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Mechano-Chemical Degradation of Switch Damping Fluids at Sliding Contacts

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Abstract— **While reactions involving adsorbed organic molecules on electrical contacts have been known for many decades, the precise reaction mechanisms leading to friction polymer formation, particularly on surfaces at low temperature, have remained largely undiscovered. These films can reduce friction and mitigate wear but they also increase electrical contact resistance. In the present study, friction coefficient and electrical contact resistance measurements obtained in parallel during specially designed tribological tests are used to probe mechano-chemical reactions between a number of different classes of fluids and metal surfaces. The results show that copper-containing surfaces promote the formation of polymerized reaction products by catalyzing the formation of radicals, even at room temperature. In the case of silicone fluids, the chemical reaction pathway by which these insulating deposits are formed in the presence of copper has been determined. The relative reactivity of electrical contact alloy surfaces for mechano-chemical degradation of silicone, and the electrical behavior of deposits from other potential damping fluids are discussed.**

Keywords—silicone, sliding contacts, friction polymer, degradation

I. INTRODUCTION

The formation of high molecular weight deposits by mechanical action alone on electrical contacts operated in silicone (polydimethylsiloxane, PDMS) fluid was reported by Dugger et. al in 2014 [1]. While silicone decomposition in arcing contacts is well known [2-5], the mechanism referred to in [1] was related only to mechanical contact, as the presence of a voltage across the contacting bodies was not required for deposit formation. Nuclear magnetic resonance (NMR) spectroscopy was used to identify specific radicals in the deposit, which supported that the dominant reaction involved oxidation at the pendant methyl group on the silicone molecule. Methyl oxidation creates radicals that subsequently crosslink to form an insoluble deposit that collects on metal contact surfaces nearby. This reaction pathway was independently proposed by Tamai in 2012 [6]. The author reported a power level below which relays did not fail, and explained that this power level is the result of the competitive processes of deposit creation due to heating in discharges and mechanical removal by sliding. Hence, the power level below which relays did not fail is a function of relay design, including contact force. While Tamai demonstrated in this work that silicone would thermally decompose to a mixture of SiO_2, carbon and crosslinked PDMS as a function operating power conditions, he did not explore mechanical contact alone. While Tamai indicates that methyl oxidation can lead to silicone crosslinking at moderate temperature [6], our previous work [1] showed that this polymerization reaction can be catalyzed by metal surfaces at room temperature, and can occur without current flow.

In the present work, further study of metals and alloys contacting in various dielectric fluids has been conducted in order to obtain a better fundamental understanding of the reactivity of metal surfaces in damping fluids, and to identify a damping material more suitable for use in fluid-filled accelerometers that are subjected to mechanical vibrations. The formation of deposits at mechanical contacts can be damaging to such devices since polymerized insulating deposits formed while the contacts fret against one another in the rest position can interfere with correct signal generation during operation when the contacts slide across the areas where vibration previously occurred.

II. EXPERIMENTAL PROCEDURES

A. Solids

Pin-on-flat sliding experiments described below were performed using a polished hemispherical pin or ball of 1.6 mm radius sliding on a polished (both with 20 nm Ra surface roughness) flat. The Neyoro-G® and Paliney-7® materials [7] represent those used in a fluid-filled accelerometer of interest. The other metals were used in pure (at least 99.9 at.%) form. The nominal compositions of metals used for testing are shown in Table 1. The Paliney-7® alloy contains mostly Pd, Ag and Cu, while Neyoro-G® is an Au-Cu alloy containing Pt and Ag as minor alloying elements.

TABLE I. NOMINAL SAMPLE COMPOSITIONS IN ATOMIC PERCENT

Sample	Pd	Ag	Cu	Pt	Ni	Zn	Au
Paliney-7	34.8	29.4	23.3	5.4	NA	1.6	5.4
Neyoro-G	NA	6.0	33.0	6.3	NA	2.2	52.5
Au	NA	NA	NA	NA	NA	NA	99.9
Cu	NA	NA	99.9	NA	NA	NA	NA

B. Fluids

The contact sliding experiments were conducted using several fluids. The base fluid was 20 cSt PDMS (PMX-200, Xiameter Corporation). In addition, a perfluorinated polyether (PFPE Uniflor 8900, Nye Synthetic Lubricants), and a multiply-alkylated cyclopentane (MAC 1001, Nye Synthetic Lubricants) were used, both with pour points (lowest usable temperature) of -50°C or lower. The former is a fluorocarbon, and the latter a synthetic hydrocarbon. These fluids have low vapor pressure and have been used for space mechanism lubrication. Another synthetic hydrocarbon investigated was poly-alpha olefin (Synfluid PAO4, Chevron Phillips Chemical Company), developed for demanding industrial and transportation lubrication applications. Select fluid properties are shown in Table 2. All fluids have viscosity near 20 cSt at 20°C, but viscosity as a function of temperature varies widely, particularly at cryogenic temperatures, as shown in Fig. 1.

TABLE II. SELECT FLUID PROPERTIES

Property	PDMS	PFPE	MAC	PAO
Pour Point, C	-65	-80	-59	-69
Surface Tension, mN/m	20.6	23		27
Specific Gravity at 25C	0.95	1.81	0.84	0.82
Refractive Index	1.4		1.465	1.456
Flash Point, C	204	NA	300	226

C. Electrical Contact Tribometer

A commercial tribometer (CSM Instruments Nanotribometer) was significantly modified and used for the measurements described here. A photograph of the instrument is shown in Fig. 2. The tribometer was modified so that a flat sample could be held within a PTFE fluid cup mounted on a piezoelectric stage to allow the surfaces to be mechanically abraded at low sliding amplitude while submerged in about 5 mL of fluid. The flat surface and the ball holder were both fitted with copper wires so that a 4-wire electrical contact resistance measurement could be made at the contact. A source-measure unit (SMU) was used to probe the electrical behavior of the contact while in the fluid environment.

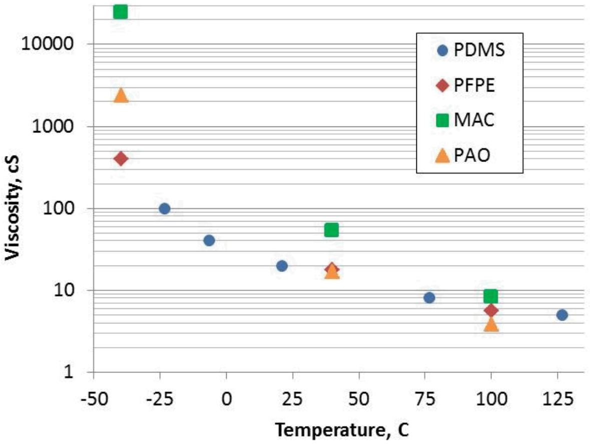

Fig. 1. Viscosity as a function of temperature for damping fluids tested.

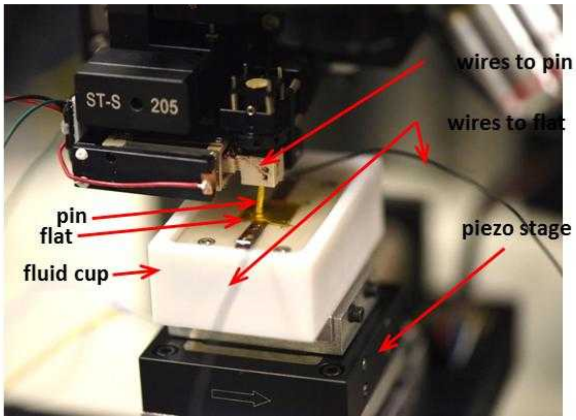

Fig. 2. Modified CSM Nanotribometer used for electrical contact tribology measurements.

The experiments were typically conducted as follows: Freshly polished and cleaned flat and pin specimens of the desired metals were placed in the tester, and the fluid cup was filled with the desired test fluid.

Mapping Phase: The electrical contact behavior was first mapped over a sliding track 2 mm long using 50 mN applied force on the pin, a probe current of 20 mA, and an open circuit potential of 1.1 V while the sliding contact was submerged in fluid.

Abrasion Phase: The pin and flat samples were both electrically grounded, and the track length was adjusted to 1 mm in the center of the 2 mm long track previously mapped. Using this smaller track, the pin was rubbed over the surface at 1 mm/s in the track direction, but with the piezo stage operating at 100 Hz with an orthogonal displacement having an amplitude of 50 μm and constant velocity. The pin therefore followed a path such as that shown in Fig. 3 over the 1 mm long track. Sliding was continued for 100 passes over the 1 mm track with the piezo stage operating.

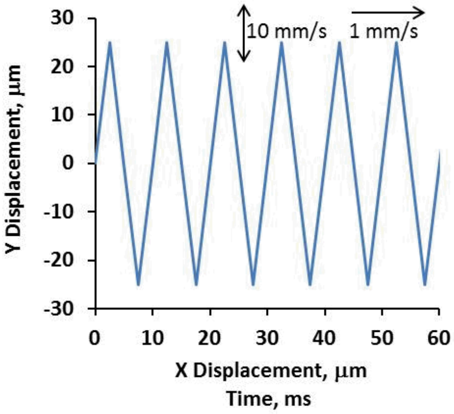

Fig. 3. Sliding path of hemispherical pin on the flat during the abrasion phase.

Deposit Characterization Phase: After abrading the surfaces submerged in the test fluid as described above, the track length in the slow sliding direction was increased to the previous 2 mm length, the pin was returned to the origin of the first 2 mm track, and the 20 mA, 1.1 V open circuit conditions were used once again to map the electrical contact resistance of the surface. In this way, the pin was made to travel over the ends of contact created during the abrasion phase, so that any reaction products deposited just outside of the contact would be slid over and electrical contact resistance measured.

D. *Screening Test for Fluid Reactions*

Reactions between copper and various damping fluids during mechanical contact alone were further investigated using a "tumble test," as described in [1]. Briefly, a polyethylene bottle of 200 ml volume was filled approximately 20% full with commercially pure copper balls 3.2 mm in diameter. The damping fluid was added to the bottle until the balls were just submerged. The bottle was then sealed and made to tumble end over end lengthwise in a rotary tumbler at 6 rev/min. At this speed the balls would fall from one end of the bottle to the other as it rotated, created a high rate of mechanical contact events between the metal balls in the presence of the damping fluid. At the conclusion of the test, about 2 cm^3 of the fluid was centrifuged in a vial to separate metal wear particles from the fluid, and to cause any reaction product to settle to the bottom. The fluid above the settled particles and reaction product was decanted off, and a small sample of the remaining fluid collected with a pipette for analysis.

E. *Fluid Chemical Analysis*

Analysis of the fluids from the tumble test was performed using nuclear magnetic resonance (NMR) spectroscopy. NMR is a nucleus specific technique allowing details about the local chemistry and bonding for the molecules of interest to be determined. In the present study NMR was employed to probe the degradation or aging by-products of the fluids that were formed while in contact with the metal surface. Silicon (^{29}Si) solution NMR provides information about the condensation reaction products involving Si-O crosslinks due to degradation of PDMS. Proton (^{1}H) solution NMR was used for the determination of radical presence in the PDMS and hydrocarbons (MAC and PAO). ^{19}F NMR was used to examine degradation of the PFPE.

III. RESULTS AND DISCUSSION

A. *Electrical Contact Tribometer Tests*

The sliding electrical contact resistance (ECR) data is presented in the form of contour maps, showing electrical contact resistance as color contours on a log scale from 1 to 1000 mΩ. Resistance is plotted as a function of position along the 2 mm sliding track (Y axis) and as a function of repeated cycles of sliding over the same track (X axis). The contact resistance for Neyoro-G® on Paliney-7®, Cu on Cu, and Au on Au sliding in PDMS fluid are shown in Fig. 4. In the case of Neyoro-G® on Paliney-7®, elevated contact resistance can be seen outside of the area mechanically abraded without current flow, indicating the accumulation of a resistive deposit at the ends of the 1 mm track. This deposit was easily seen in scanning electron microscope (SEM) images of the track in backscattered electron mode, highlighting atomic number differences. The copper sliding pair exhibits elevated contact resistance throughout the 2 mm sliding track, while the self-mated gold sliding pair shows no difference in contact resistance within or just outside the ends of the 1 mm abraded track. The white contours at the ends of the sliding track in the gold-gold contact are due to missing data at increasing cycle numbers rather than high electrical resistance. The friction coefficient became so high in these areas that the pin did not slide over the full 2 mm distance programmed. These measurements, as well as the NMR spectra of fluid tumbled with copper balls, confirmed the hypothesis that copper in the electrical contact alloys was particularly reactive toward PDMS degradation. No degradation of the fluid was observed in the gold on gold sliding tests.

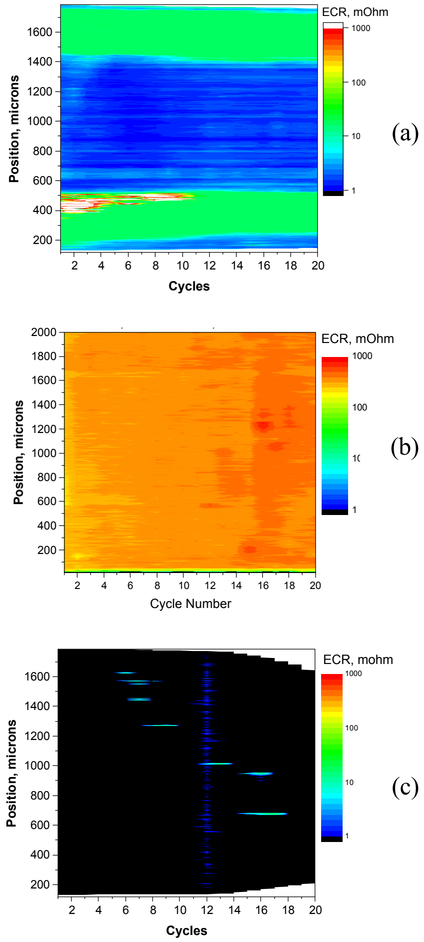

Fig. 4. ECR as a function of position and cycles for Neyoro-G® on Paliney-7® (a), copper on copper (b) and gold on gold (c) sliding in 20 cSt PDMS fluid in air.

Alternative damping fluids for the accelerometer application were investigated by performing sliding of the

Neyoro-G® on Paliney-7® contacts in the presence of these fluids, and examining the ECR performance of the contact. Fig. 5 shows the results of ECR maps of sliding contact in the fluorocarbon and hydrocarbon fluids. Contact resistance in the PFPE fluid exhibits values of several to 10s of mΩ, but do not vary substantially over the entire sliding track. Both the MAC and PAO synthetic hydrocarbons exhibit similar variability in ECR over the abraded and non-abraded areas of the track. Therefore, from ECR measurement alone, all of the alternative fluids appear to resist radical formation and crosslinking better than the baseline PDMS fluid. However, SEM examination of the wear tracks from PFPE, MAC and PAO tests indicate some differences in performance. While no low atomic number deposits were observed after the sliding tests in PFPE, both of the synthetic hydrocarbons showed a small amount of low atomic number deposit formed adjacent to the wear tracks. This observation prompted an examination of fluid degradation in the presence of copper, using the "tumble test" and NMR spectroscopy.

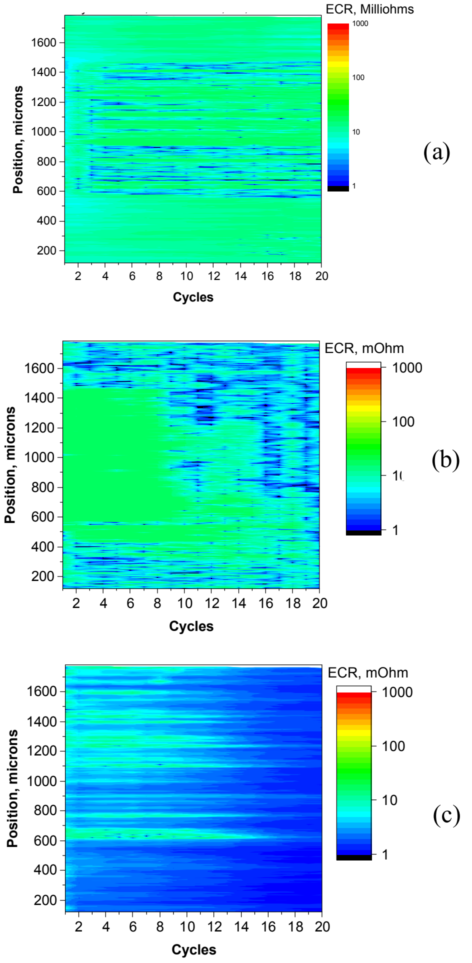

Fig. 5. ECR as a function of position and cycles for Neyoro-G® on Paliney-7® sliding in PFPE (a), MAC (b), and PAO (c) fluids in air.

B. *Fluid Chemistry*

Each of the alternative fluids was tumbled in containers with copper balls as described above. Analysis of the centrifuged fluid samples by NMR revealed some degree of interaction of the hydrocarbon fluids with copper to produce reaction products. The NMR spectra of relevant regions are shown in Fig. 6. Red circles in the figure indicate peaks not present in the NMR spectrum of new fluid, which are evidence of mechano-chemical reaction between the fluid and the copper balls.

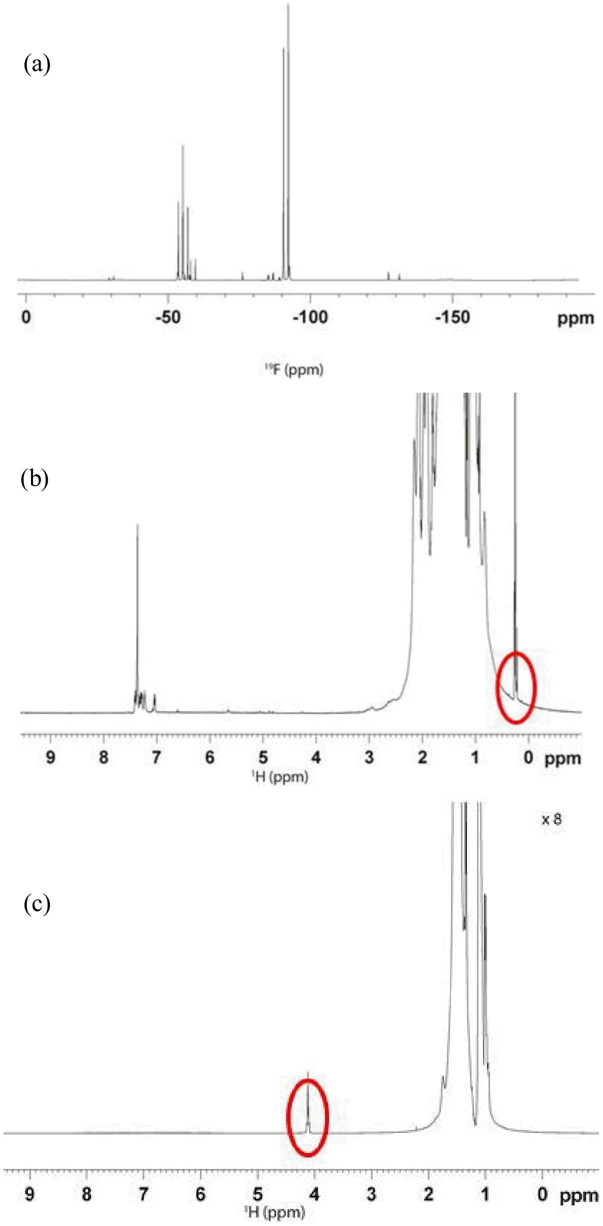

Fig. 6. NMR spectra from PFPE (a), MAC (b), and PAO (c) after tumling with copper balls. The red highlighted peaks were not present in the NMR spectra of new fluids. The PFPE fluid (a) did not exhibit changes.

No differences in the ^{19}F spectrum from PFPE before and after tumbling were detected, indicating the absence of any reaction between the fluid and copper balls that could be detected by NMR.

The results of the ECR tribometer tests and NMR spectroscopy of damping fluids that are alternatives to the baseline PDMS suggest that the alternatives are far less reactive with the electrical contact alloys than the base PDMS fluid. ECR tribometer results showed that the fluids did exhibit some differences in resistivity from one another, attributed primarily to the ability of the adsorbed film to remain in the contact during sliding, and related to the strength of chemisorption of the damping fluid molecules. However, very little impact to ECR was measured after abrading the electrical contact alloys in the presence of the damping fluids. NMR spectroscopy on fluid samples before and after tumbling with copper balls (representing a reactive component of the electrical contact alloys) did indicate some radical formation in the synthetic hydrocarbons due to mechanical contact. However, no reaction products were detected in the tumbled PFPE fluid.

IV. CONCLUSIONS

The reactivity of several metal surfaces and damping fluids was investigated to identify alloy constituents and alternative damping fluids that resist mechano-chemical degradation. ECR tribometer tests with pure copper and gold surfaces in PDMS fluid showed that copper promoted the degradation of PDMS even more so than did the Neyoro-G® and Paliney-7® electrical contact alloys. No degradation in contact resistance of the gold surface was detected, indicating that gold does not catalyze the radical formation and crosslinking of PDMS observed with copper or the copper-containing alloys. One solution to the resistive deposits formed in PDMS-filled accelerometers would therefore be to insure that sliding surfaces are gold or gold plated. Pure gold structural elements are not compatible with device requirements, and in addition to the expense associated with gold plating, there are concerns about process controls to insure adhesion and repeatability. An alternative solution is to change the damping fluid to remove the degradation-susceptible chemistry from the accelerometer. Of the synthetic fluorocarbon and hydrocarbon fluids investigated, all exhibited significantly reduced reactions with the electrical contact alloy surfaces and pure copper surfaces, than the baseline PDMS fluid. NMR spectroscopy showed that the PFPE fluid was particularly stable against reactions associated with mechanical abrasion of copper surfaces in the presence of the fluid.

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[7] Alloy names are trademarks of the Deringer-Ney Company, Bloomfield, CT.