Lubrication Lab Call

Advanced Lubricant Technology - Technology Innovation, Design, and Synthesis

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Project ID: FT048

F&L Lubrication Lab Call - Lubricant Technology - *Innovation, Discovery, Design, and Engineering*

Three Thrust Areas, 4 National Labs, Multiple Industrial Partners
Lab Call Project Support for FY17 - $3M @ 75%

- **Thrust I - Surface and Lubricant Interactions**
  - ANL, ORNL
- **Thrust II - Technology Innovation, Design & Synthesis**
  - PNNL, ANL, ORNL
- **Thrust III - Lubricant Effects on Combustion and Emissions Control**
  - ORNL, NREL

Overview: Thrust II
Technology Innovation, Design, and Synthesis

Timeline

- Lab Call Lubricant research project supporting DOE/industry lubricant-technologies projects
- October 15, 2016-September 30, 2019
- FY17 - 50% complete

Budget

Project funded by DOE/VT:

FY17: 3M overall; 985K Thrust II (75% level)

Goals/Barriers

- By 2020, identify and validate lubricant technologies that further a 4% fuel economy goal by:
  - Reducing parasitic asperity and hydrodynamic friction losses by 25%
  - Low-viscosity lubricants improve fuel economy, but present challenges to reliability and durability.
- GF-5 testing platform

Partners

- ANL; ORNL; PNNL and multiple Industrial Partners

Relevance and Project Objectives

- Relevance:
  - 250 M vehicles
  - 10-12 MBBL/day
  - 5MMT CO_2/day
  - Café 2025 – 55 mpg
- Trust II Objectives:
  - Develop advanced base fluids, additives, and materials/coatings that reduce parasitic friction losses by 25%
  - Minimize viscous shear losses through hybrid base fluid design
  - Design Viscosity index improver additives that reduce friction (multifunctional)
  - Design new base fluids that intrinsically reduce friction through chemical functionality
  - Introduce colloidal additives to reduce wear and scuffing
  - Discover new coating technologies to increase durability and reduce friction
- Impact: increase fuel economy, reduce CO_2 emissions via drop-in-lubricant

Project addresses fuel economy improvements from a molecular level, through novel additives designs, hybrid base fluids and surface coatings

FY17 Milestones – Project and Thrust II Specific

Lab	Task	Milestone	Date*	Status
All		Develop downselect criteria, select baseline configuration (2009/GF4 or 2015/GF5), and identify paths (base fluids, additives, and coatings) to pursue.	FY17Q1	March 30, 2017 Completed
ANL	2.1	Blend and measure rheological properties of binary and ternary ultra-low viscosity hybrid basefluid from PAO, SHC, Esters, PAG	FY17 Q2	In progress; on track
ANL	2.2	Synthesize colloidal FM, AW and EP functional additives with appropriate encapsulator.	FY17 Q2	In progress; on track
ANL	2.3	Development of VN family coatings with catalytic components of and CuNi	FY17 Q2	In progress; on track
ANL	2.3	Testing Coating performance – Wear/ friction and scuffing performance of VN family catalytically active nano-composite coatings with base fluids.	FY17 Q4	In progress; on track
PNNL	2.2	Continue the development of multifunctional VIIs	FY17 Q2	In progress; 3 month delay
PNNL	2.1	Synthesize base fluids which are multifunctional	FY17 Q2	completed
PNNL	2.2	Develop protocols for the synthesis of extreme pressure additive moieties built in viscosity index improvers.	FY17 Q4	In progress; on track
ANL	2.1	Measure friction, wear and scuffing behavior of hybrid base fluid under different contact conditions	FY17 Q4	In progress; on track
ANL	2.1	Measure the friction, wear and scuffing performance of colloidal additives blended into ultra-low viscosity PAO base fluid	FY17 Q4	Not yet started
PNNL	2.1	**Evaluate friction and wear in novel base fluids**	FY17 Q3	75% Complete, on track

* These dates were projected at full funding level; the actual dates will shift

Approach/Strategies

How can we achieve 4% FE improvement?

- Efficient Additives to reduce friction:
  - Multifunctional additives
    - Built-in Functionality to reduce friction
    - Built-in Functionality to address extreme pressure
  - Colloidal additives for friction, wear, scuffing and enhanced thermal control
- Base Fluids to reduce viscosity and friction:
  - Hybrid base fluids with ultra low viscosity: formulate binary, ternary and quaternary fluids
  - Multifunctional to address rheology, friction and wear without additives: Methacrylate-based fluids or composite for fluids
- Coating technologies for next generation cars:
  - VN coatings can potentially eliminate stringent requirements from lubricant

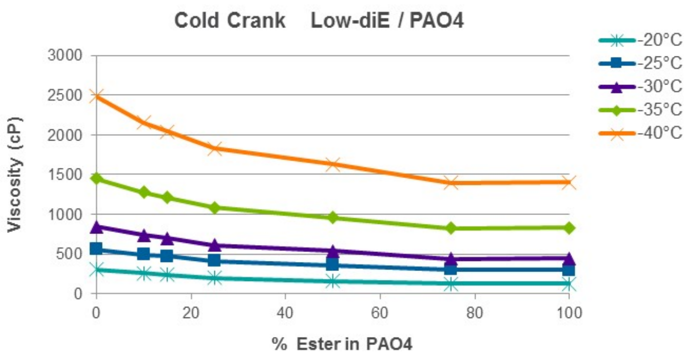
Go/No-Go FY18Q2

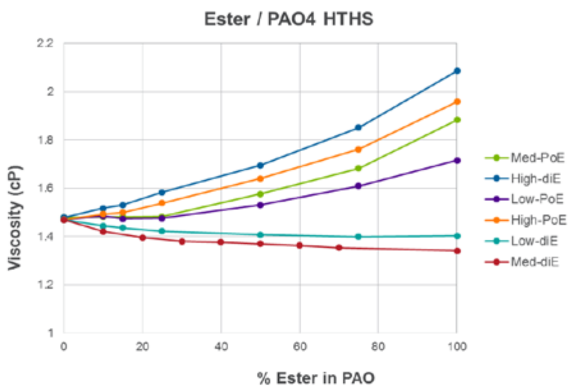
Identify and demonstrate state-of-the-art low-viscosity lubricant systems that reduce friction by 20% over baseline (GF5) without reducing durability.

Technical Accomplishments

Ultra-low viscosity hybrid base-fluid

- Blended binary fluids of several types of low-viscosity ester and PAO4 in different ratios.
- Measured three viscosities of fluid blends – kinematic, CCV, HTHS
- Building data base of viscosities for various composite fluid blends towards a semi-empirical thermodynamic model development

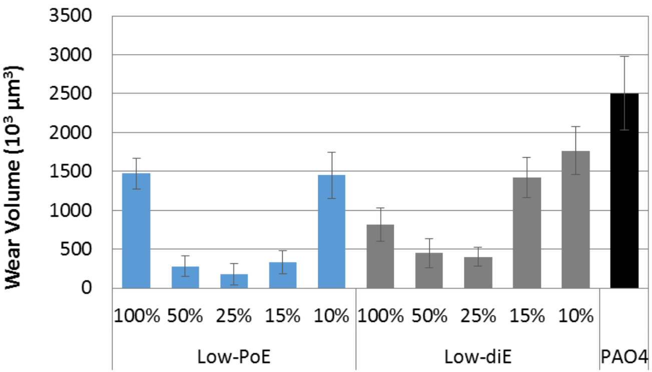


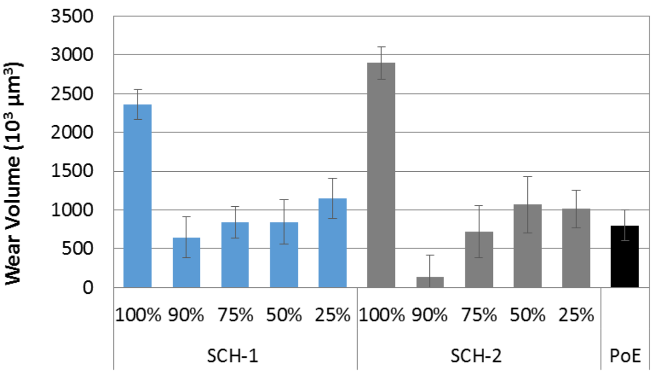


Technical Accomplishments
Ultra-low viscosity hybrid base-fluid (ANL)

- Evaluated rheological properties of binary hybrid fluids (PAO/ester and SHC/ester)
- Evaluated the wear performance of PAO and 2 different esters (polyol ester, PoE and diester, diE) and two types of SHC with polyol ester.
- Identified minimal wear for
  - Ester-PAO in the range of 15-25 % ester
  - Ester-SHC in the range of 10-25% polyol ester

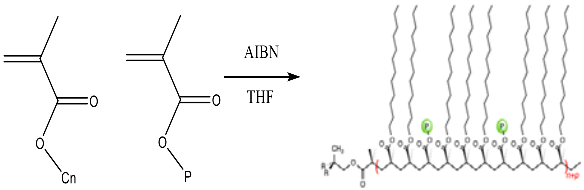
Conclusion:
Achieved competitive wear results for hybrid base fluids





Technical Accomplishments
Multifunctional Base Fluids (PNNL)

- Low molecular weight polymethacrylates not previously explored as base stocks
- They can possess functionality usually provided by additives, towards friction and wear control
- Soluble in Group III oil and PAOs
- Due to lower MW than traditional VIIS, these polymers are more stable to shear
- Amenable to scale-up



Comp ID	Conc in 4Yubase (w/w)	Polymer Composition*	KV40 (cSt)	KV100 (cSt)	VI
61828 62A	50%	M1:PM1/ - 1:0.15	504.5	66.89	210
61828 62B	25%	M1:PM1/ - 1:0.15	91.9	17.81	213
61828 62C	12.5%	M1:PM1/ - 1:0.15	40.67	8.80	204
61828 62D	25%	M1:PM2/ - 1:0.15	54.41	11.73	217
61828 62E	12.5%	M1:PM2/ - 1:0.15	35.46	7.61	191
61828 63A	25%	M1 homopolymer	75.39	18.05	260
61828 63B	12.5%	M1 homopolymer	40.83	9.52	228

Results:

- Even at low MW, the neat polymers are too viscous
- Function as additives at high level (10-12%)
- High VIs
- Shear stability evaluation – in progress

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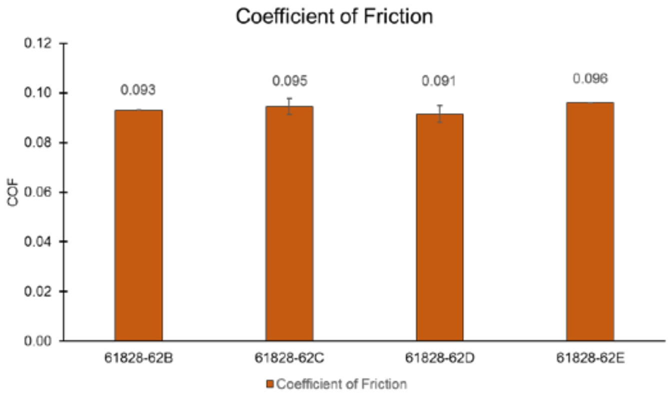
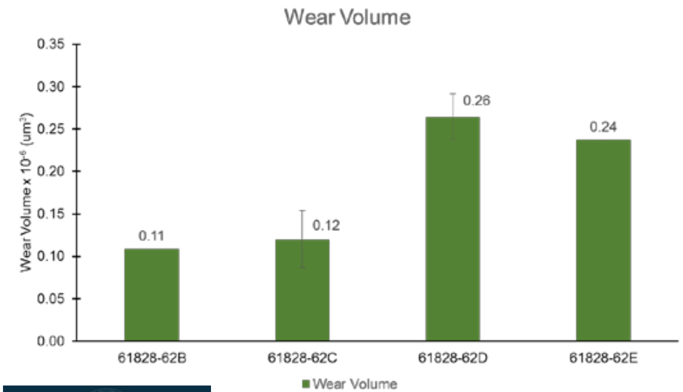
Technical Accomplishments

Multifunctional Base Fluids Tribological Evaluation (PNNL and UC Merced)





- COF is independent of:
  - Concentration of the composite/VM in base fluid
  - Nature of the polar co-monomer
- Wear is
  - Dependent on the polarity of the co-monomer (N versus O – containing)
  - Independent of the concentration of the composite in base fluid

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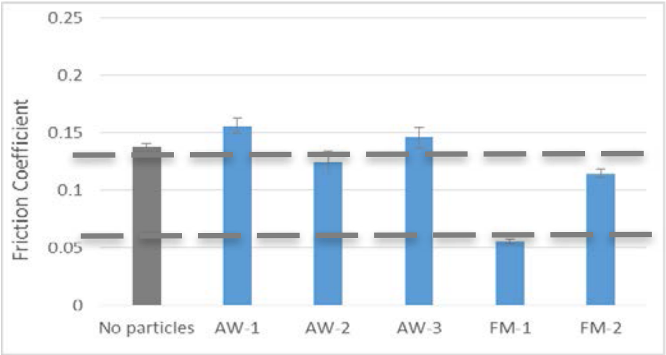
Technical Accomplishments

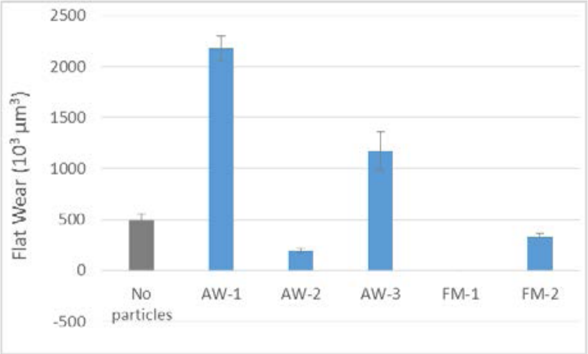
Multifunctional colloidal additives (ANL) -

- Deliver sustainable friction reduction via encapsulation technology
- Engineer tribochemical (boundary) films structure

Results:

- Identified several FM, AW, EP and TD particles that do not affect rheological properties.
- Investigated nano-mechanical properties of colloidal tribofilms
  - Two FM candidates colloidal systems (MoS_2 and Cu)
  - Three AW candidates colloidal systems (Al_2O_3, SiO_2, ZrO_2)
- Tribological performance of several colloidal systems in ultra-low viscosity base stock similar or superior to benchmark performance.

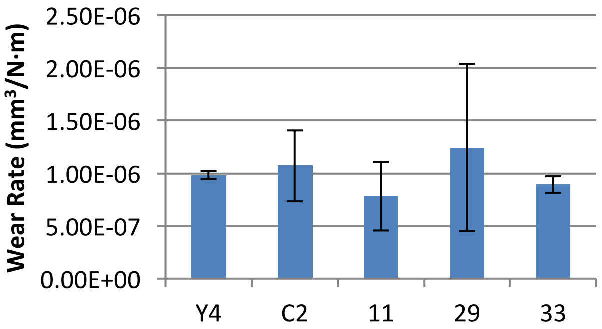




Friction coefficient and flat wear in reciprocating sliding for AW and FM colloidal additives systems

Technical Accomplishments

Multifunctional Viscosity Index Improvers (PNNL) -

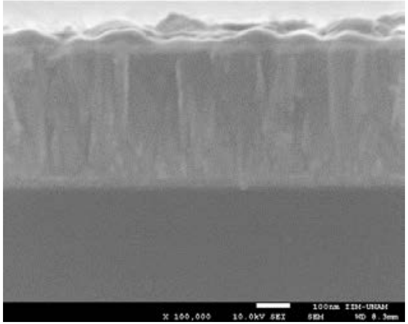


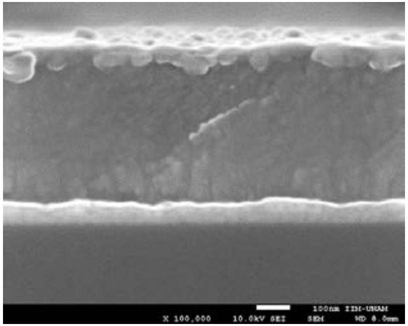
- C2 is a PAMA VII commercial benchmark
- 11, 29 and 33 are inventive compounds
- This project is a continuation of LDRD funded effort
- Synthetic efforts to include different IL moieties
- Defining methodology in progress

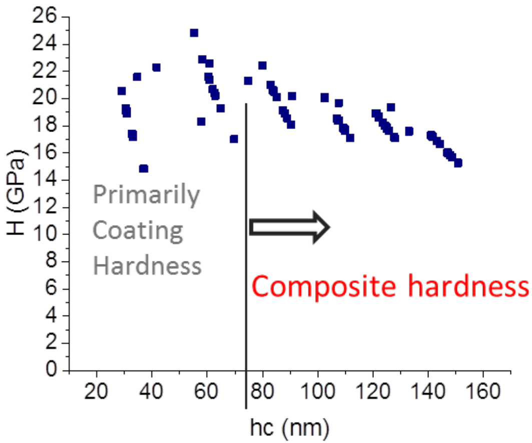
Sample #	Composition (Polar component)	type	KV 25 (cSt)	KV 40 (cSt)	KV 100 (cSt)	VI
62127-11	20% amine	random	44.39	25.19	5.78	184
62127-29	20% IL	random	40.90	23.66	5.29	166
62127-33	10% IL	random	42.53	24.09	5.52	178.5

Technical Accomplishments

Coating Optimization and Characterization







- Columnar structure disappeared with Ni addition into Vanadium Nitride which results in a more dense/compact structure.
- Morphology determined by SEM
- Excellent adhesion to steel substrate: Rockwell C Coating adhesion test reveals that adhesion falls into HF1 category
- Coating Hardness is around 20 GPa

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year.

Collaboration and Coordination

Argonne National Laboratory: Leads the entire project; Provides friction and wear expertise to further tasks within Thrust 2 (G. Fenske; R. Erck, N. Demas, O. Ajayi, C. Lorenzo-Martin, A. Erdemir, O. Eryilmaz, G. Ramirez).

Oak Ridge National Laboratory: Engagement in meetings; participate in various phases of Thrust 2 with substantial involvement starting FY18

UC Merced, University of California: Ran simulations of small molecular architectures to predict shear thinning (A. Martini, U.S. Ramasamy); Conducted friction and wear measurements of polymeric additives

Afton Chemical: Kindly provided DI package to prepare finished lubricant. Interested in multifunctional VIIs and will become more engaged in further testing as PNNL compounds are down selected and scaled-up.

Infineum: ANL will be getting partially formulated fluids for colloidal additives studies from Infineum. Collaboration in place.

USDA: Agreement with USDA Lab. in Peoria to include bio-derived ester (potential DOE-USDA joint effort)

Remaining Challenges and Barriers

- **Ultra-low viscosity hybrid base-fluid**
  - Need for rapid simultaneous measurement of viscosity and density of various composite fluids as a function of temperature.
- **Multifunctional base fluids**
  - Even at low molecular weights, polymethacrylates are too viscous
  - These will be further tested as additives
- **Multifunctional colloidal additives**
  - Suspension of colloidal particles with time
  - Compatibility with other additives in the package
- **Development of multifunctional viscosity modifiers**
  - Delays encountered in the hiring process
  - Delays in receiving key starting material, methacryloyl chloride
  - Select most suitable polymer synthesis methodology
- **Coatings**
  - None, however tribo-testing activities depend on receiving base/partially formulated oils.

Proposed Future Work

- Ultra-low viscosity hybrid base-fluids
  - Rheological study and data base of more composite fluids
  - Formulation of semi-empirical thermodynamic model for rheological properties
- Multifunctional base fluids
  - Evaluate wear for all analogs in the series
  - Investigate shear stability
- Multifunctional colloidal additives
  - Optimization of colloidal additive systems for AW, FM, EP and TD properties.
  - Determination of nano-mechanical properties of colloidal tribofilms
- Development of multifunctional viscosity modifiers
  - Evaluate friction and wear of IL polymers
  - Synthesize polymers containing other IL pairs
- Coatings
  - Evaluate friction and wear performance of catalytically active nano-composite coated surfaces with base and partially formulated oils.

Any proposed future work is subject to change based on funding levels

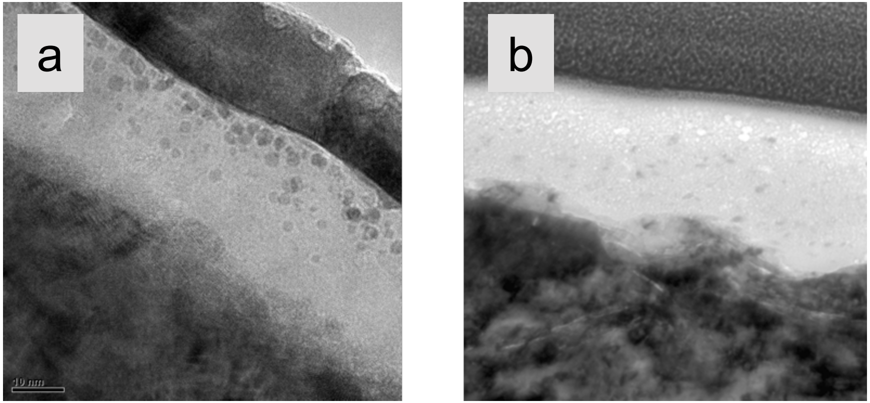
Summary

- Each laboratory is leveraging their expertise to contribute to friction and viscosity control technologies
- By using the alloying principle better properties were obtained from the composite than the individual components (hybrid base fluids)
- Minimal wear was obtained for Ester-PAO in the range of 15-25 % ester
- Prepared base oil composites that are expected to control viscosity, friction and lower shear losses, as compared to viscosity index improvers
- Delivered AW and FM colloidal additives with competitive tribological performance
- Multifunctional VIIs encountered synthetic challenges due to their unique structure and thus delays, however we are now back on track
- Incorporation of Ni into VN coatings improved density and hardness of the resulting coating

Backup Slides

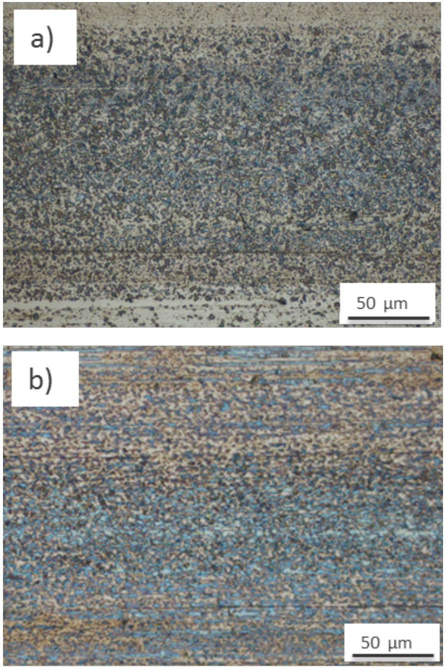
Multifunctional colloidal additives (ANL)
Structure of colloidal tribofilms

- Tribofilm from colloidal additives is similar to ones from current chemical additives system:
  - Surface morphology is similar (optical micrographs)
  - Mixed amorphous-crystalline structure (TEM micrographs)



TEM micrograph of tribofilm from a) FM colloidal additive and b) chemical additives

Optical micrograph of tribofilm from a) AW colloidal additive and b) chemical additives



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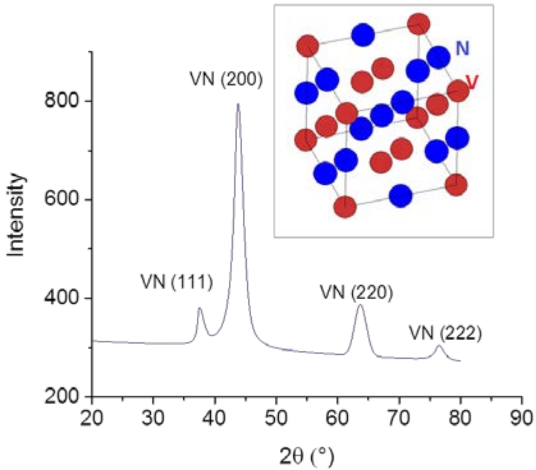
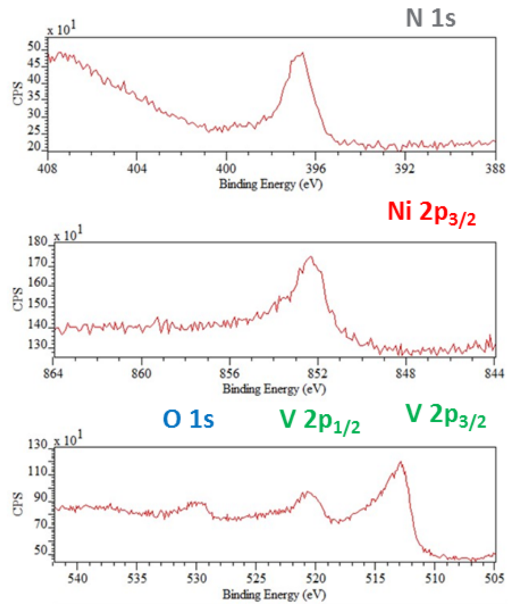
Coatings

Coating Microstructure and Composition





- XRD confirms VN phase
- XPS results shows that coating has 9.5% Nickel:
  - O 10.85 at.%
  - N 35.44 at.%
  - V 44.3 at%
  - Ni 9.41 at.%

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