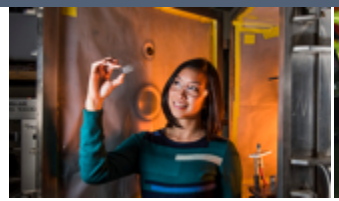
SAND2022-14617C

Sandia National Laboratories

Tribopolymer Film Formation on Sliding Electrical Contacts Exposed to Siloxanes



Nic Argibay[1], John Curry[2], Don Susan[2], Mike Dugger[2]

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Holm Conference, Tampa FL
October 26, 2022

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Introduction

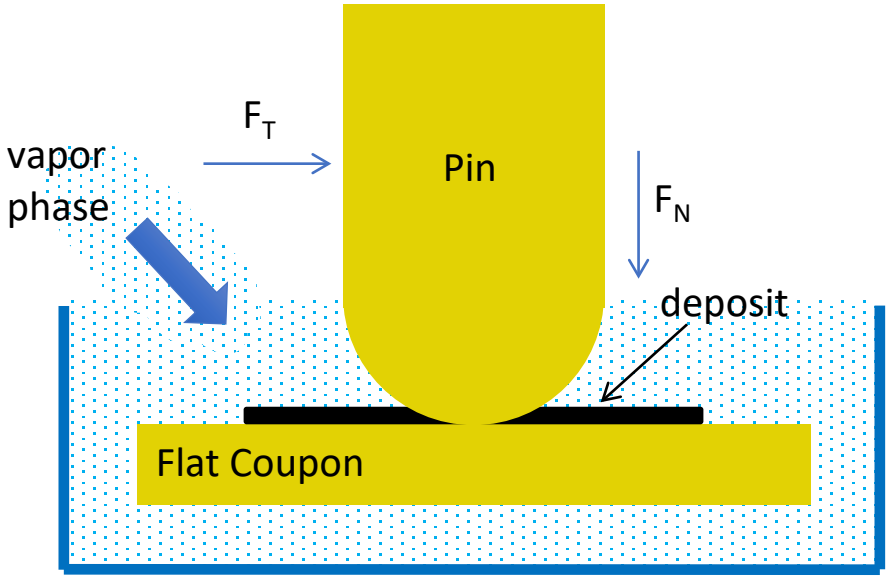
- Friction polymer (tribopolymer) formation was studied in a laboratory environment with outgassing epoxy (Loctite EA9394), i.e. vapor-phase environment. Build on previous studies of film formation in *liquid* silicone oil (PDMS – polydimethylsiloxane), *Mike Dugger et al., Holm Conference 2015.*

- Friction polymer formation from a specific outgassing vapor species, octamethyltrisiloxane (OMTS), has also been confirmed in the laboratory.

- Sliding contact friction experiments are discussed.

  - Electrical contact resistance (ECR) measurements correlate to film formation as well.

  - Morphology, thickness, and chemical signature of the tribopolymer film on precious metal electrical contact alloys (Paliney-7, Neyoro-G, Deriney -72) will be outlined.



Electrical Contact Resistance is a longstanding issue of concern

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
Materials Science and Engineering, and Engineering Design and Integration Centers
Sandia National Laboratories
Albuquerque, New Mexico, USA
mtdugge@sandia.gov

2015

A Tribochemical Investigation of the Reaction Products on Pd Plated Contacts

A. Shinchi *, Y. Imada, F. Honda and K. Nakajima

1995

THE FORMATION OF FRICTIONAL POLYMERS ON NOBLE METAL SURFACES

Ernest Rabinowicz and Scott W. Webber

Department of Mechanical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139, U.S.A.

1982

EFFECT OF LUBRICANTS ON FRICTION POLYMERIZATION AND THE CONTACT RESISTANCE OF PALLADIUM

Morton Antler
Bell Telephone Laboratories, Inc.
Columbus, Ohio 43213 U.S.A.

1982

TABLE IV — BEHAVIOR OF VARIOUS SLIDING SURFACES IN BENZENE VAPOR

(4 × 10^6 Wipes, 170-Micron Stroke, 120 Cycles/Sec, 30-gm Force)

...d, in Benzene-Saturated Air)

Hermance and Egan, 1958

SCR-18

Sandia Corporation

REPRINT

CONTACT-RESISTANCE SYMPOSIUM

BENDIX AVIATION CORPORATION,
KANSAS CITY DIVISION
SANDIA CORPORATION

JUNE 14, 1957
ALBUQUERQUE, NEW MEXICO

Those compounds which produced the largest amount of polymer under the same conditions were principally the aromatic hydrocarbons, including:

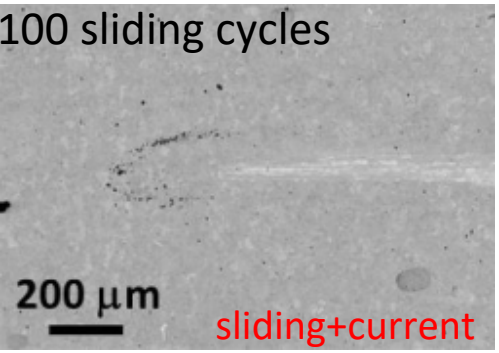
Benzene	Crotonaldehyde
Toluene	Butyraldehyde
Xylene	Cyclohexanone
Naphthalene	Limonene
Cyclohexene	Styrene
Acrolein	Benzaldehyde
Acrylonitrile	

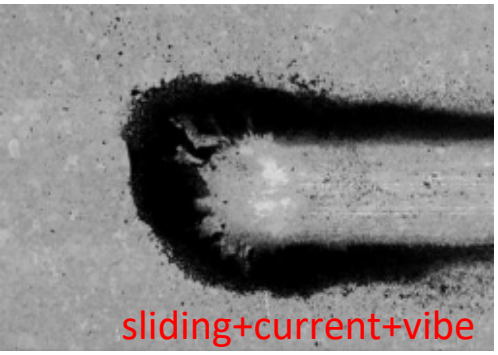
Ney Handbook, 1960

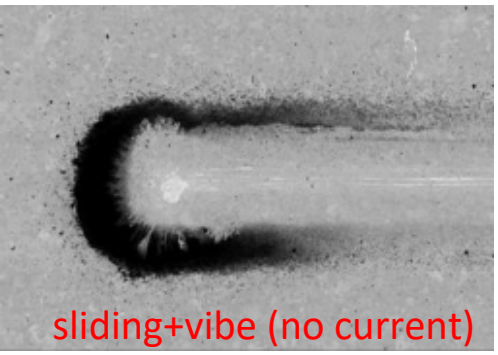
Frictional polymer ranges in color from a light brown to black after enough has formed so that it is readily visible in its powdery amorphous form. Fortunately, it is rather fragile material and readily pushed to the side of the wiper track by the sliding motion. It takes on an electrostatic charge readily and clings to the metallic surfaces adjacent to the areas of contact,

History: Friction Polymer Formation in *Silicone-Fluid Filled Devices* (~2014-present)

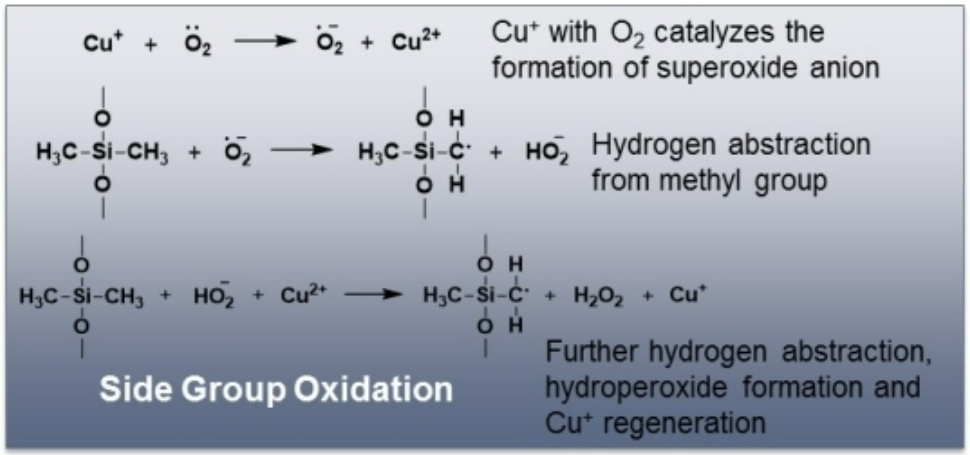
Backscatter Electron Image, 100 sliding cycles







Demonstrated Reaction Pathway



New peaks associated with PDMS radicals

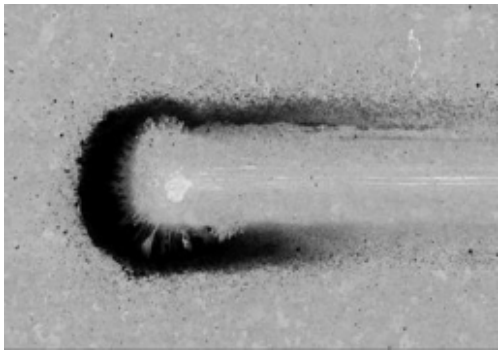
Nuclear Magnetic Resonance (NMR) Spectroscopy

- Crosslinked PDMS deposit is created during mechanical contact, *without current* (*M.T. Dugger et. al, Holm Conference 2015*)
- Todd Alam, Characterization of PDMS (SiCO) thin film growth on Copper Metal Surfaces, National ACS Meeting, 2014.

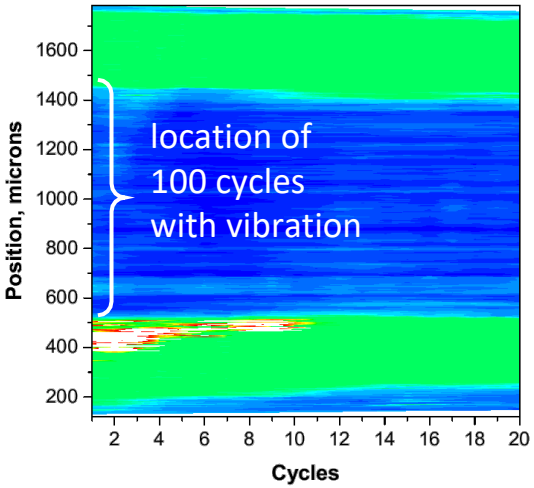
PDMS = polydimethylsiloxane

History: Contact Resistance Maps in PDMS Fluid

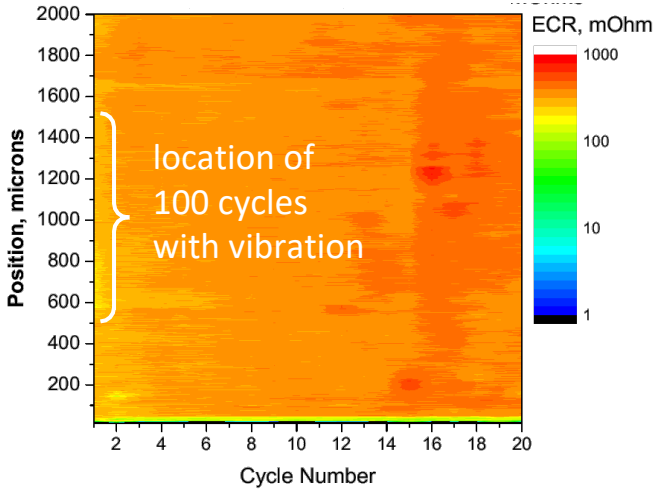
20 cS PDMS fluid, 50 mN load



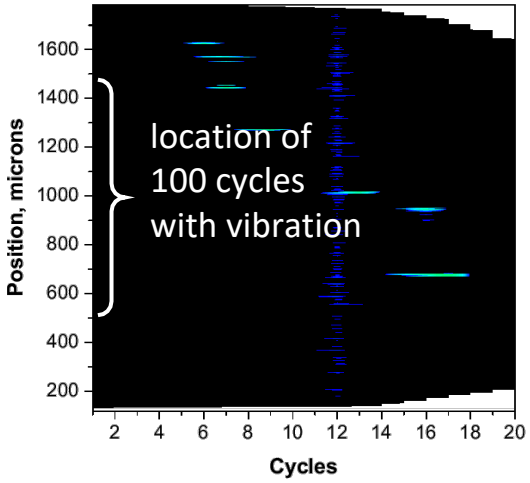
Paliney-7 on Neyoro-G



Cu on Cu



Au on Au

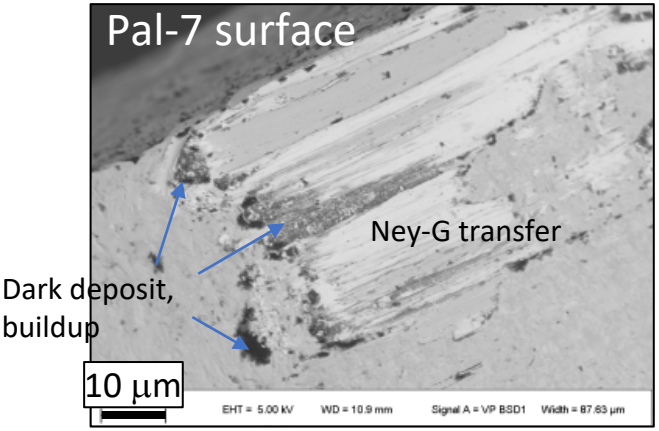


- Electrical contact alloys form insulative deposits at edges of sliding track
- Cu exhibits ECR of 100's of mΩ everywhere
  - dynamic deposit formation during ECR mapping
- Au exhibits ECR of a few mΩ everywhere; no deposit formation

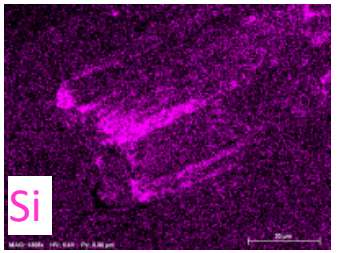
(methyl side group oxidation that leads to PDMS crosslinking does not occur in self-mated gold contacts)

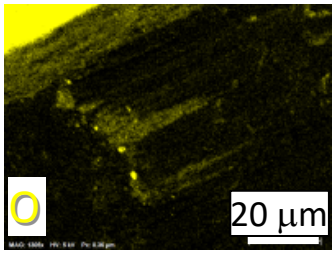
Recent issue: High electrical contact resistance in sliding precious metal contact pairs due to *Epoxy Outgassing Effects*

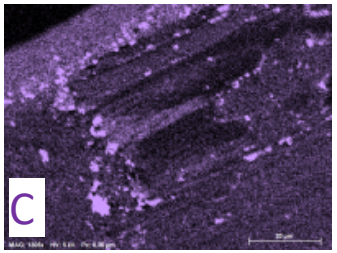
- Investigation *suggested* that friction polymer formation (and other contamination) was a key aspect of high contact resistance. Si-C-O in the film, source is less obvious in this case.
- Epoxy outgassing was identified as a likely source of film formation. Frictional (sliding) contact is required to polymerize this layer.

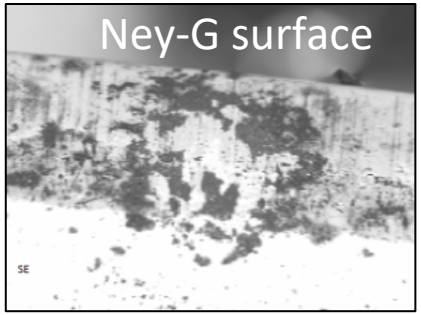


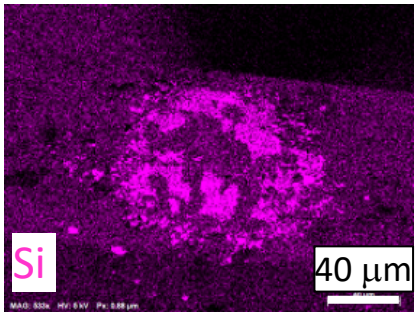
EDS maps show Si, C, O in dark areas

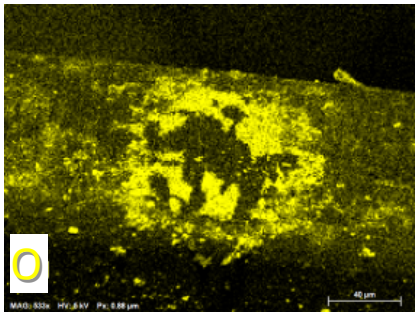


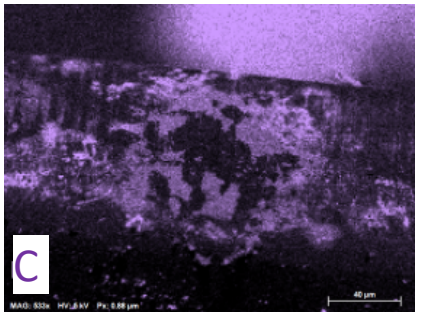






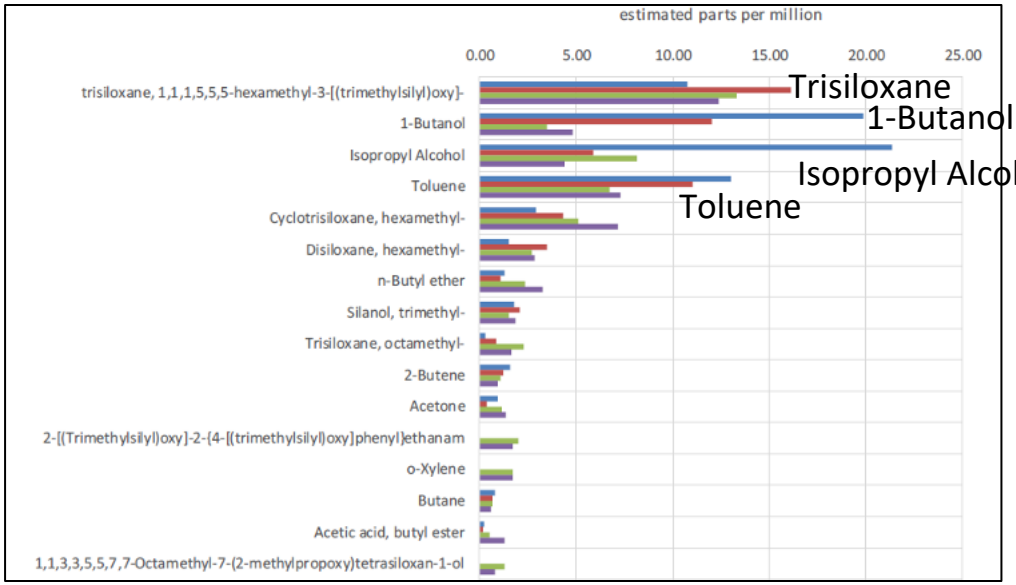






Outgassing Species from Epoxies

RGA Anaylsis



Outgassing analyses from electrical components with 3 different epoxies present. Results show siloxanes, alcohol, toluene, acetone, etc.

Some known “bad actors” for friction polymer formation

Epoxies present:

EC-2216 (no longer used)

Abelfilm (used as solid preform disk)

EA-9394 (Loctite)

Those compounds which produced the largest amount of polymer under the same conditions were principally the aromatic hydrocarbons, including:

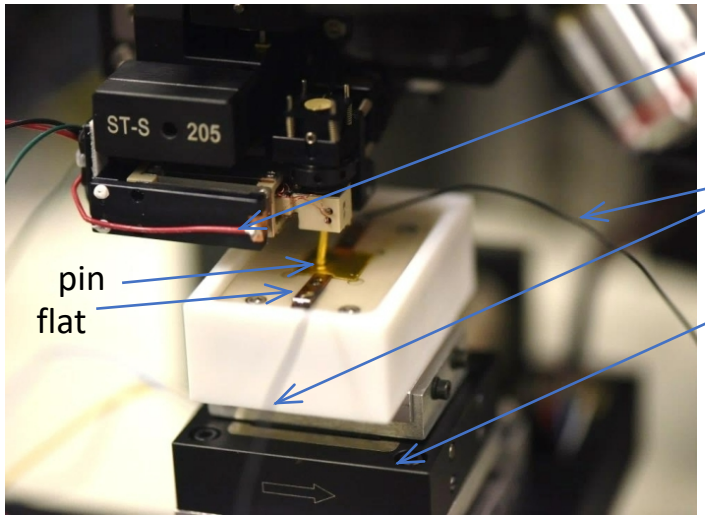
Benzene	Crotonaldehyde
Toluene	Butyraldehyde
Xylene	Cyclohexanone
Naphthalene	Limonene
Cyclohexene	Styrene
Acrolein	Benzaldehyde
Acrylonitrile	

Ney Handbook, 1960

Frictional polymer ranges in color from a light brown to black after enough has formed so that it is readily visible in its powdery amorphous form. Fortunately, it is rather fragile material and readily pushed to the side of the wiper track by the sliding motion. It takes on an electrostatic charge readily and clings to the metallic surfaces adjacent to the areas of contact,

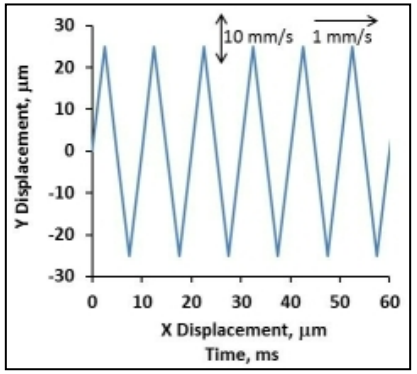
Can We Reproduce this Phenomenon in the Laboratory?

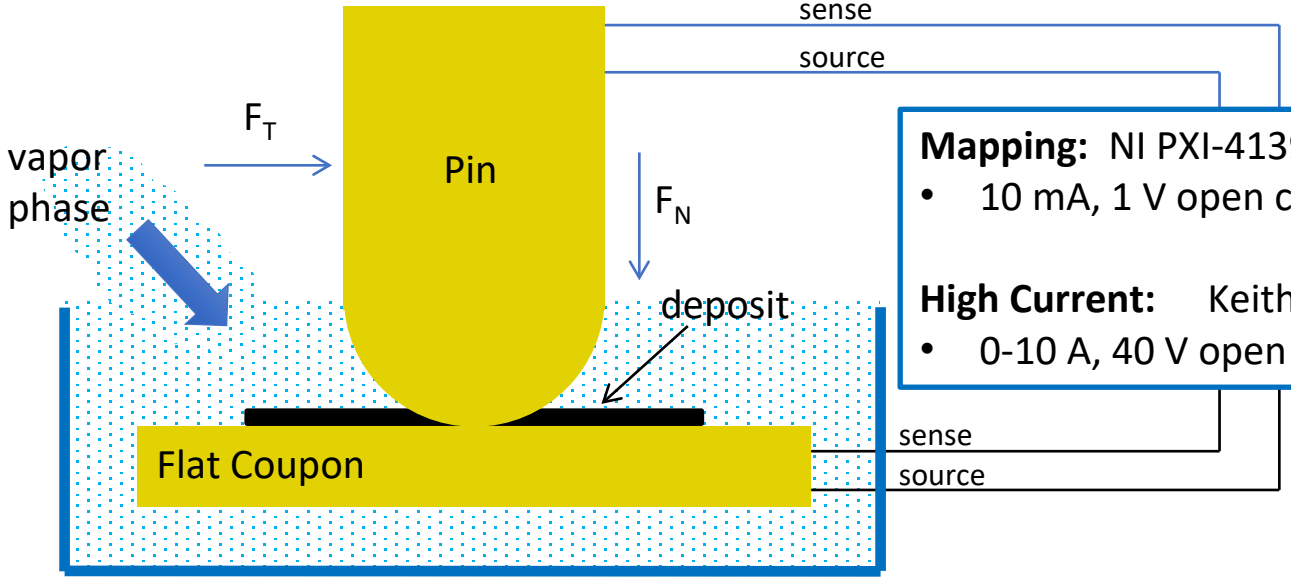
Experimental Setup



Nanotribometer modified for 4-wire Electrical Contact Resistance measurement

Simulated vibration during testing. ECR and friction coefficient mapped as a function of position



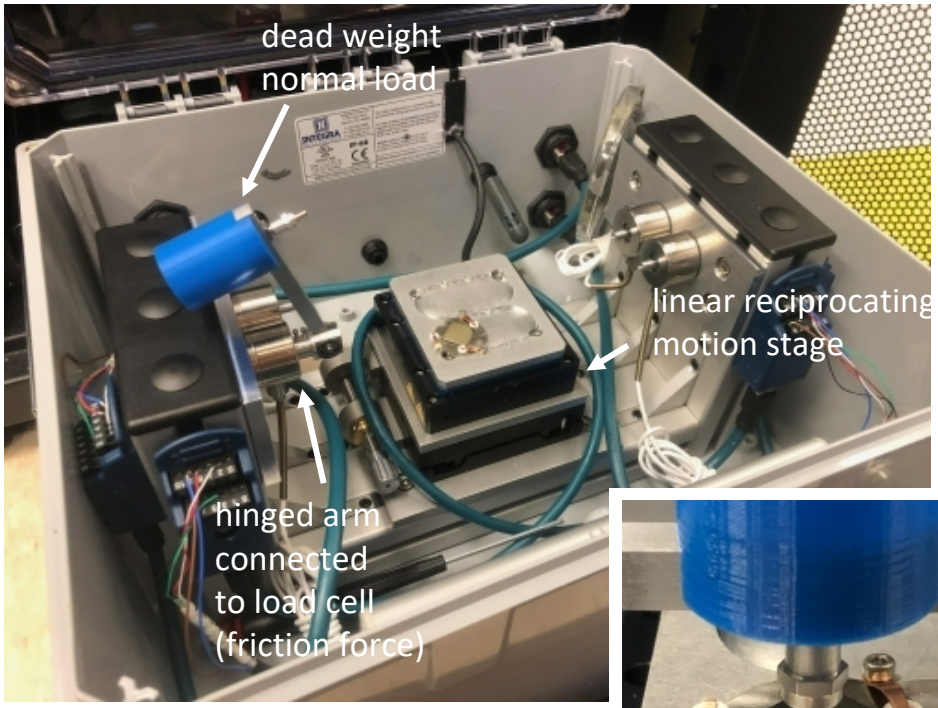


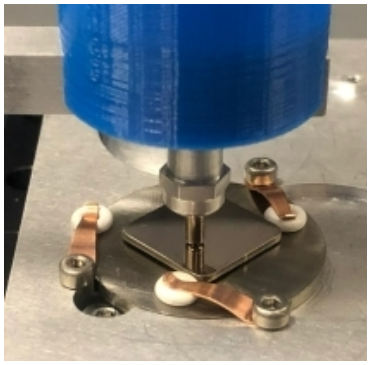
Mapping: NI PXI-4139 Source Meter
- 10 mA, 1 V open circuit limit

High Current: Keithley 2651A High Power SMU
- 0-10 A, 40 V open circuit limit

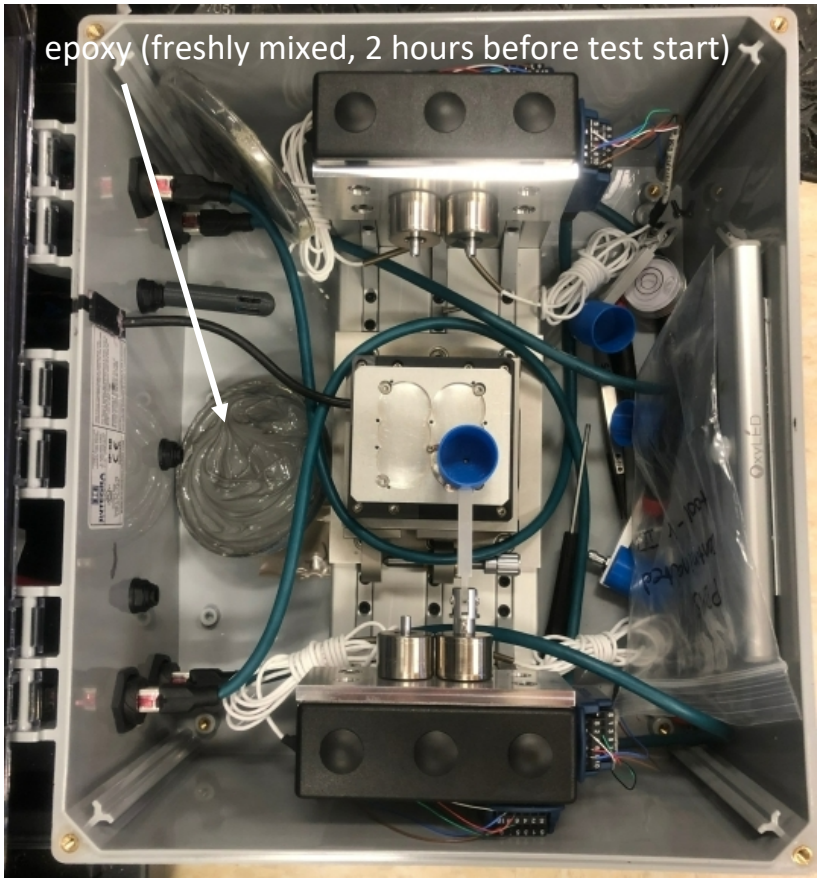
Vapor phase injected directly at the contact surfaces.
Vary concentration

High Throughput Friction and Wear Test Module





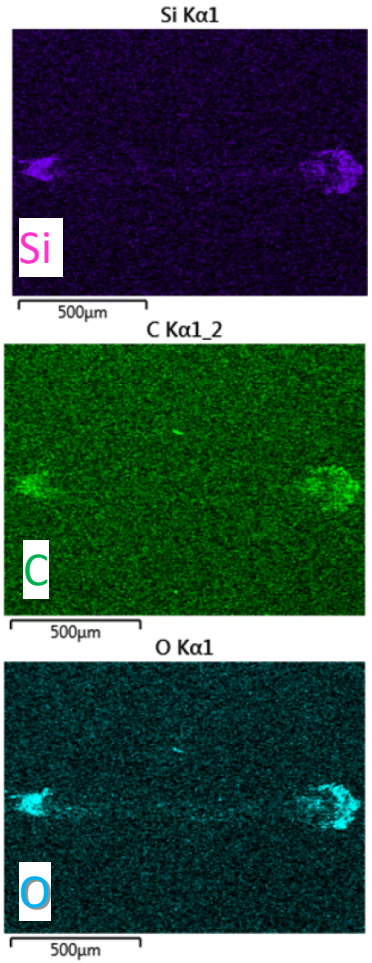
Each module can accommodate 4 parallel experiments in a controlled environment (gas and humidity).

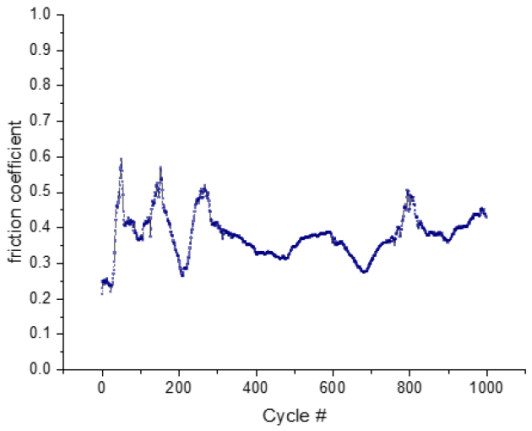


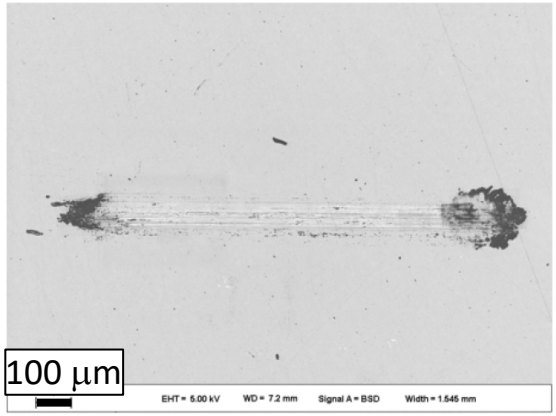
- Initial focus was testing with particular epoxy “EA9394” (Loctite)
- Outgassing studies showed volatile amines (from curing agent), reactive silanes (bonding agent), and methanol formation
- Amines and silanes are volatile and reactive at room temp.

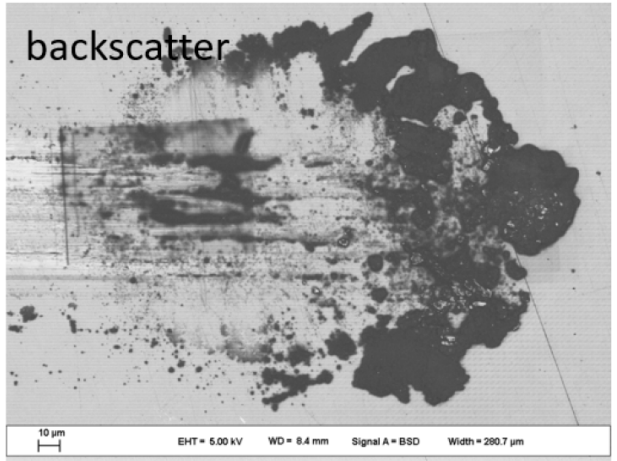
The Answer is Yes – Below, SEM/EDS Analysis (5kV)

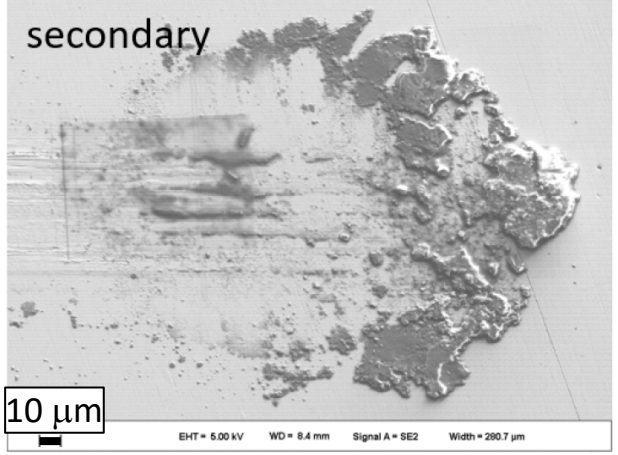
Environment: Ambient air sealed inside a chamber with curing epoxy.
Materials: Neyoro-G (Au/Cu alloy) pin, Paliney-7 (complex Pd-based alloy) disk. Both alloys in high-strength, precipitation-hardened condition.
Test Conditions: 1 mm/second sliding speed, contact force of 100 mN, 1000 cyles









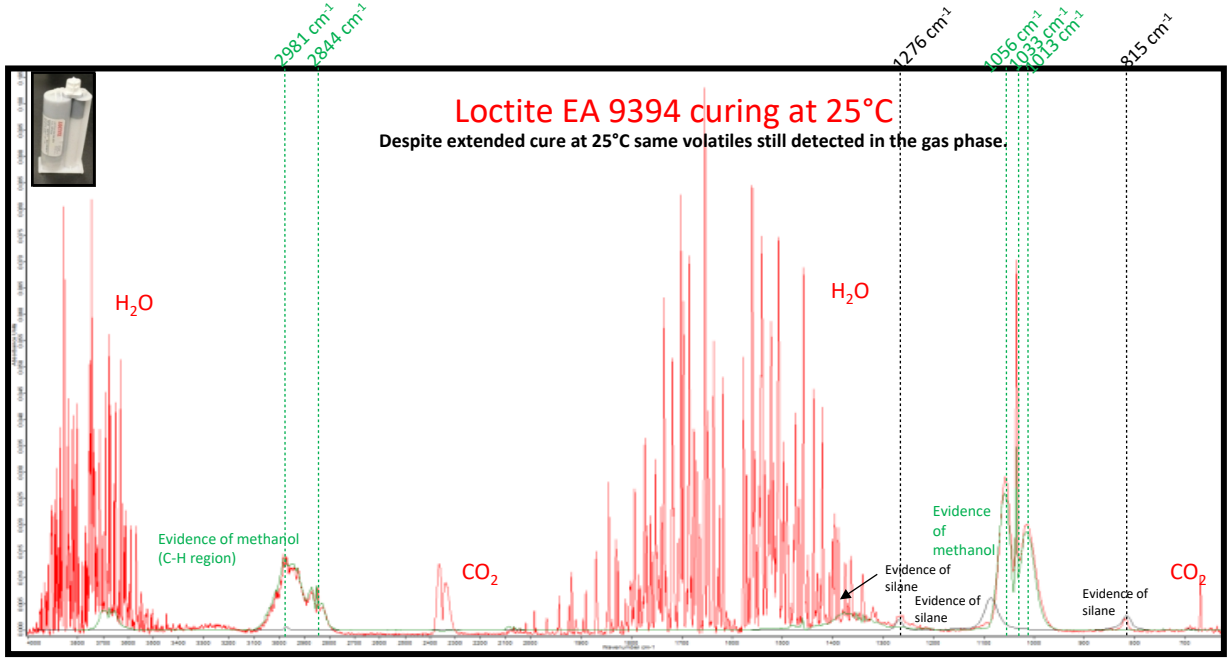


What *IS* the Actual Insulative Film Forming on these surfaces?
Results: IR Analysis of EA9394 Epoxy

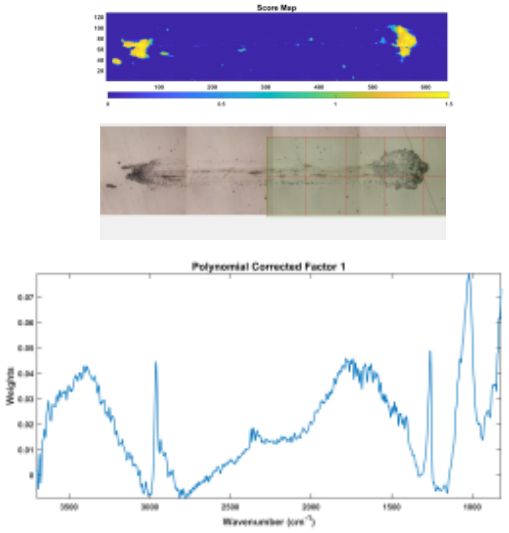
- Band at 1261 cm^{-1} is consistent with Si-CH_3 deformation
- Broad signal from 950 – 1150 cm^{-1} is consistent with Si-O-Si stretch
- Band at 2961 cm^{-1} is also consistent with Si-CH_3 asymmetric stretch

i.e. consistent with silane/siloxane

- These bands have overlap with the methanol assignment below



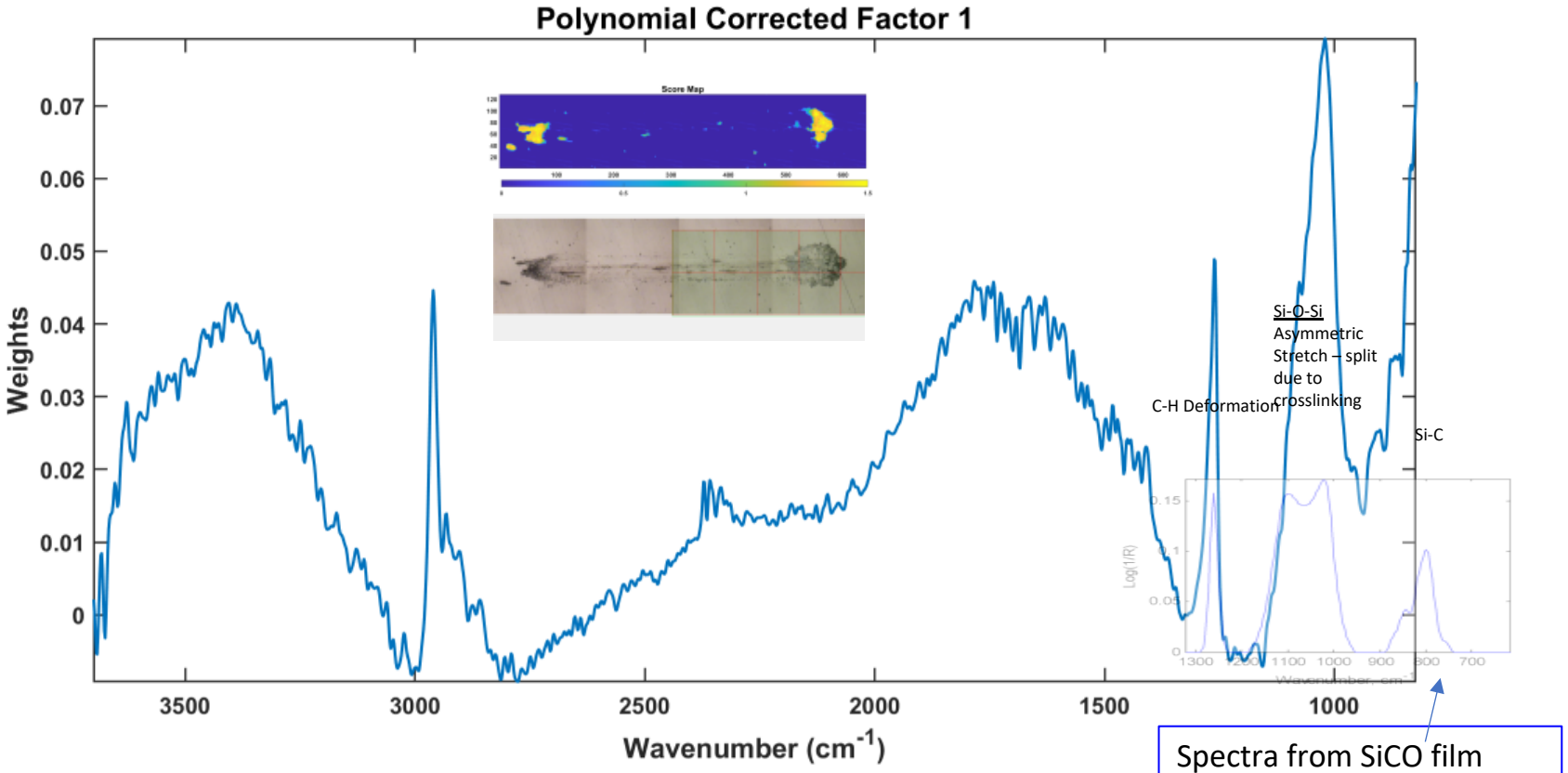
"Loctite EA 9394 Aero" Methanol - Reference Octamethyl-cyclotetrasiloxane - Reference



IR scan from the wear track friction polymer

- Results indicate that EA9394 does indeed give off silane/siloxanes
- From a reactive silane coupling agent…unusual for an epoxy

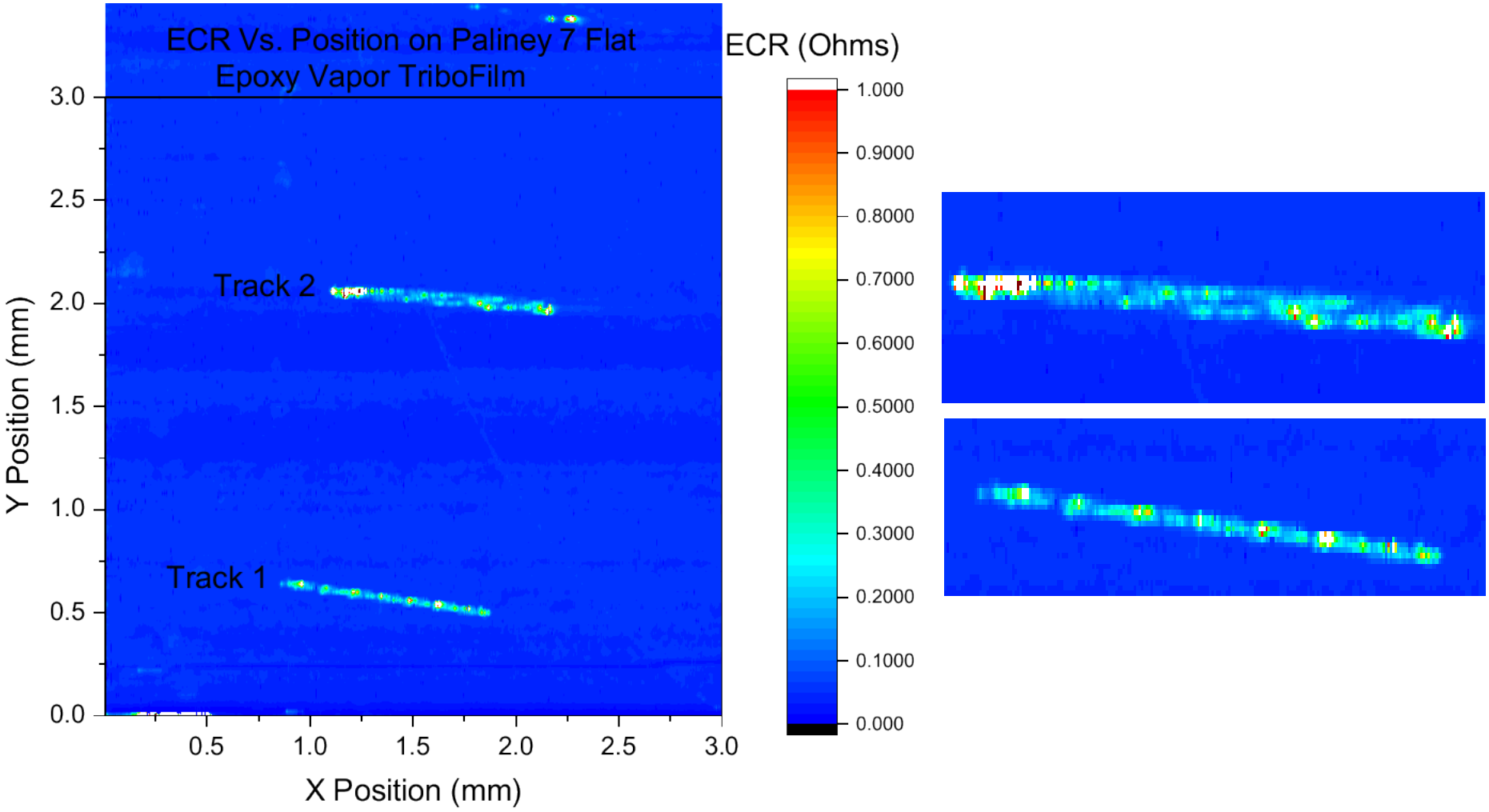
IR Analysis of Friction Polymer Film and Comparison to (historical) SiCO Film Formed in liquid PDMS



- Results indicate the film contains silane/siloxane polymer along with methanol and water present
- The same type of film was observed several years ago, associated with silicone-oil filled devices (PDMS fluid-filled devices)

High electrical contact resistance (ECR) measured in wear tracks (not just at the ends)

Representative ECR maps, same spherical Ney-G tip with lower load of 50 mN, 4-wire measurement
Current source 20 mA, voltage limit 1.1 V, mapping speed 0.1 mm/sec

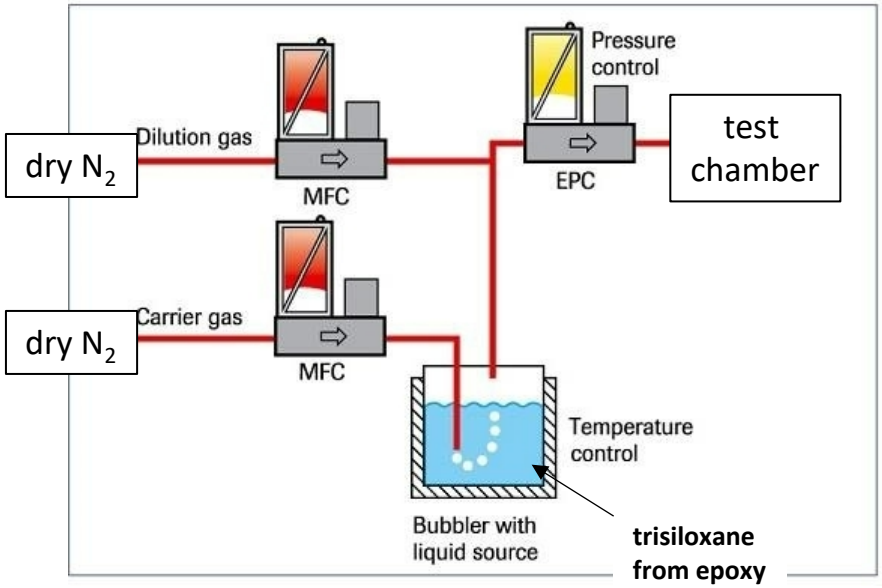


ECR ≥ 1 ohm in various locations, especially near ends of wear track

Outgassing epoxy: complex mixture of many vapor species. Desire to investigate *individual outgas constituents* in controlled experiments. Identify "Bad Actors"…

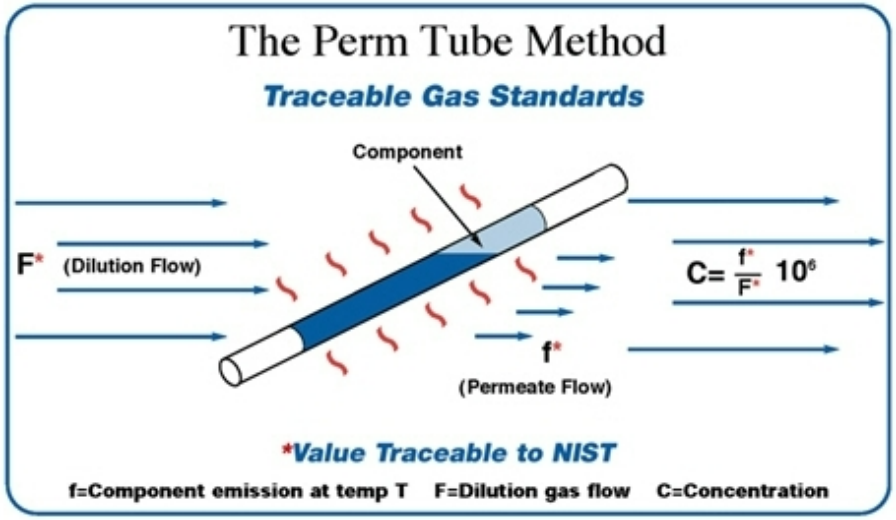
Two complementary methods to deliver controlled gas species

Method 1: Bubbler Mixing System
(coarse concentration control but greater range)



Reference: https://www.bronkhorst.com

Method 2: Permeation Tube
(fine control/narrower range; high purity)

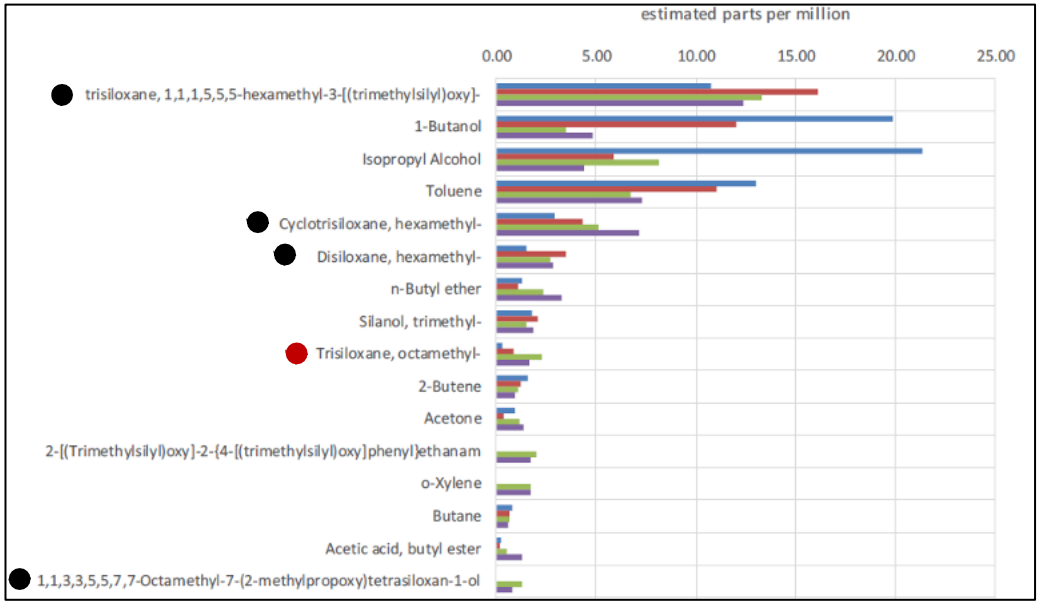


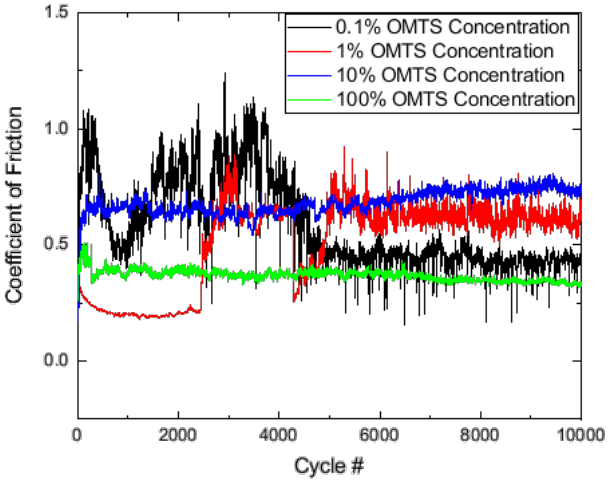
Reference: https://kin-tek.com

Both methods can be used to investigate tribofilm formation due to exposure to species identified as potentially problematic from gas analysis on actual electromechanical components.

Pin-on-Disk Friction Testing in an Individual Outgassing Species: Octamethyltrisiloxane (OMTS) $C_8H_{24}O_2Si_3$

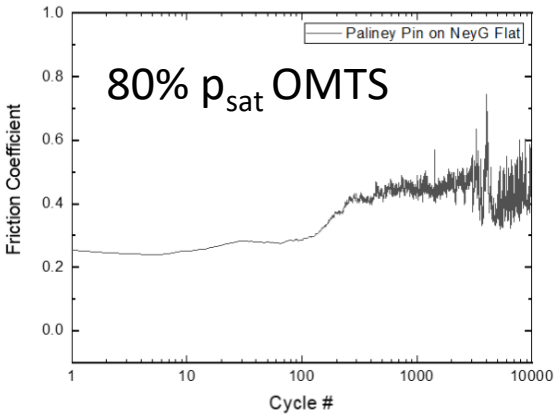
- 1 SCFH of dry N_2 mixed with 5 SCFH of OMTS-saturated N_2. This mixture gives 80% p_{sat} of OMTS

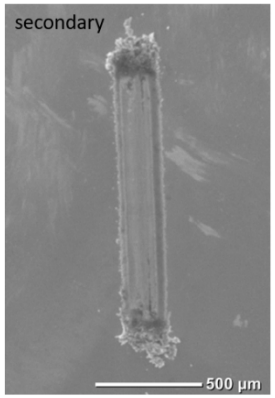


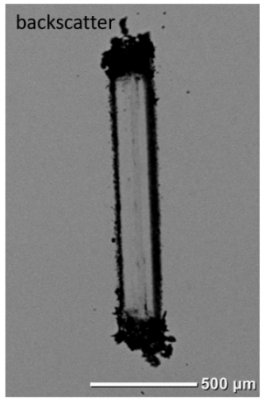


Friction experiments up to 10,000 cycles

- Friction coefficient generally increases until ~100% OMTS saturation
- This fully saturated or practically 'liquid-immersed' condition shows evidence of less well-adhered tribofilm
- Could be easier to remove or push aside the film during testing



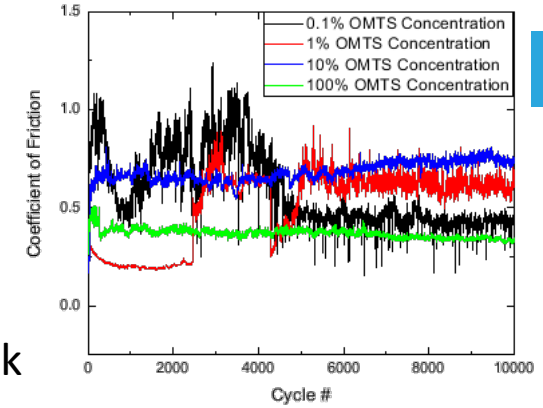


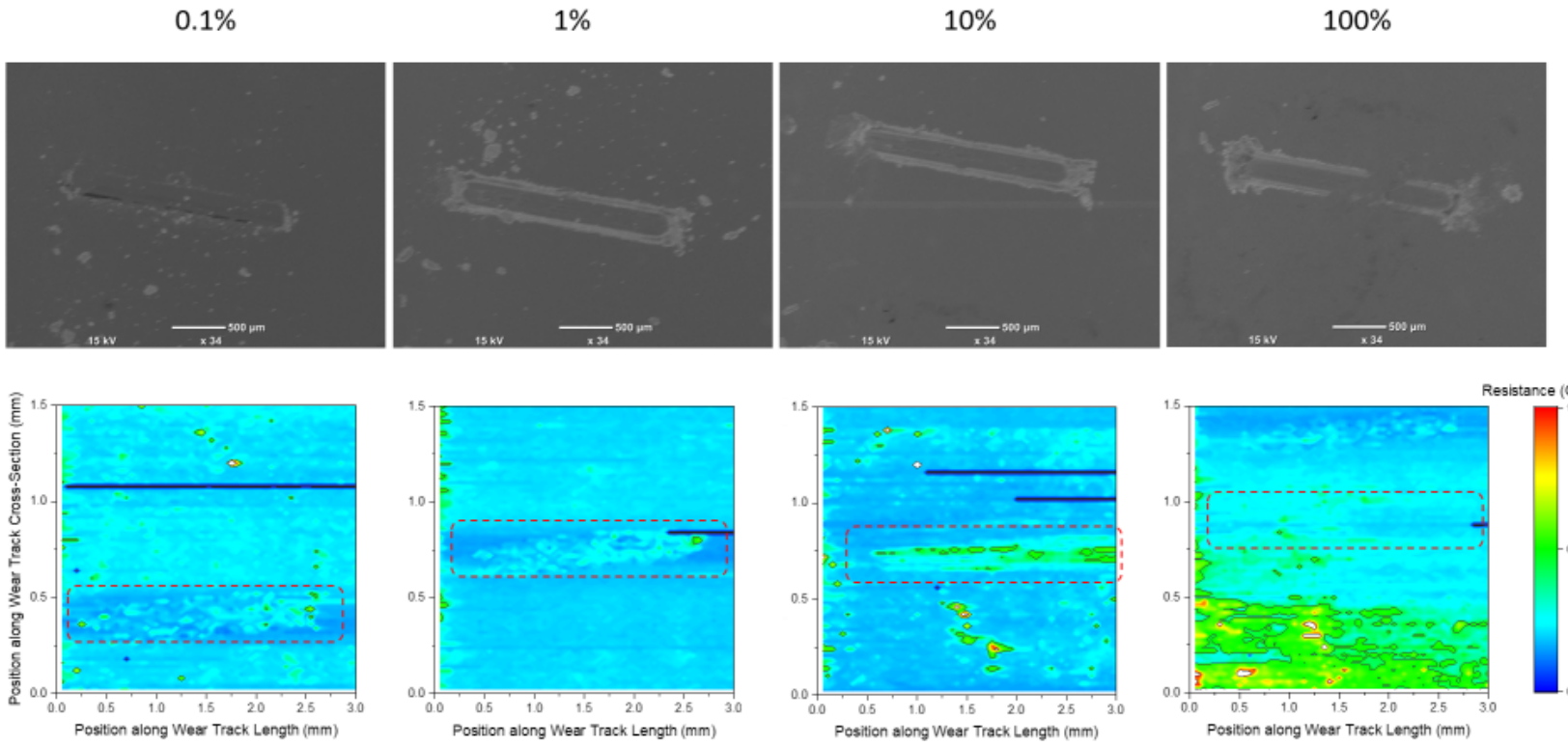


Friction polymer formation from 'OMTS alone'

SEM Micrographs and ECR Results for tests in OMTS environments

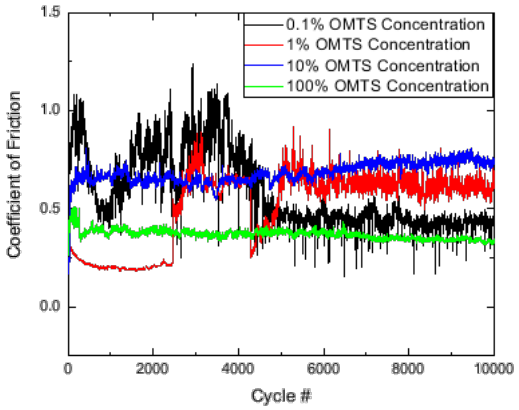
- OMTS/N_2 mixtures to generate 0.1 to 100% of saturation (liquid meniscus observed in 100% OMTS tests)
- 100 mN contact force, 1 mm/sec sliding speed, 3mm track



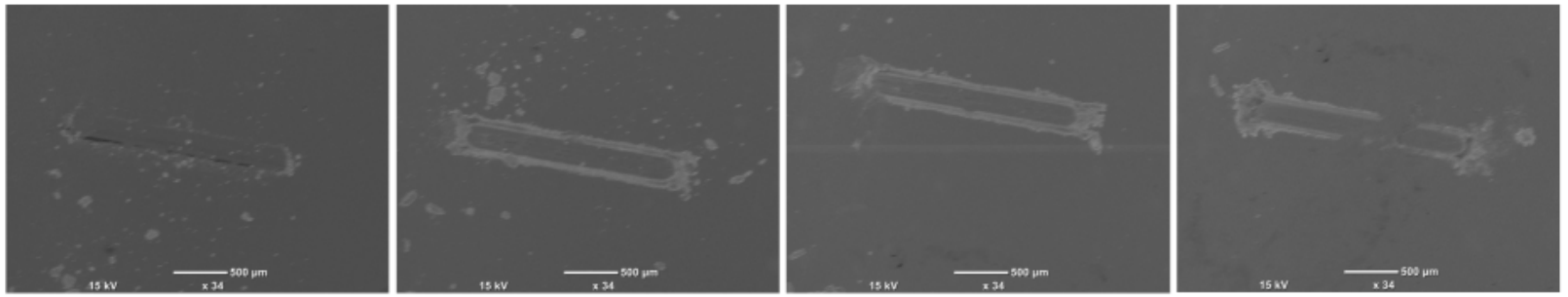


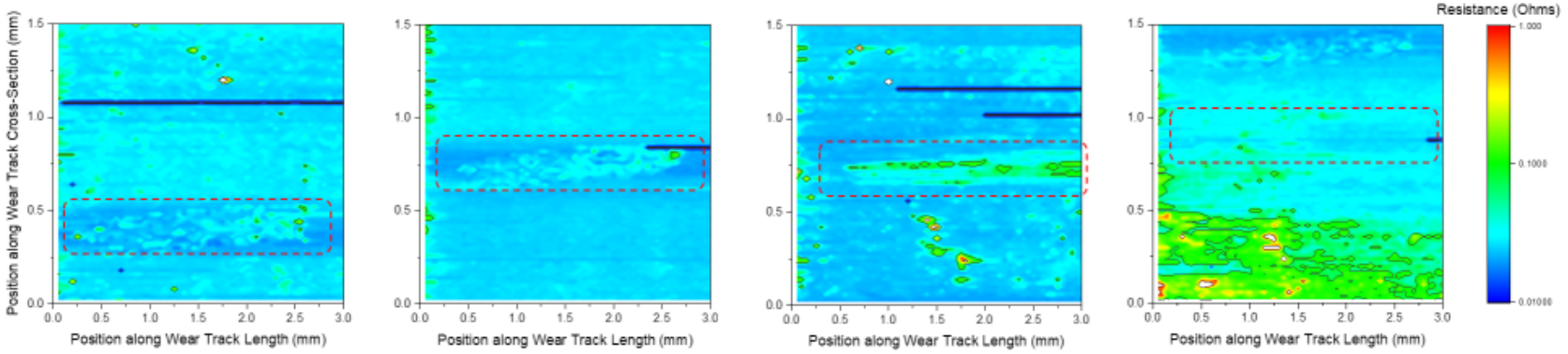
SEM Micrographs and ECR Results for tests in OMTS environment

- OMTS/N_2 mixtures to generate 0.1 to 100% of saturation (liquid meniscus observed)
- 100 mN contact force, 1 mm/sec sliding speed



0.1% 1% 10% 100%





Summary

- Insulative tribofilm formation was studied in an outgassing epoxy environment and an individual outgas species (OMTS). Tribofilm “friction polymer” is reliably produced in laboratory sliding friction experiments.

- The surface films result in significantly elevated electrical contact resistance (ECR). Results are similar to those produced in (liquid) silicone oil (PDMS) in previous work.

- Persistent tribofilm is produced with increasing concentration of OMTS, resulting in more significant current interruption, with the exception of 100% condition. For the 100% (liquid) OMTS condition, it is possible that the film is less well-adhered than that formed in the vapor environment. More work needed to confirm.

- Careful selection of epoxies, or better yet removal of epoxies from electromechanical assemblies is recommended if robust low-resistance sliding electrical contact is needed.

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Stephanie DeJong (IR Analysis)
Mat Celina (epoxy analysis)
Bonnie McKenzie (SEM/EDS)
Daniel Perry (FIB analysis)

<u>Tribology experiments</u>
Brendan Nation, J. Wellington-Johnson
Damian Gallegos-Patterson
Frank Delrio, Brian Wisler
M. Jones, J. Varga

Backup Slides

Paliney®-7 (ASTM B540)

Element	Weight %
Palladium	34.0-36.0
Silver	29.0-31.0
Copper	13.5-14.5
Gold	9.5-10.5
Platinum	9.5-10.5
Zinc	0.8-1.2

Trace impurities of Ir, Os, Rh, Ru, Fe

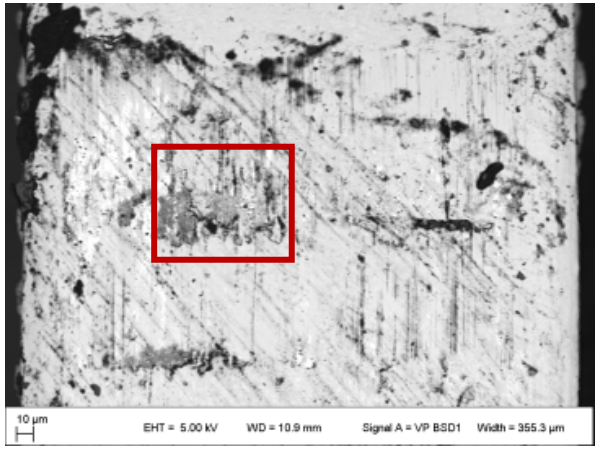
Neyoro®-G (ASTM B541)

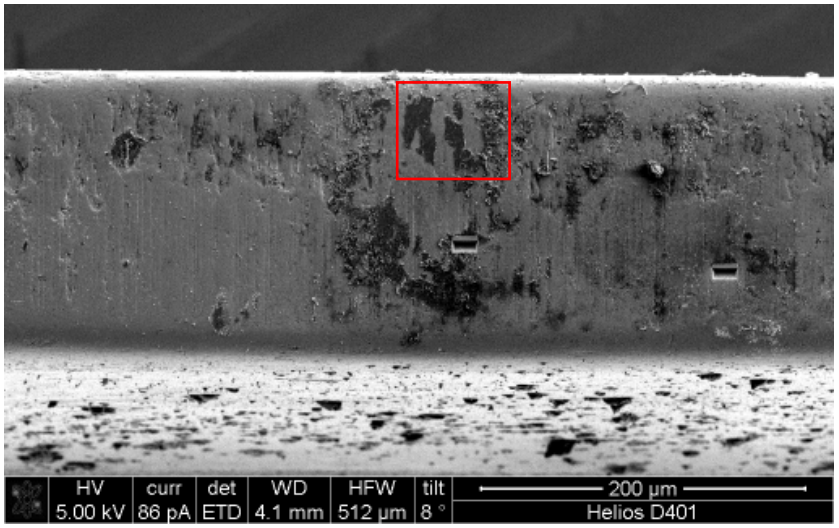
Element	Weight %
Gold	70.5-72.5
Copper	13.5-15.5
Platinum	8.0-9.0
Silver	4.0-5.0
Zinc	0.7-1.3

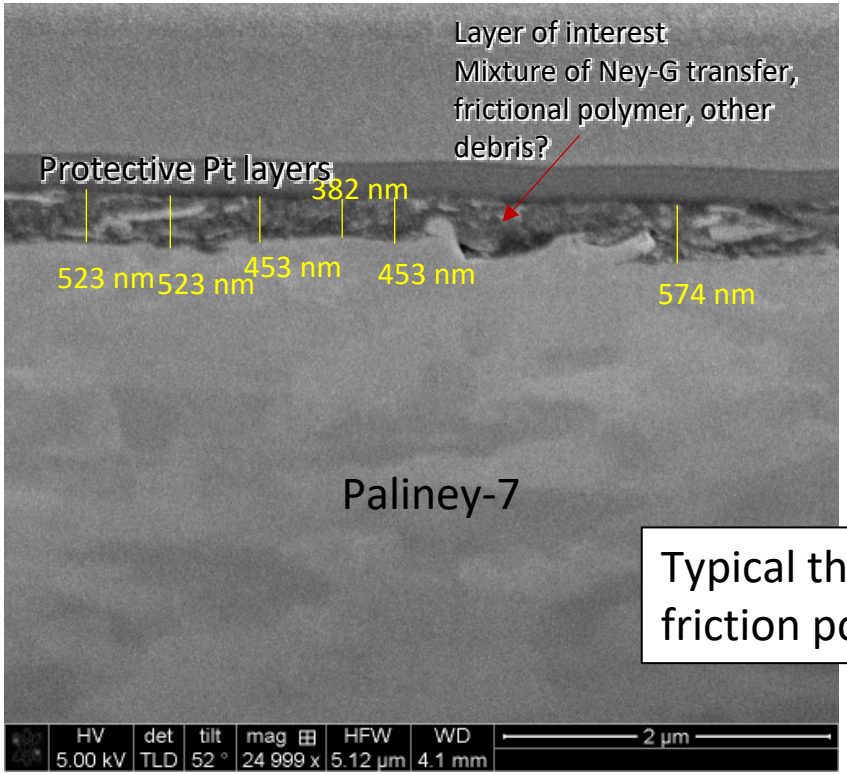
Trace impurities of Ir, Os, Rh, Ru, Fe

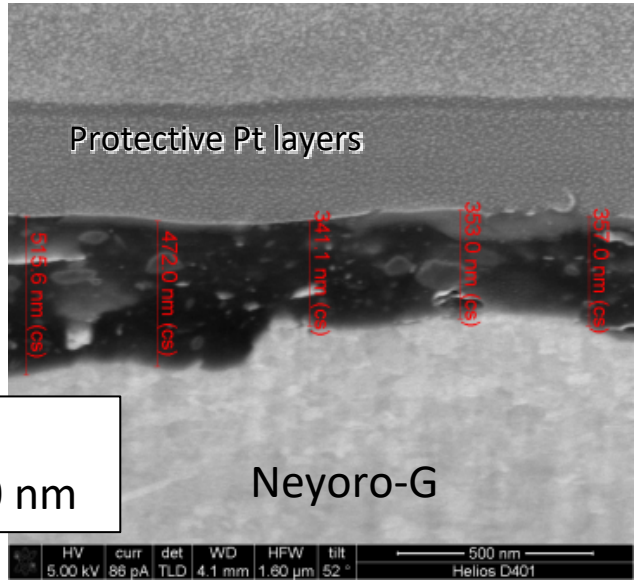
®Paliney and Neyoro are registered tradenames of Deringer-Ney Inc., Bloomfield, CT

Focused Ion Beam (FIB) Analyses of Sliding Contacts





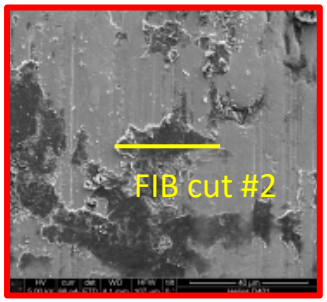




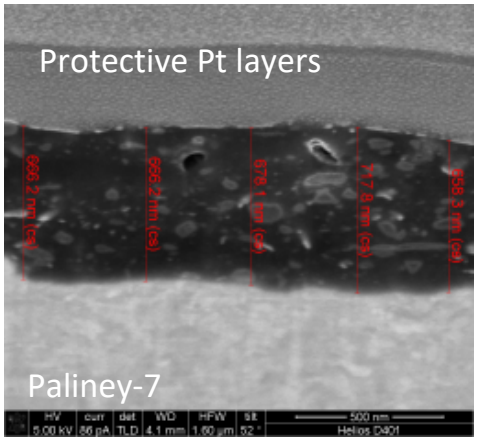
Typical thickness of the friction polymer is ~500 nm

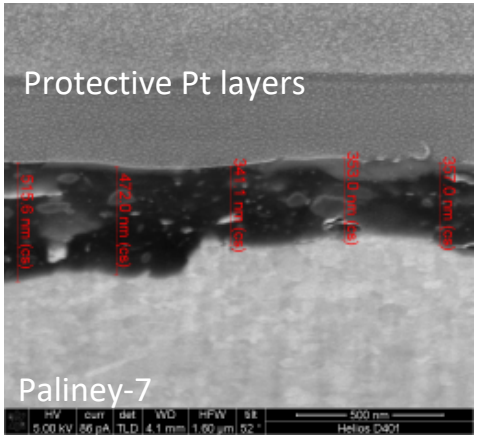
FIB Cuts: Actual sliding contacts vs. Films produced in the Laboratory

Actual sliding contacts



Thick friction polymer buildup, up to 720 nm thick





Laboratory: FIB cut results Wear Track 10