Ionic Liquids as Novel Lubricants and Additives*

Jun Qu[1], John J. Truhan[2], Huimin Luo[1], Sheng Dai[1], Peter J. Blau[1]

[1]Oak Ridge National Laboratory

[2]University of Tennessee (currently at Caterpillar)

*Research sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy under Contract No. DE-AC05-00OR22725.

Needs for Improved Lubricants

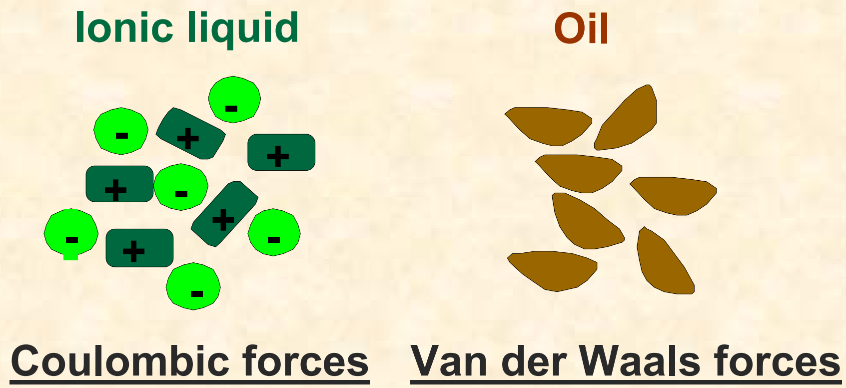
- **In transportation sector, 10~15% of the energy generated in automobile engines is lost to friction.** In addition, production engine oils
  - are one of the barriers for higher combustion temperatures to increase engine efficiency, limited by their low thermal stability above 250^o C, and
  - contribute hydrocarbon exhaust emissions due to oil blow-by and burn-out.

A new class of more effective, environmentally-friendly lubricants could lead to huge energy savings.

Introduction to Ionic Liquids

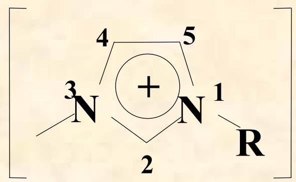
- **Ionic liquids (ILs) are composed of cations and anions, in stead of neutral molecules.**
  - Currently being used as green solvents in chemical synthesis, electrochemistry, catalysis, etc.

- **Properties**
  - Inherent polarity
  - High thermal stability
  - Negligible volatility
  - Non-flammability
  - High flexibility of IL molecular design
  - Economical and environmentally friendly synthesis

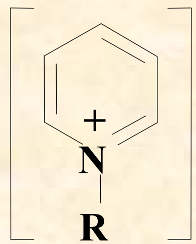


Typical Molecular Structures of Ionic Liquids

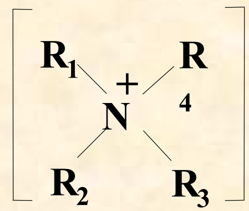
Common cations:



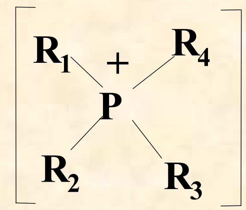
1-alkyl-3-methyl-imidazolium



N-alkyl-pyridinium



Tetraalkyl-ammonium



Tetraalkyl-phosphonium

($R_{1,2,3,4}$ = alkyl)

Common anions:

water-insoluble → **water-soluble**

$[PF_6]^-$
$[(CF_3SO_2)_2N]^-$ (or Tf_2N^-)
$[(C_2F_5SO_2)_2N]^-$ (or $BETI^-$)
$[BR_1R_2R_3R_4]^-$

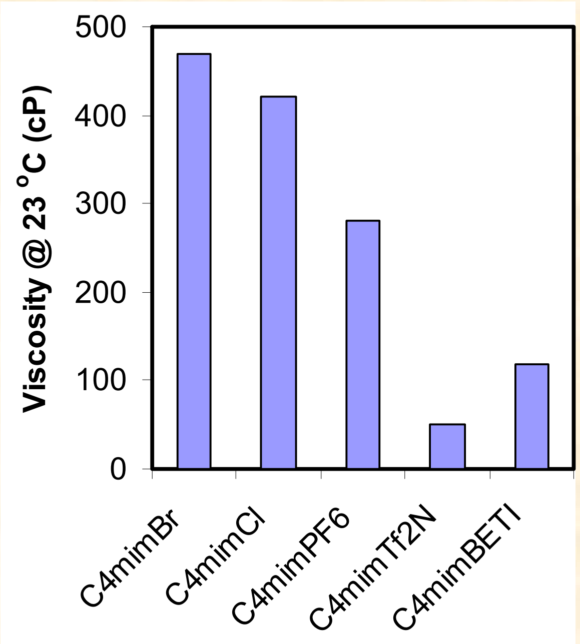
$[BF_4]^-$
$[CF_3SO_3]^-$

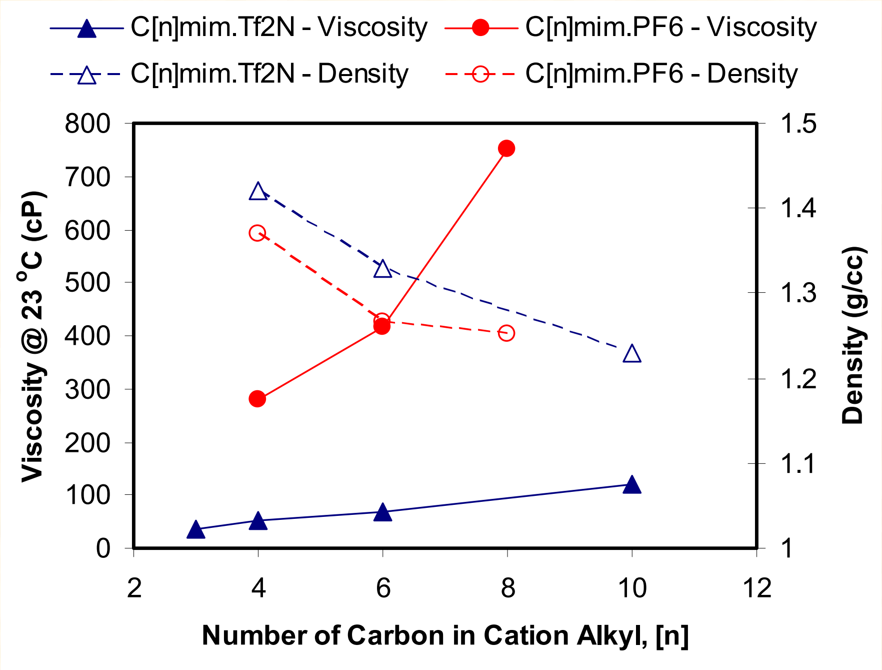
$[CH_3CO_2]^-$
$[CF_3CO_2]^-$, $[NO_3]^-$
Br^-, Cl^-, I^-
$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

ORNL has been active in various areas of ionic liquids research since early 1990s, with a well equipped organic synthesis laboratory.

Viscosity Strongly Correlates to Molecular Structure

- Examples
  - With same cation, Cl^-, Br^-, or PF_6^- generate higher viscosities than Tf_2N or BETI.
  - With same anion, higher # of carbon in alkyl of cation leads to higher viscosity and lower density.





ILs have a Wide Range of Viscosities

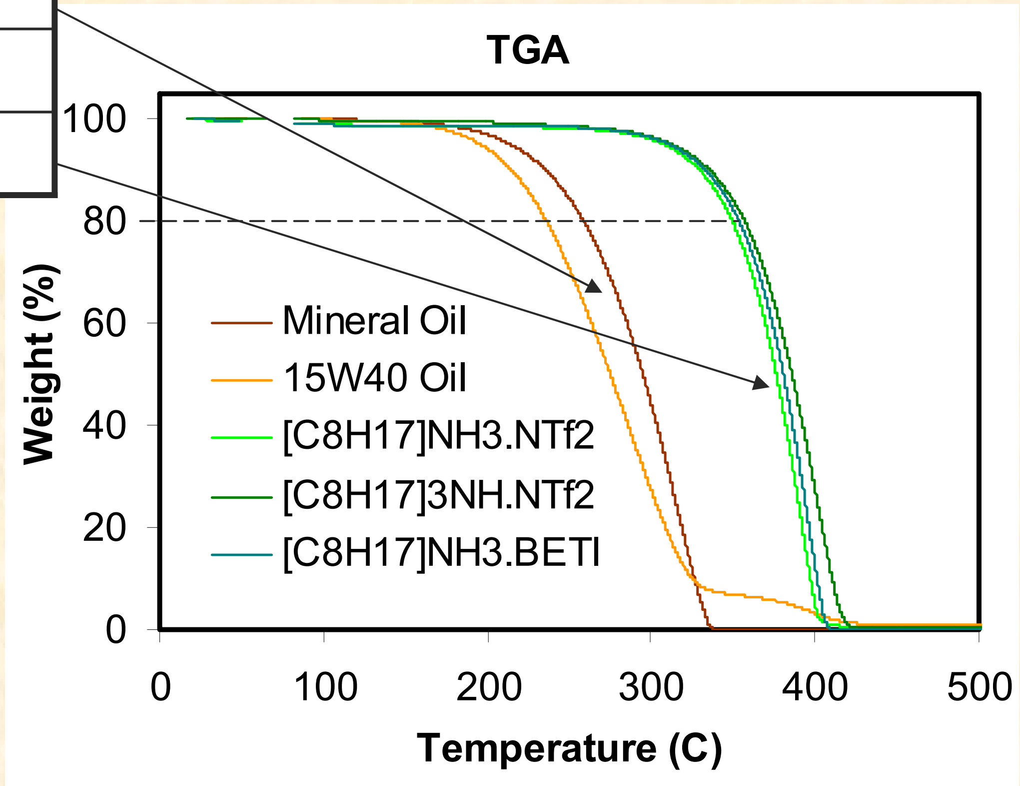
- Densities of ILs are in a narrow band, 1.03-1.46 g/cc @ 23 ^{o}C;
- **Viscosities of ILs vary in a wide range**, 50-1500 cP @ 23 °C.

	Lubricants	ρ (g/cc) @ 23 °C	η (cP) @ 23 °C	η(cP) @ 40 °C	η (cP) @ 100 °C	*Viscosity Index*
Hydrocarbon oils	Mineral Oil	0.86	159	56	6.3	78
	15W40 Oil	0.86	229	91	11.3	128
Imidazolium ionic liquids	C_4mim.PF_6	1.37	281	108	13.3	110
	C_6mim.Br	1.16	*>1500*	630	*n/m**	*n/m**
	C_4mim.Tf_2N	1.42	51	25	5.8	152
	C_{10}mim.Tf_2N	1.23	122	53	8.8	135
	C_8mim.BETI	1.34	169	69	9.5	99
Ammonium ionic liquids	$[C_6H_{13}]_3NH.Tf_2N$	1.12	170	72	9.7	113
	$[C_8H_{17}]_3NH.Tf_2N$	1.06	219	89	11.7	124
	$[C_8H_{17}]NH_3.Tf_2N$	1.37	331	125	14.2	100
	$[C_2H_5]_3NH.BETI$	1.48	163	67	9.3	87
	$[C_8H_{17}]NH_3.BETI$	1.45	763	265	*n/m**	*n/m**

**n/m - not measured*

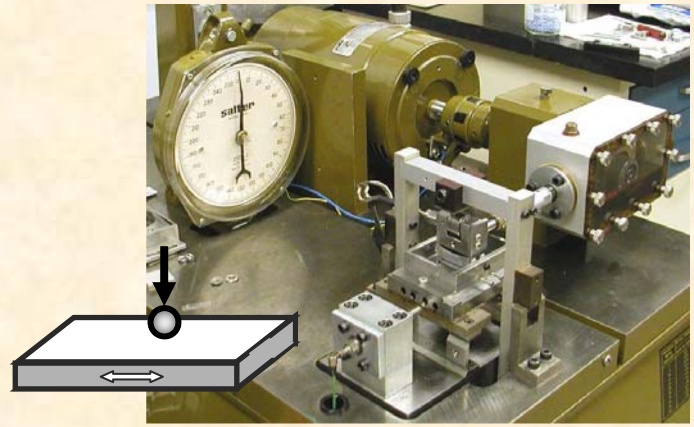
ILs Have High Thermal Stability

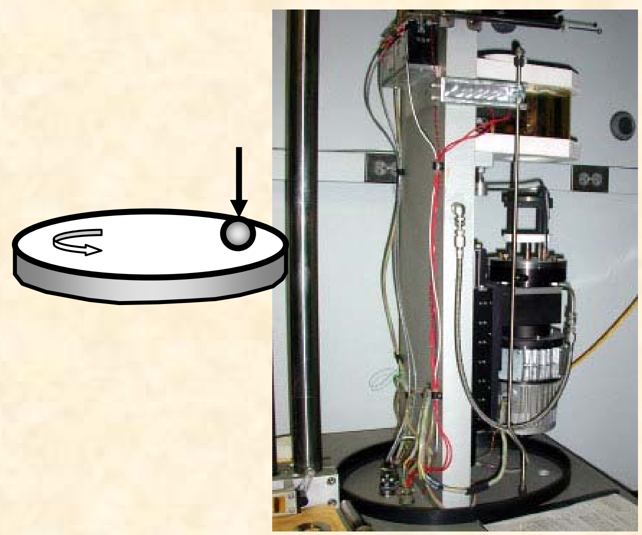
Lubricant	T_{onset} (^oC)
15W40 oil	236
$C_{10}mim.Tf_2N$	>400
$[C_8H_{17}]_3NH.Tf_2N$	357



Tribological Evaluation

- Materials
  - Al 1100, Al 6061-T6, Al 319
  - Counterface: AISI 52100 steel
- Lubricants:
  - 8 imidazolium ionic liquids
  - 5 ammonium ionic liquids
  - Mineral oil and 15W40 engine oil
- Testing temperature: RT and 100 ^{o}C
- Test configurations:
  - Ball-on-flat reciprocating sliding
  - Pin-on-disk unidirectional sliding





Friction Screening Tests

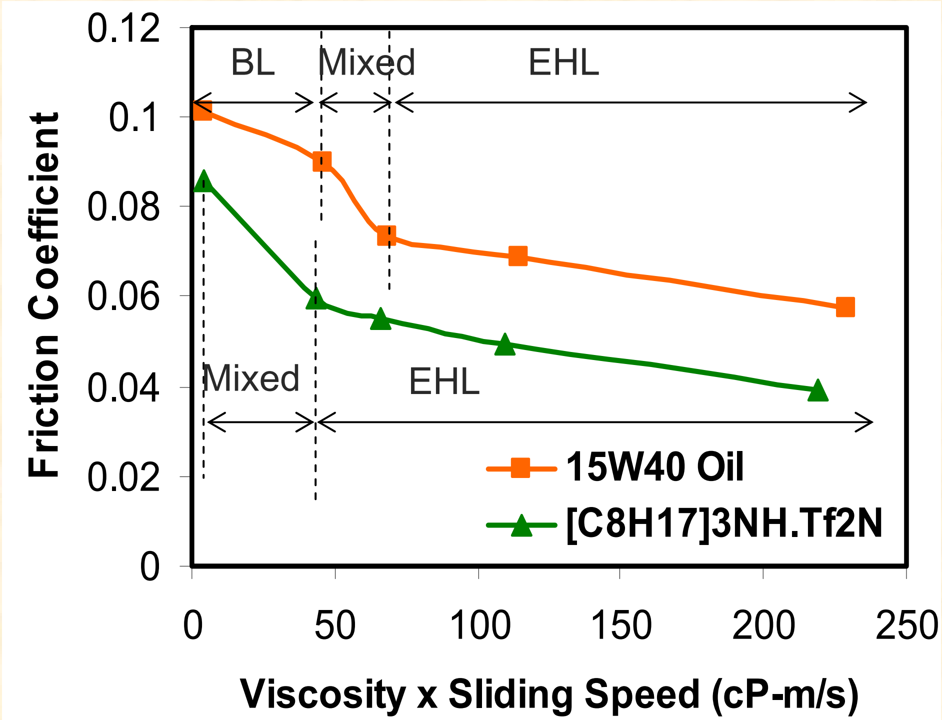
	Lubricants	η @ 40 °C (cP)	COF
Hydrocarbon oils	Mineral oil	56	0.10
	15W40 diesel engine oil	91	0.09
Imidazolium ionic liquids	C_6mim.Br	630	0.09
	C_4mim.Cl	136	0.21
	C_4mim.PF_6	108	0.18
	C_6mim.PF_6	153	0.20
	C_8mim.PF_6	245	0.07
	C_{10}mim.Tf_2N	53	0.16→0.10
	C_8mim.BETI	69	0.21
Ammonium ionic liquids	$[C_6H_{13}]_3NH.Tf_2N$	72	0.11
	$[C_8H_{17}]_3NH.Tf_2N$	89	0.06
	$[C_8H_{17}]NH_3.Tf_2N$	125	0.07
	$[C_2H_5]_3NH.BETI$	67	0.20
	$[C_8H_{17}]NH_3.BETI$	265	0.08

Friction Reduction by ILs in All Lubrication Regimes

- $[C_8H_{17}]_3NH.Tf_2N$ produced 20-35% lower friction than 15W40 Engine Oil in all lubrication regimes.
- Suppress the transition from EHL to boundary lubrication *(Stribeck curve shifted to the left)*;

AISI 52100 steel against Al 6061-T6.

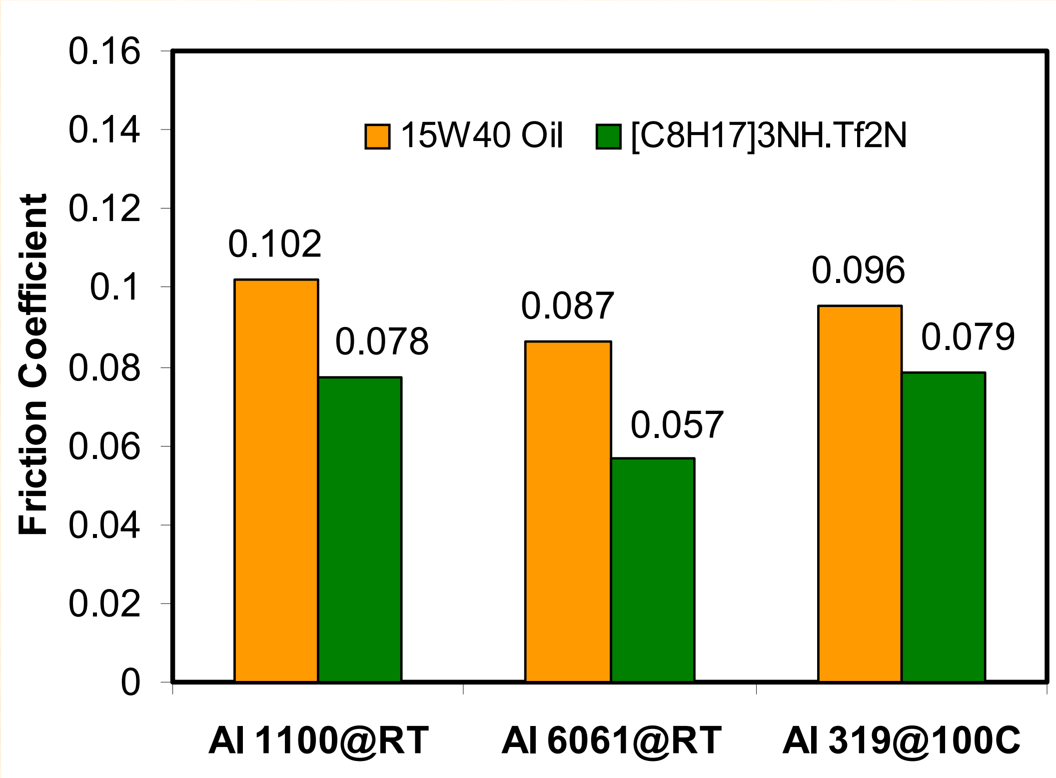
Unidirectional sliding under 38.3 N load, 0.02-1.0 m/s.



ILs Produce Low Friction

Ionic Liquid ($[C_8H_{17}]_3NH.Tf_2N$) ***vs.*** **15W40 Engine Oil**

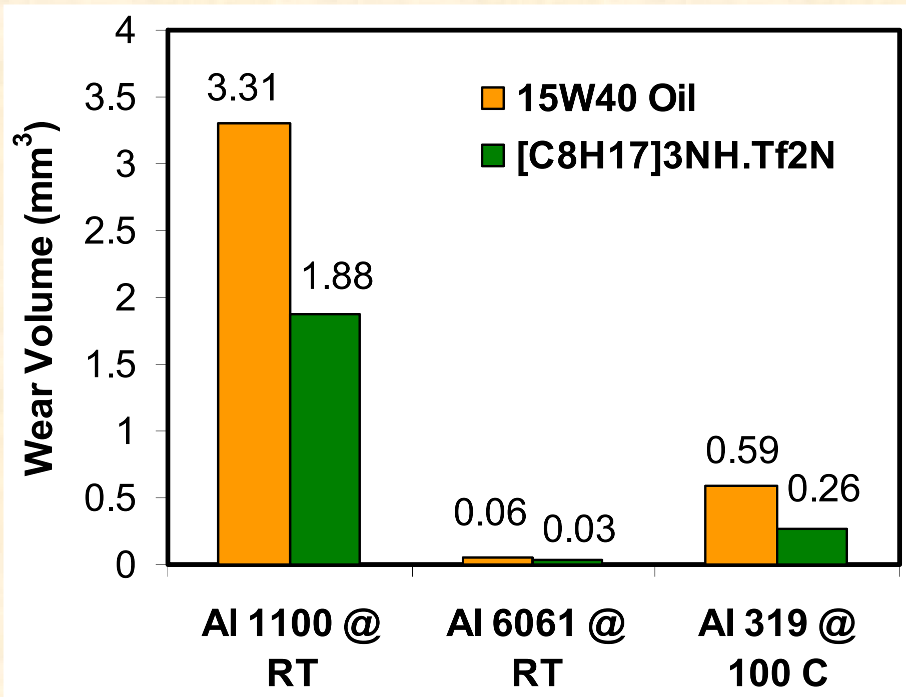
- **20-35% friction reduction for Al alloys**



ILs Produce Low Wear

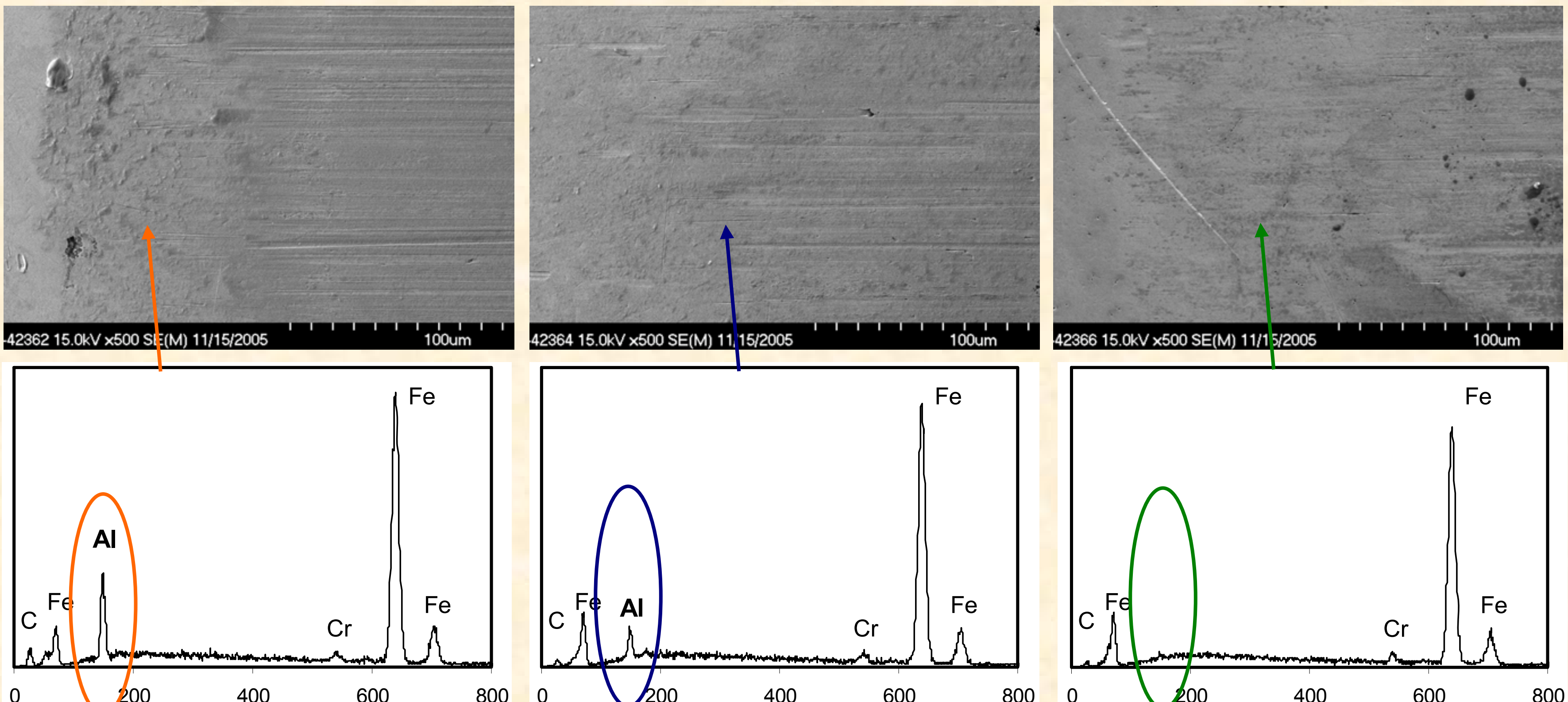
Ionic Liquid ($[C_8H_{17}]_3NH.Tf_2N$) ***vs.*** 15W40 Engine Oil

- **45-55% wear reduction for Al alloys**
- Virtually no wear on steel balls



Aluminum Had Less Material Transfer (Adhesive Wear) to the Steel Counterface in Ionic Liquid Lubrication

Images of contact areas of the steel counterface



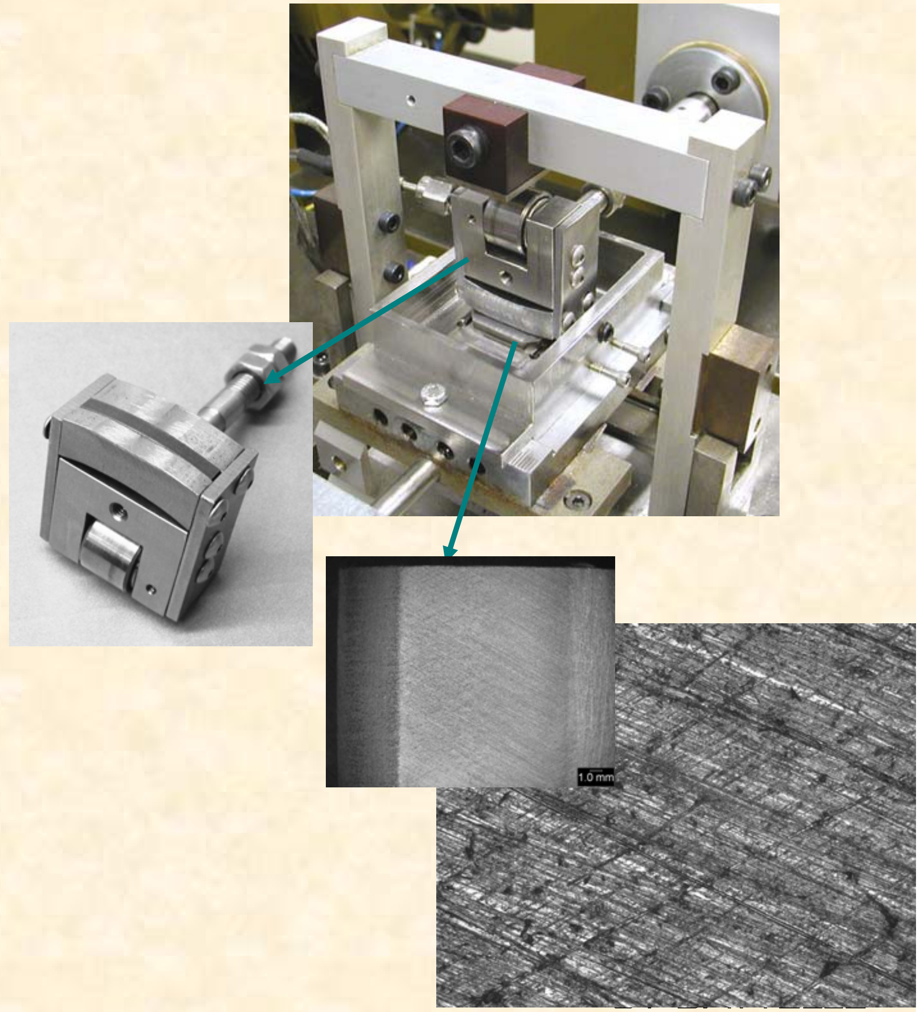
Mineral Oil

Mineral Oil + 10% $[C_8H_{17}]_3NH.Tf_2N$

$[C_8H_{17}]_3NH.Tf_2N$

Piston Ring-on-Flat Reciprocating Sliding Test (ASTM G 181-04)

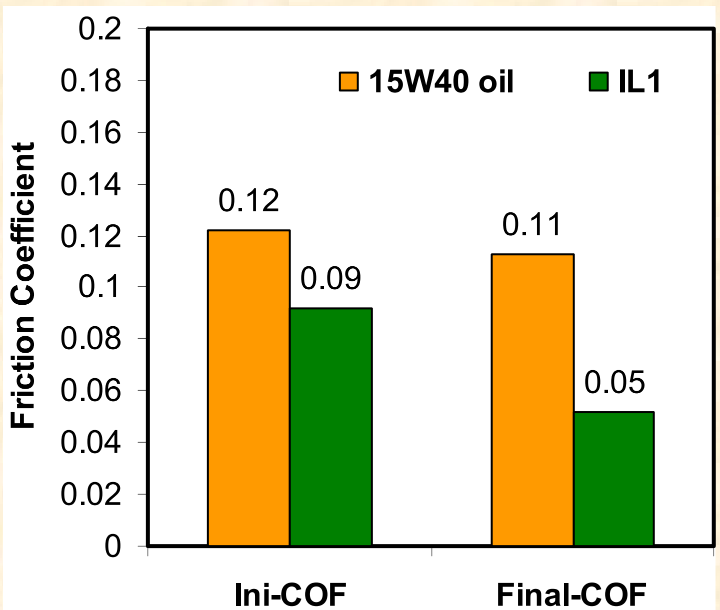
- **Materials**
  - **Slider: Cr-plated piston ring**
  - **Flat: Grey cast iron with simulated honing marks**
- **Lubricants**
  - **15W40 diesel engine oil**
  - **IL1 ($[C_8H_{17}]_3NH.Tf_2N$)**
- **Temperature: 100 ^oC**
- **Normal loads: 240 N**
- **Sliding speed: 0.2 m/s (ave.)**
  - **10 Hz, 10 mm stroke**
- **Test duration: 6 hours**

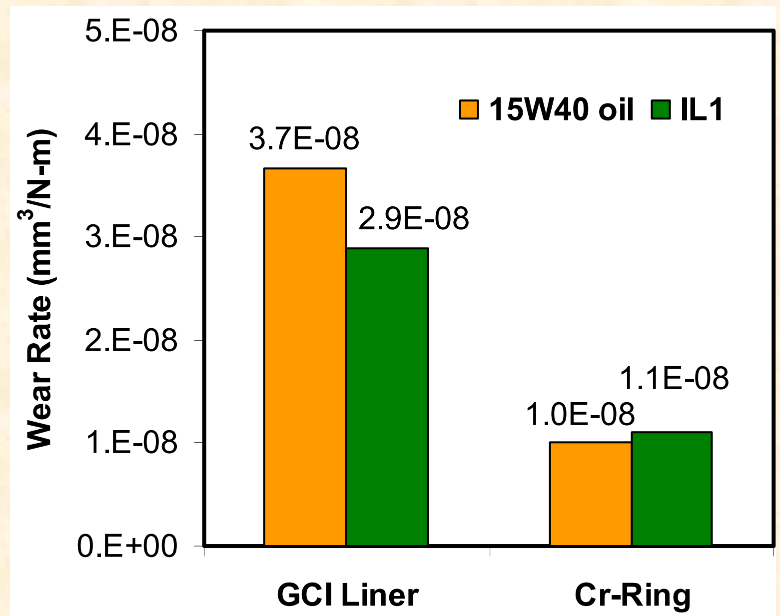


Latest Results of Piston Ring-on-Flat Reciprocating Sliding Test (ASTM G 181-04)

Compared with **15W40 oil**, $[C_8H_{17}]_3NH.Tf_2N$ (**IL1**)

- **Reduced the initial COF by 25% and the final COF by 55% at the end of the six-hour wear test.**
- **Reduced the total wear rate (flat+ring) by 15%.**





Summary

- A group of ammonium ionic liquids have been developed with promising lubricating performance and benchmarked with 15W40 engine oil.
  - 20-35% friction reduction and 45-55% wear reduction in lubricating steel-aluminum contacts.
  - 25-55% friction reduction and 15% wear reduction in lubricating Cr-plated piston rings against cast iron.
  - A surface boundary film was detected and is believed to be responsible for the firition/wear reductions.
- A U.S. Patent was filed on September 19, 2006 (Application# 11533098)

Hint: No single ionic liquid can work for all materials, but with the uncountable species available, one would expect to design appropriate ionic lubricants for specific applications.

Ionic Liquids Offer Significant Potential

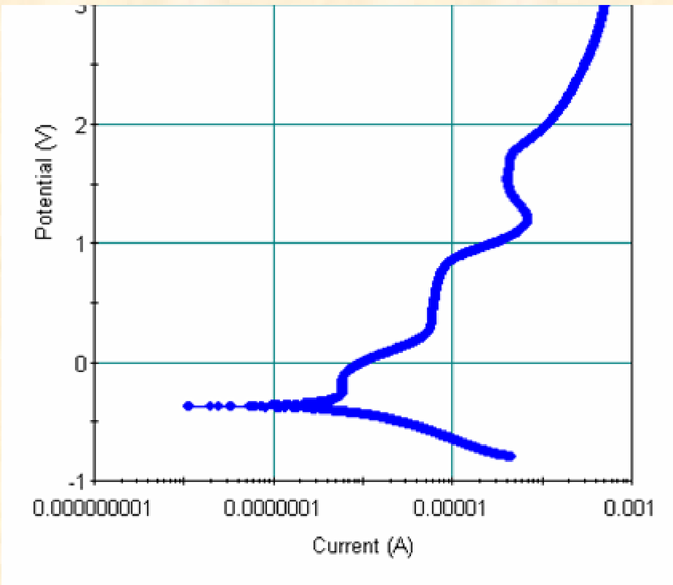
- **Reduce parasitic energy loss** by friction reduction and allowing higher engine combustion temperatures.
- **Extend service life and maintenance cycle** by wear reduction.
- **Expand the usage of lubricants to higher temperatures** with higher thermal stability.
- **Reduce air emissions** due to ultra-low vapor pressure.
- **Require fewer expensive lubricant additives** with better intrinsic properties, e.g. boundary film formability and solvent nature.
- Serve as **ashless additives for oil- and water-based lubricants**.
- An **effective replacement for catalyst-poisoning ZDDP**.
- **Safer transportation and storage** because of non-flammability.

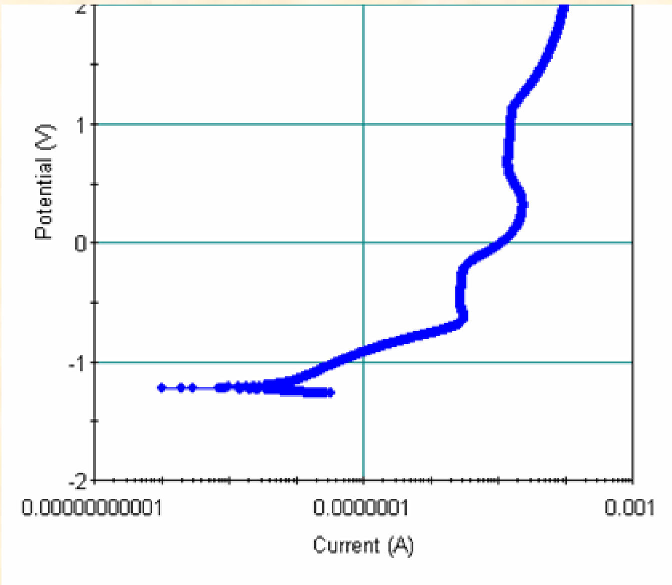
- Backup Slides -

Corrosion Behavior

Electrochemical measurement

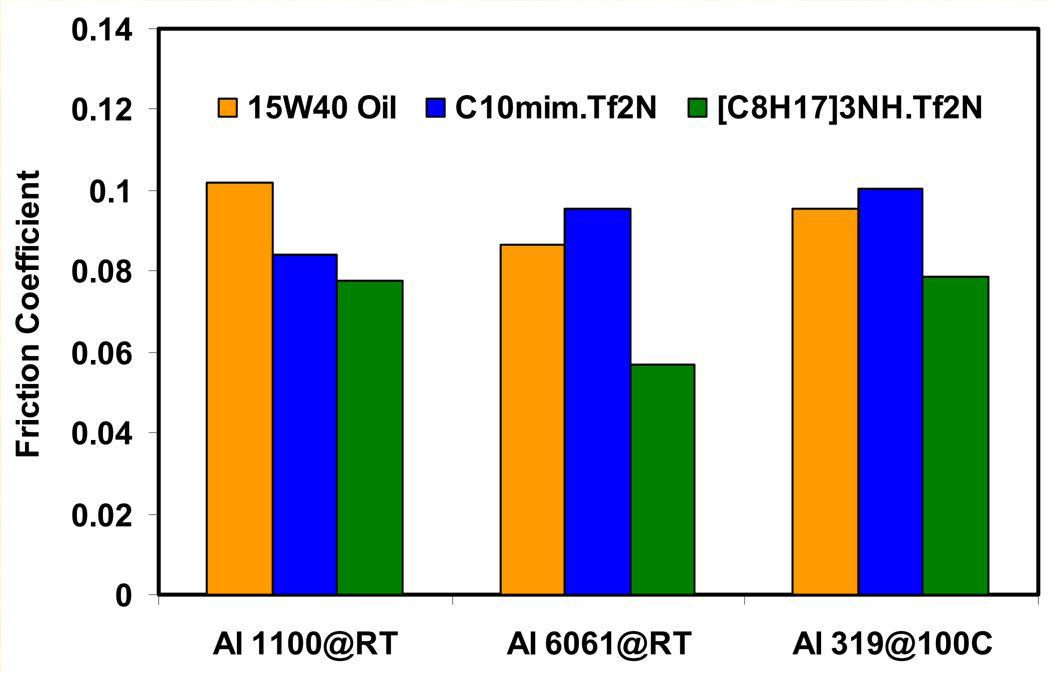
- Potentiodynamic polarization curves – both steel and aluminum showed **active-passive** corrosion behavior in [CH3(CH2)7]3NH.Tf2N.





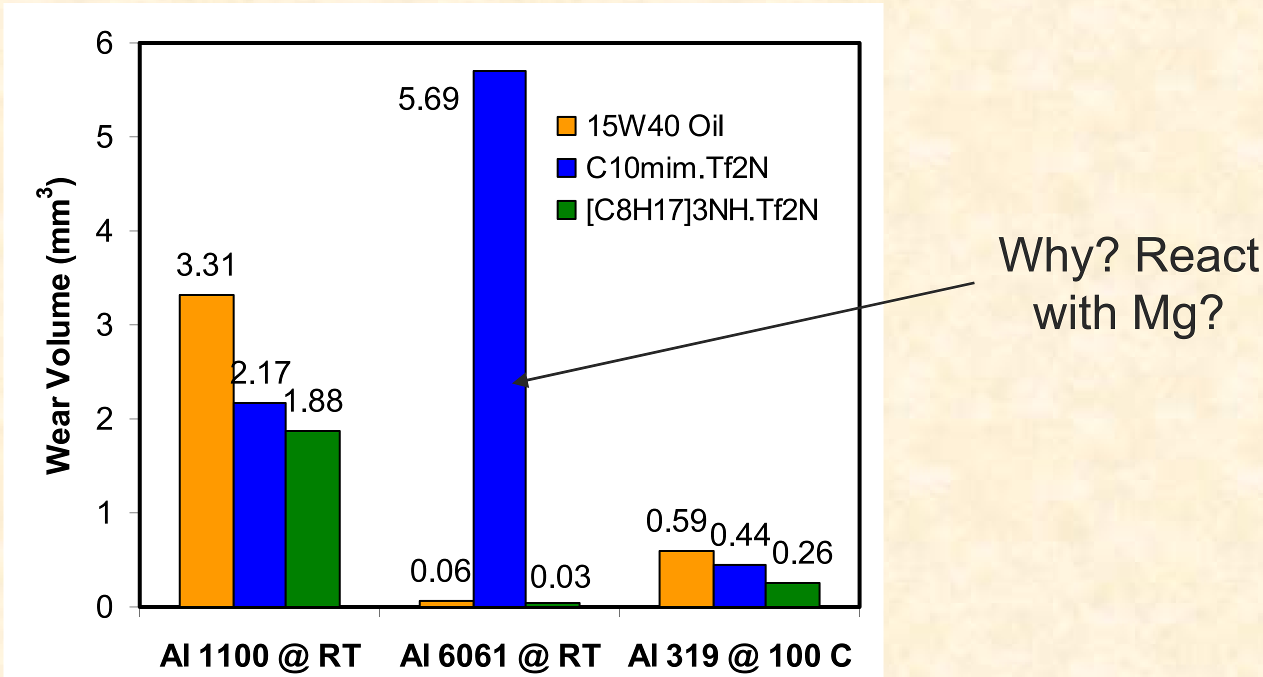
Friction Results for 3 Al Alloys

- $[C_8H_{17}]_3NH.Tf_2N$ produced lower COF by 20-35% than the 15W40 engine oil for different Al alloys.



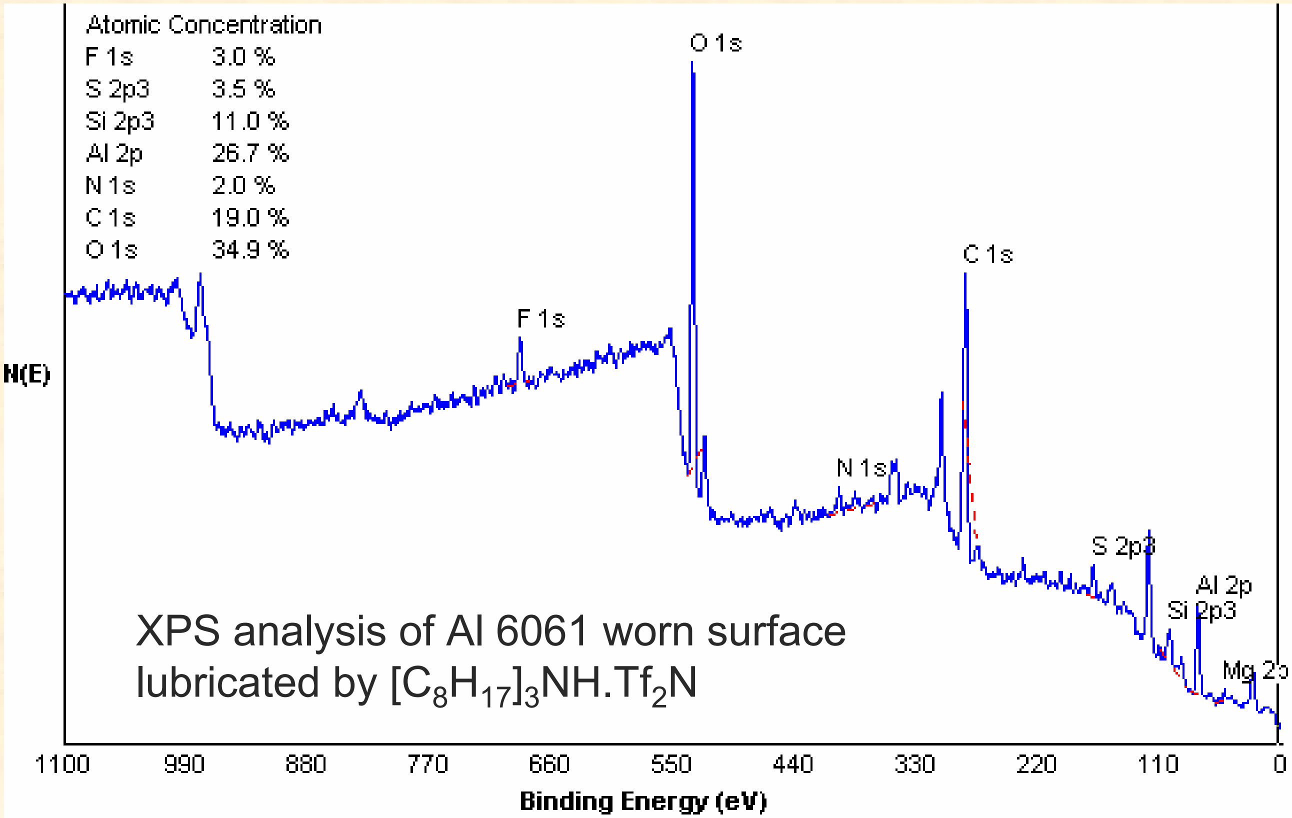
Wear Results for 3 Al Alloys

- **$[C_8H_{17}]_3NH.Tf_2N$ produced lower wear by 45-55% than that the 15W40 engine oil for different Al alloys.**
- $C_{10}mim.Tf_2N$ produced unexpectedly high wear for Al 6061.



Surface Chemistry - $[C_8H_{17}]_3NH.Tf_2N$

- Boundary films are detected on aluminum surfaces.
  - Inherent polarity and tribo-chemical reactions.



Surface Chemistry - $[C_8H_{17}]_3NH.Tf_2N$

- Possible composition of the surface boundary film: AlF_3, Al_2O_3, Al_2S_3, Al metallic phase, and organic compounds.