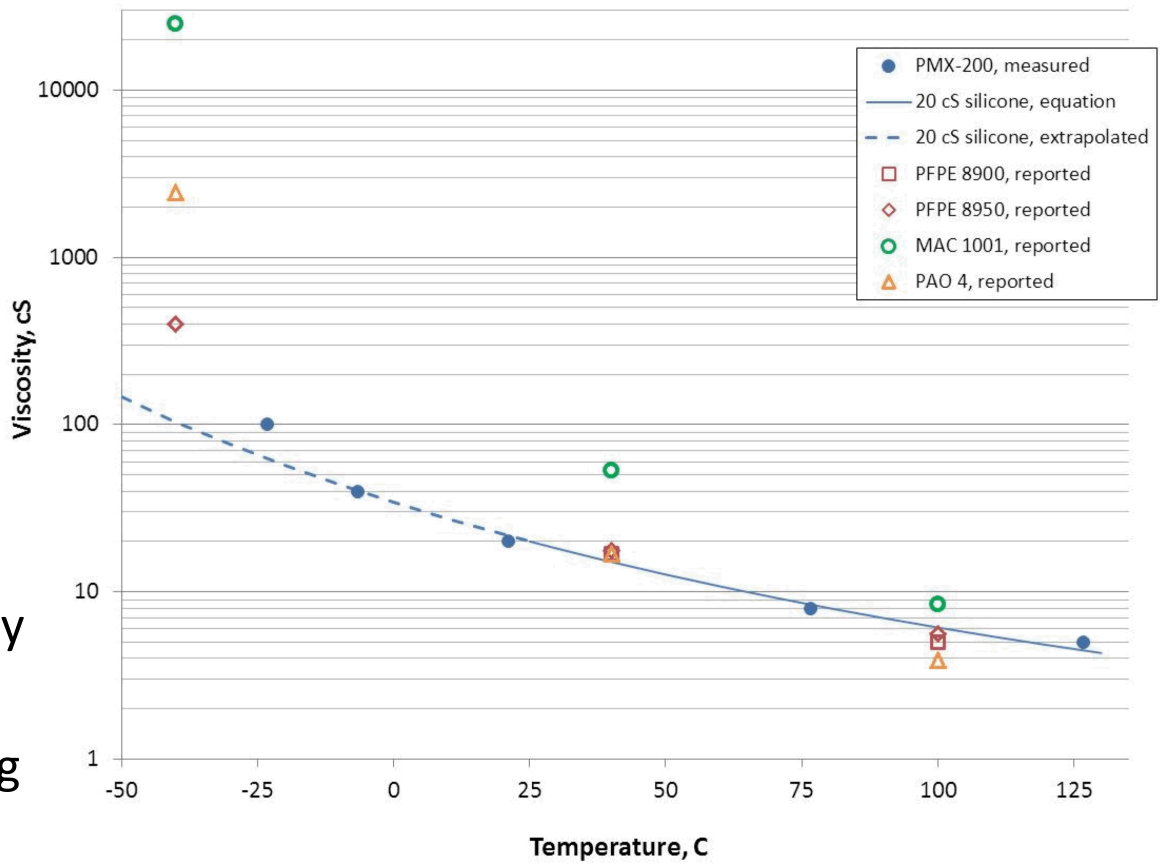
Silicone Fluids

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