sp3 nanotech®

Nanodiamond and Lubrication Applications

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January, 2014
AIChE Dallas Chapter Meeting

SP3 NANOTECH, LLC

- Founded To Commercialize New Markets For Nano-materials
  - Research, Develop And Then Spin-out New Nanotechnologies
  - Focused On Additives That *Enhance* Existing Materials

- Core Competencies
  - Working With Low-aspect Ratio Nano-materials
  - Developing Surface Chemistry For Functionalization Of Nano-materials

- Nanodiamond (Adamight™ LS) for enhancing lubricants is our first product
  - Lubricants: Reduce friction, reduce wear

FRICTION AND WEAR: A $664 Billion Problem

- Current estimates: **2-6% of GDP lost to friction and wear**
- **~1% of GDP could be saved**
  - ~$166 Billion in the U.S. alone
  - ~$664 Billion worldwide
- US Lubricants Industry: $18.7 Billion revenue in 2013

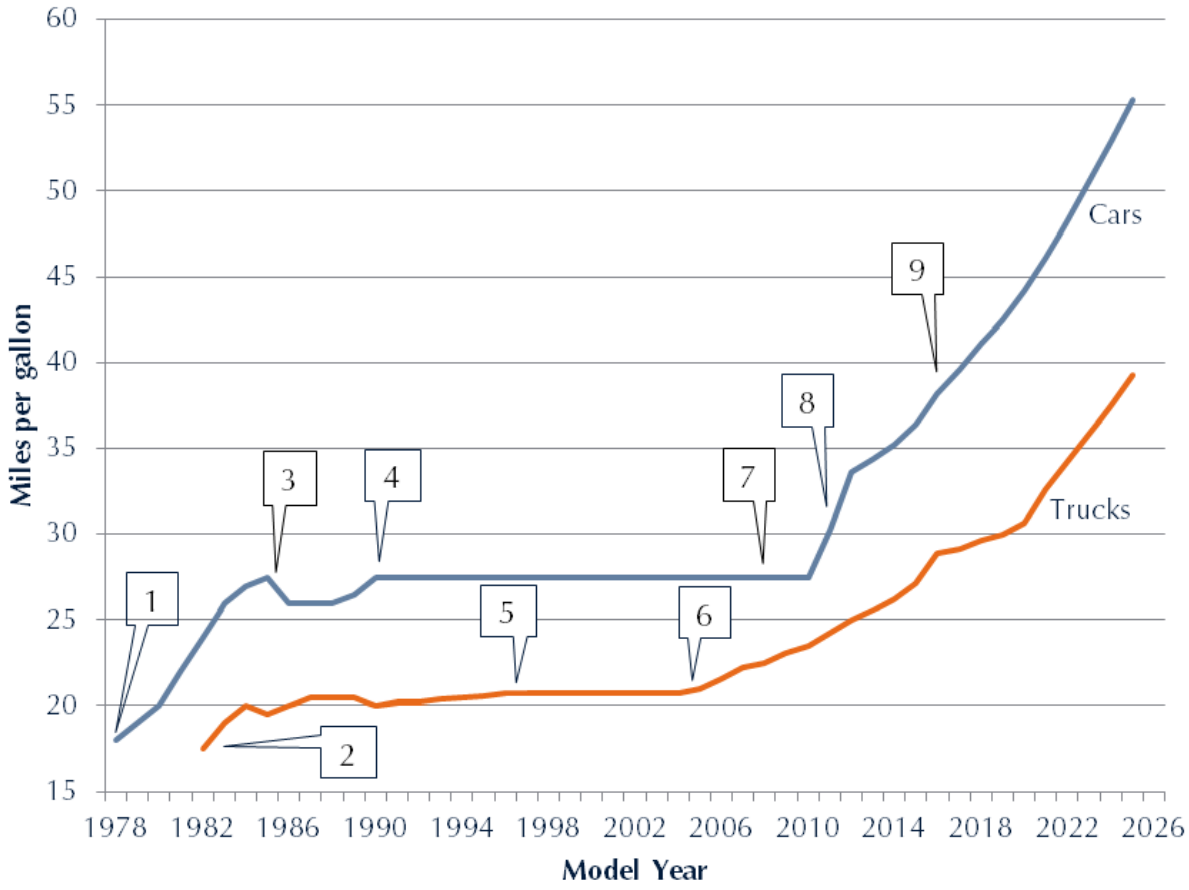
enduracoatings.com/low-friction.html

gilsonsnowblowers.com/snowparts3.html

IBISWorld Industry Report 32419
Lubricant Oil Manufacturing in the US

MOTIVATION FOR IMPROVED LUBRICANTS IN AUTOMOTIVE APPLICATIONS (53% OF U.S. LUBRICANTS MARKET)

- Higher CAFE standards
  - 54.5 MPG by 2025 (Currently 35.5 MPG)
- Longer Oil Change Intervals
  - 3,000 miles → 7,500 miles → 15,000 miles



http://www.altenergystocks.com/archives/2011/07/aggressive_new_cafe_standards_the_ic_empire_strikes_back.html

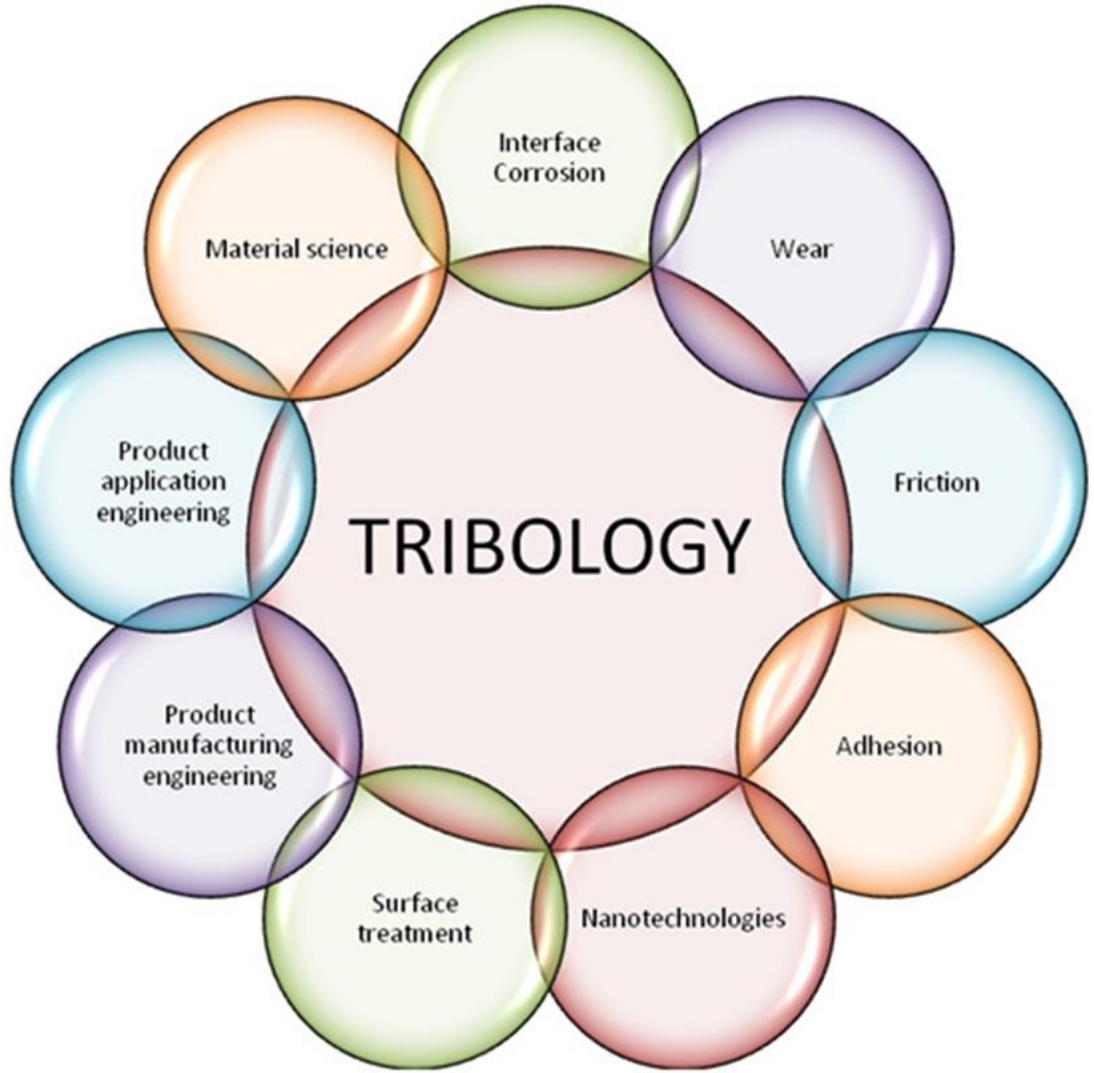
OUTLINE

- Lubrication/Tribology Basics
- Overview of Nanodiamond
- Application of Nanodiamond to Lubrication
- Application of Nanodiamond to Polymer Composites

Some Basics of Tribology

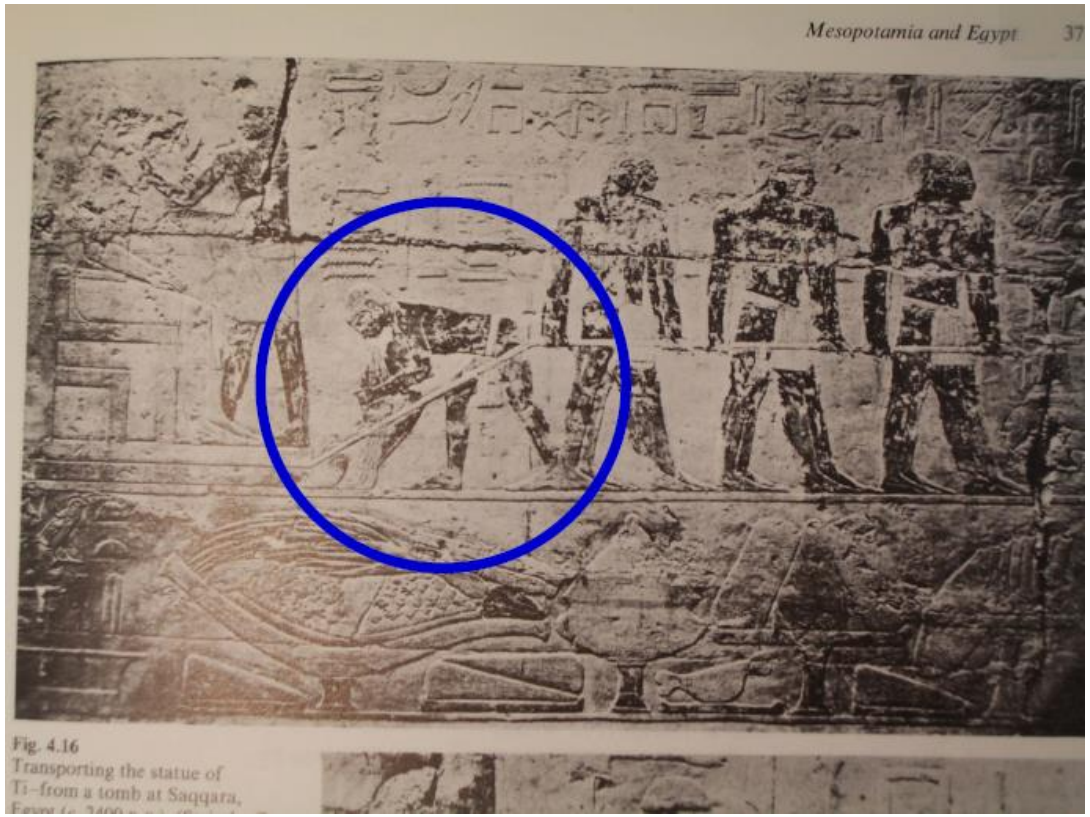
Tribology - a study that deals with the design, **friction**, **wear**, and lubrication of interacting surfaces in relative motion (as in bearings or gears)[1]

[1]merriam-webster.com

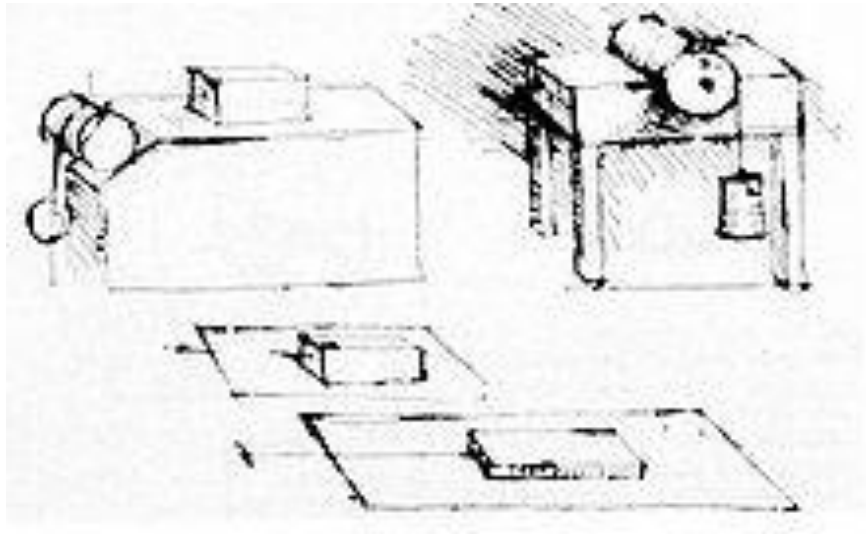


ins-thai.com/customers.html

TRIBOLOGY: AN ANCIENT ART

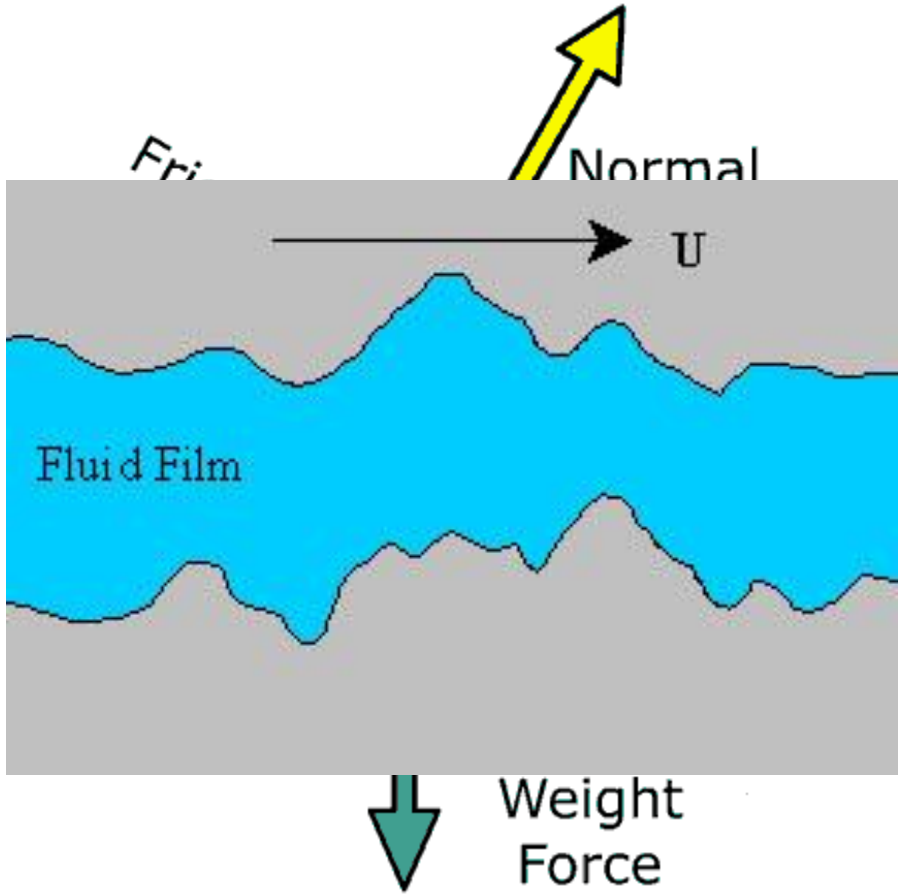


Egyptians transporting a statue and placing a lubricant (probably water) underneath the sled



en.wikipedia.org/wiki/File:Tribometre_Vinci_1.jpg

FRICTION



$$F_f = \mu F_n$$

$F_f = Frictional\ Force$

$F_n = Normal\ Force$

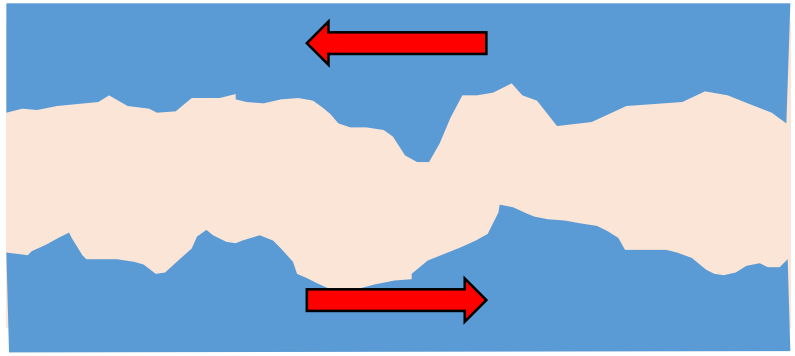
$\mu = Coefficient\ of\ Friction\ (CoF)$

www.stmary.ws/highschool/physics/home/notes/dynamics/friction/introFriction.htm

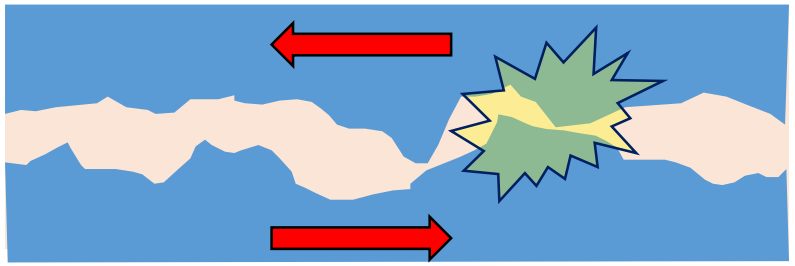
www.stle.org/resources/lubelearn/lubrication/

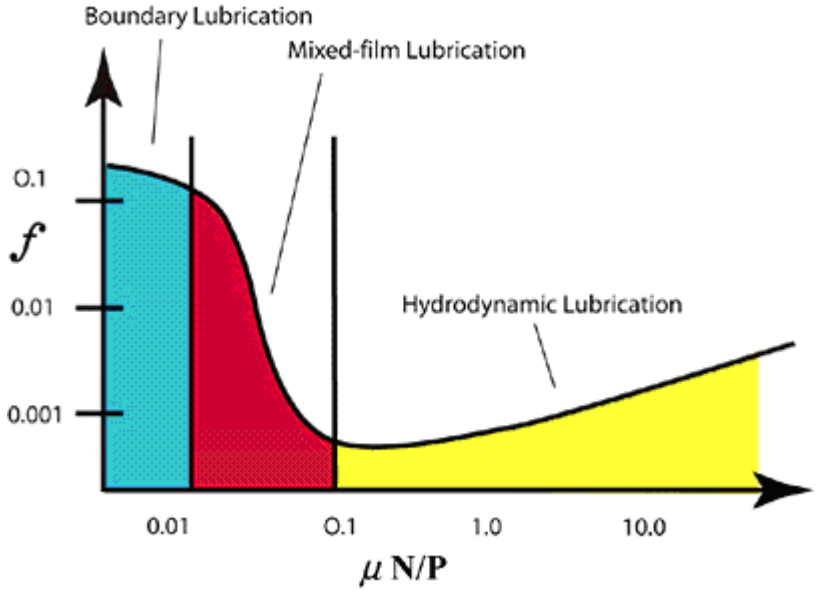
FRICTION/LUBRICATION REGIMES

Hydrodynamic Lubrication



Boundary Lubrication





f= coefficient of friction

μ = viscosity

N = speed

P = Pressure

stle.org/resources/lubelearn/lubrication/

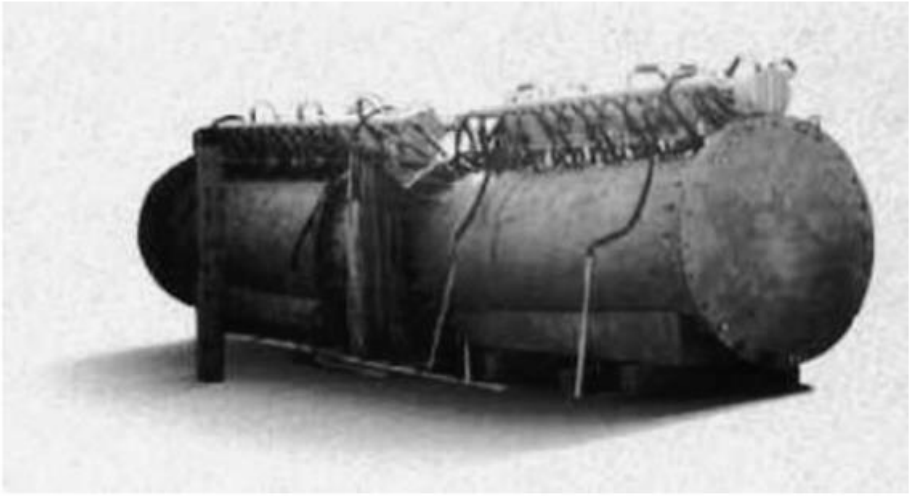
OUTLINE

- Lubrication/Tribology Basics
- **Overview of Nanodiamond**
- Application of Nanodiamond to Tribology/Lubrication
- Application of Nanodiamond to Polymer Composites

Nanodiamond

DETONATION NANODIAMOND PRODUCTION

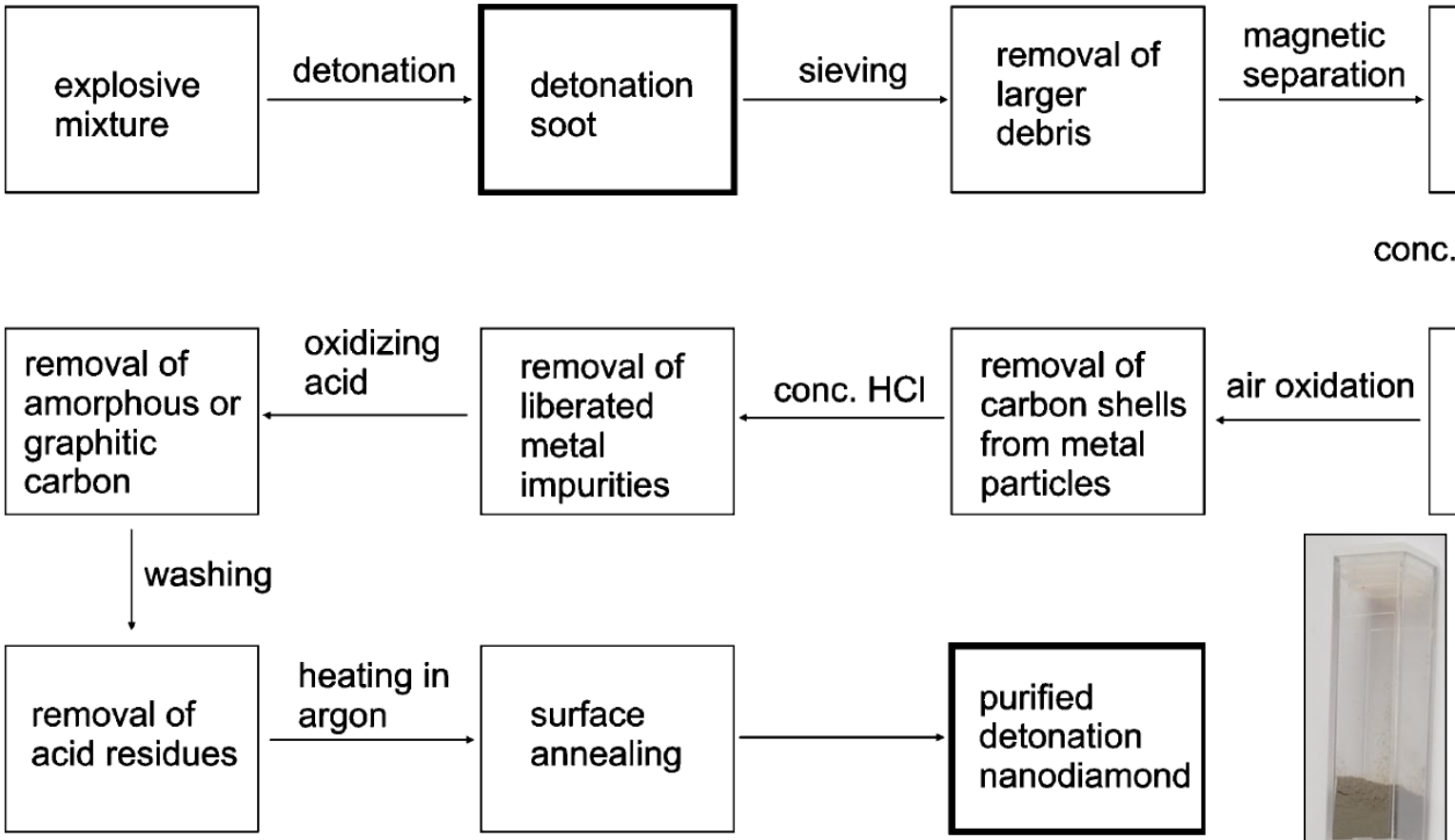
- Production technique developed by Russian scientist in 1960's
- Briefly expose graphitic carbon to high-pressure/high-temperatures (i.e. explosion)
- Produce nanoparticles of diamond
- Highly aggregated
- Until recently, primary application was as a polishing compound



Industrial Scale Nanodiamond Reactor

A. Krueger, *J. of Mater. Chem.*, 2008, 18, 1485-1492

POST-EXPLOSION PROCESSING

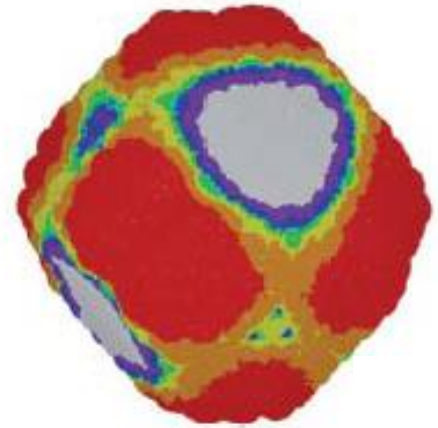


Scheme 1 Example for the purification process of detonation soot for the production of detonation nanodiamond.

J. Mater. Chem., 2008, **18**, 1485–1492 | 1487

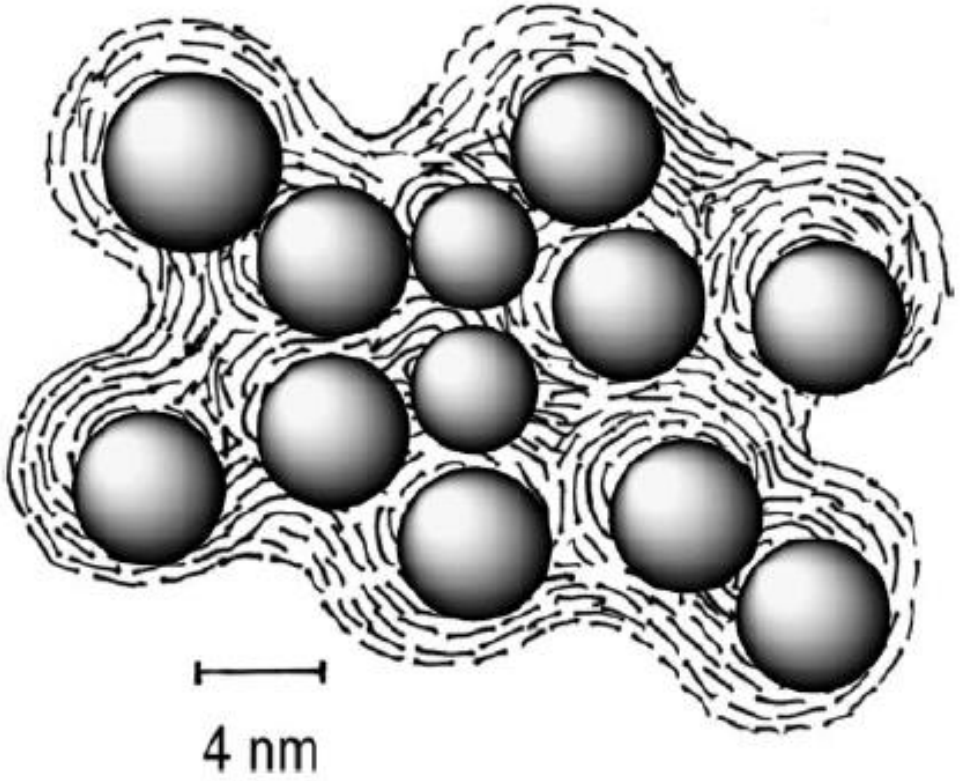
PURIFIED NANODIAMOND MATERIAL PROPERTIES

- Spheroid core crystals, <10nm
- High modulus diamond core
- High thermal conductivity
- Good dielectric properties
- Surface amenable to chemical modification/tailoring
- Synthetic product – large potential supply
- Bio- and eco-friendly



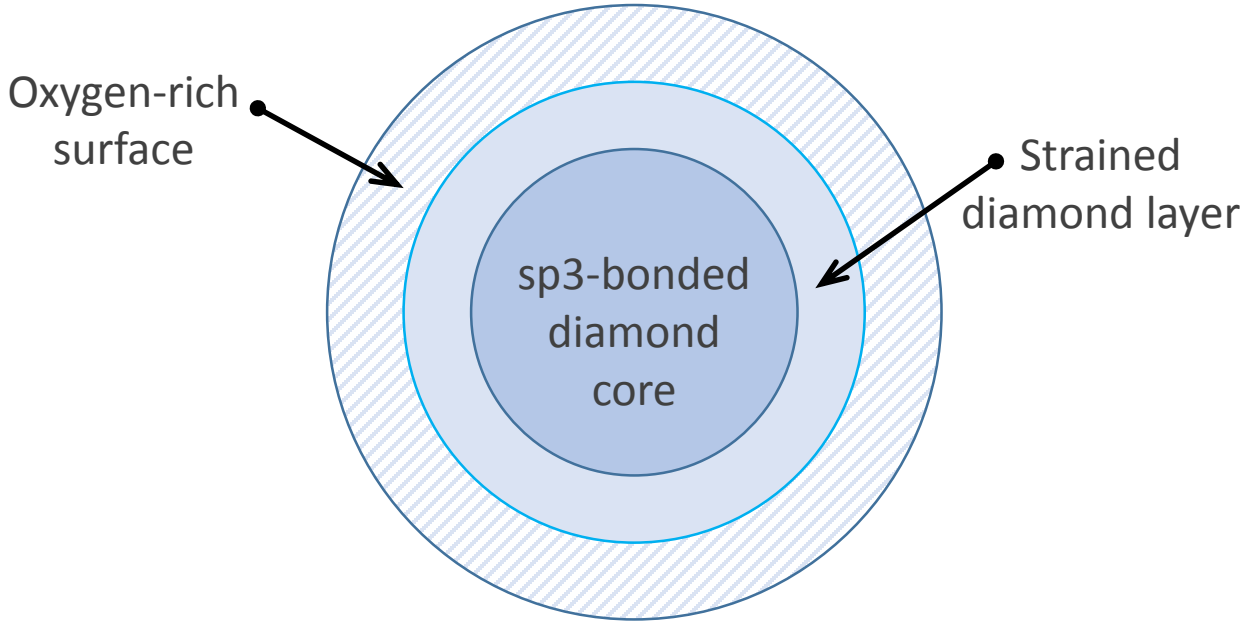
Banard, A. S., *Journal of Materials Chemistry* **2008,** 18, 4038-4041

NANODIAMOND'S 1ST PROBLEM = AGGREGATION & POOR DISPERSION



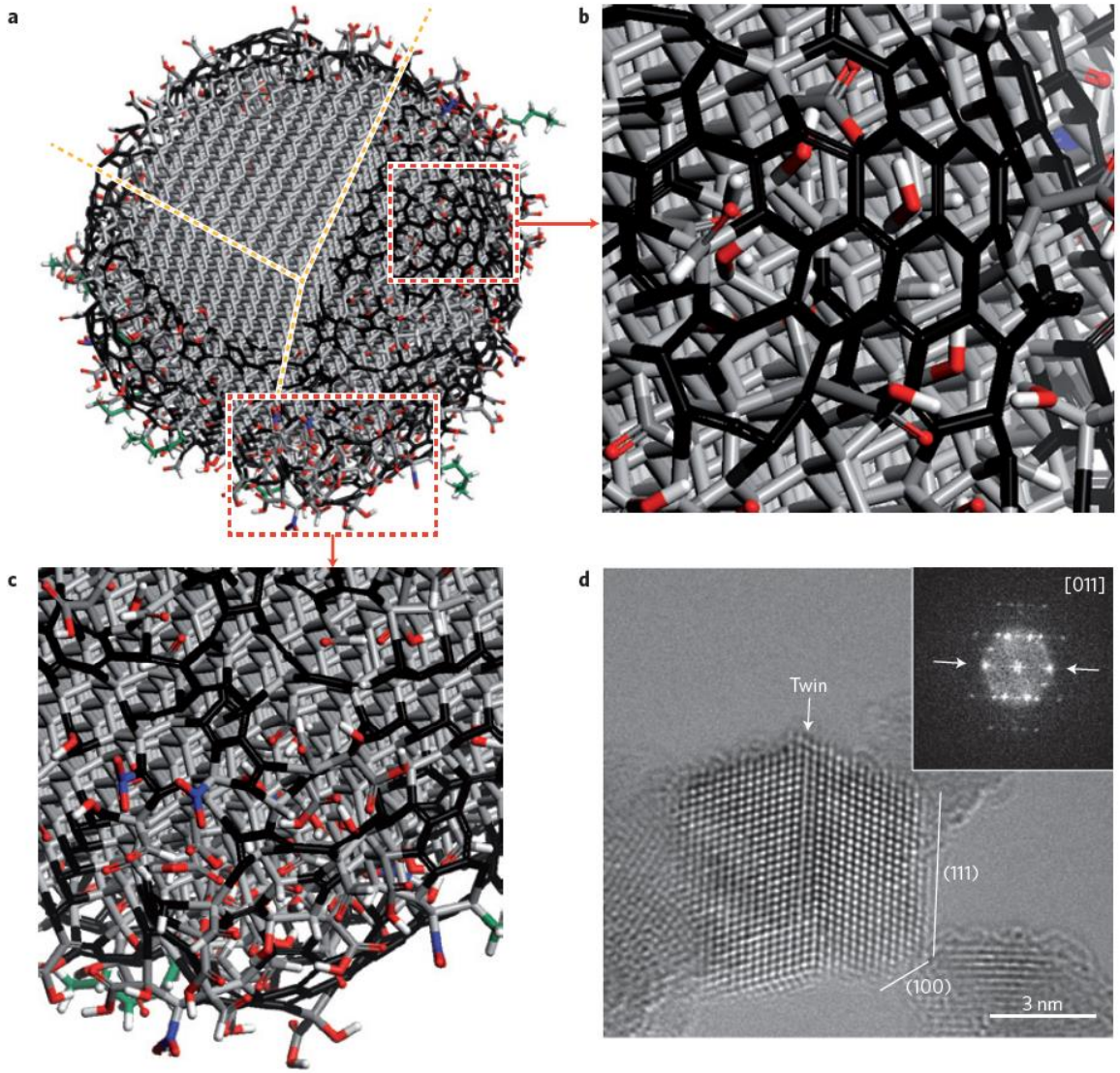
- Abrasive
- Quickly settles/falls out of solution

WHY DOES NANODIAMOND AGGREGATE?



Adapted from: Holt, K. B.,. *Philisophical Transactions of the Royal Society, A* **2007,** 365, (1861), 2845-2861.

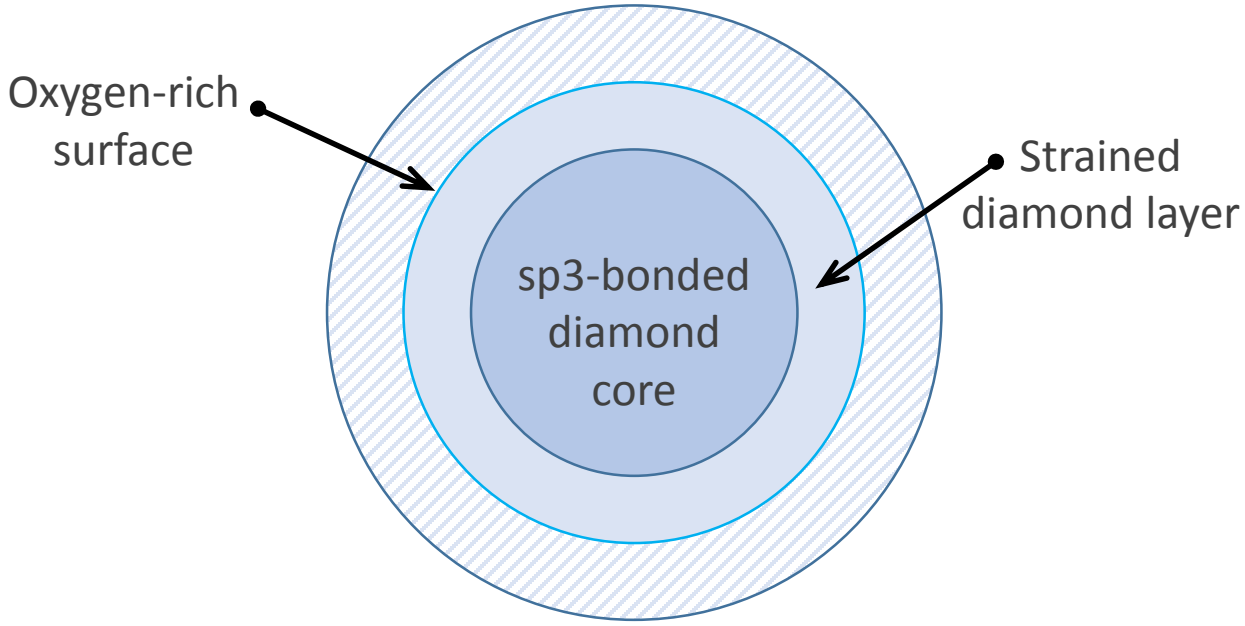
NANODIAMOND'S AGGREGATION



- Diamond (carbon) = gray
- Graphite (carbon) = black
- Oxygen = red
- Hydrogen = white
- Nitrogen = blue

Mochalin et al, *Nature Nanotechnology*, 2012, 7.

NANODIAMOND'S AGGREGATION



Adapted from: Holt, K. B.,. *Philisophical Transactions of the Royal Society, A* **2007,** 365, (1861), 2845-2861.

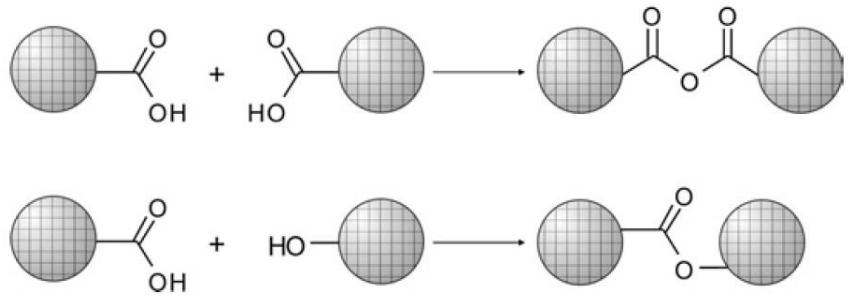
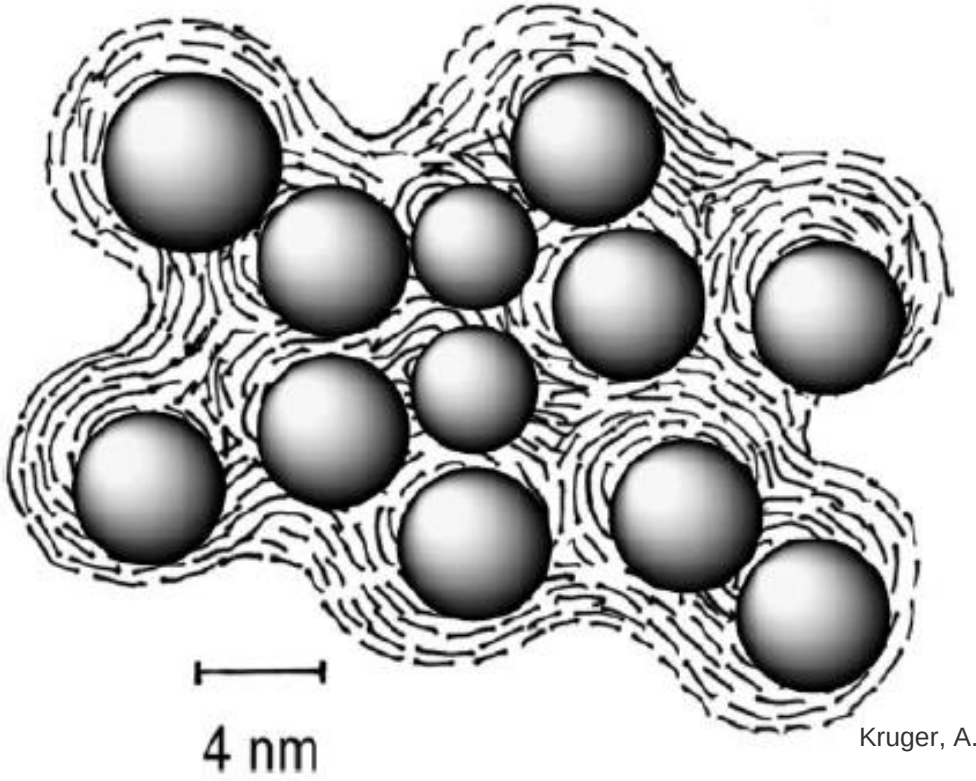


Fig. 7 A possible structure model for diamond agglomerates in detonation diamond.

J. Mater. Chem., 2008, **18**, 1485–1492 | 1487

- Aggregation may be aggravated by intra-particle covalent bonding

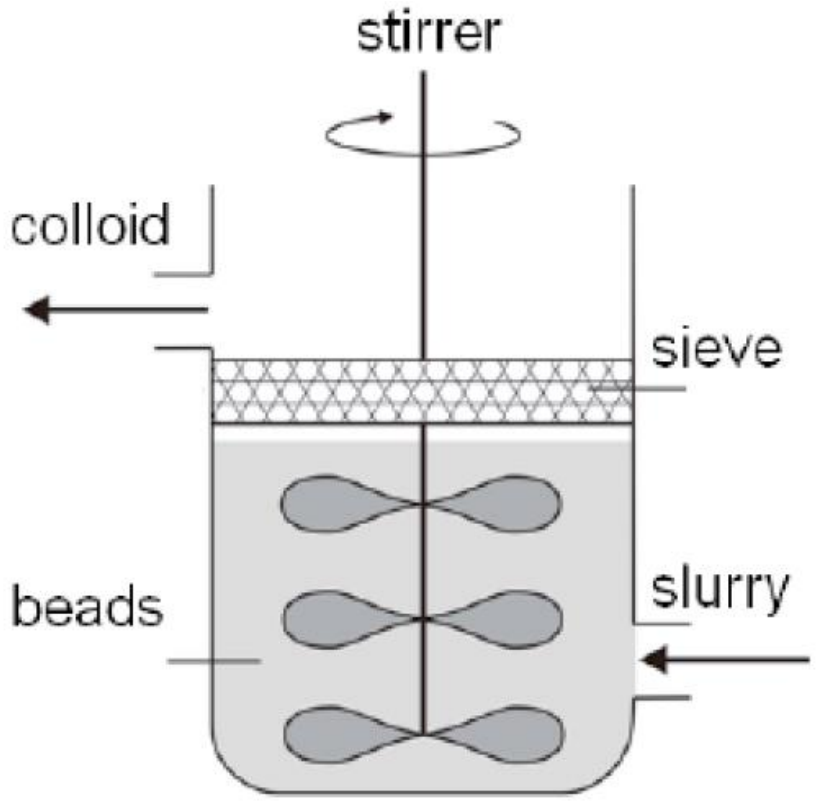
NANODIAMOND'S AGGREGATION



Kruger, A., et al., *Carbon* 43 (8), 2005

- Abrasive
- Quickly settles/falls out of solution

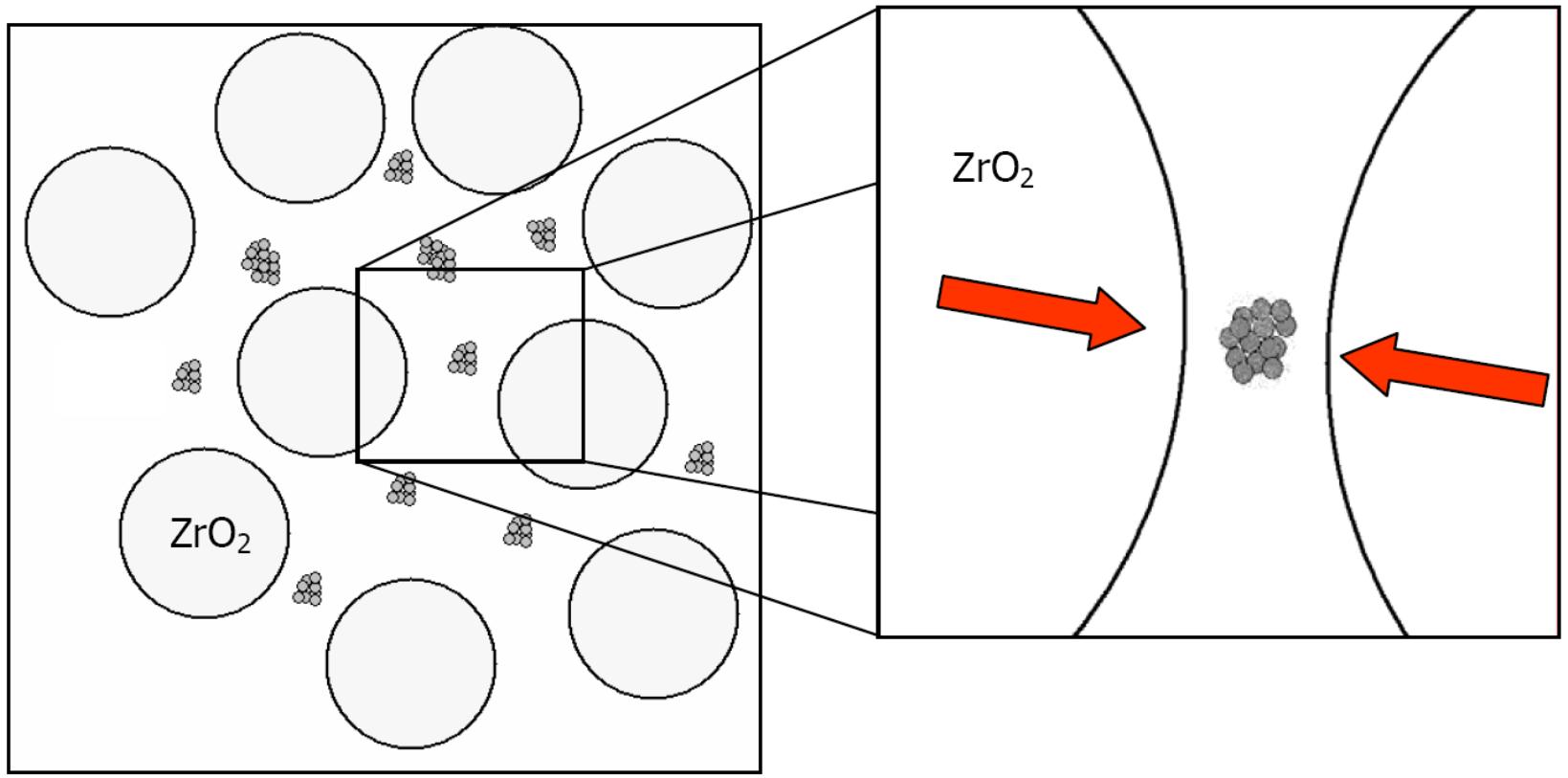
FIRST KEY TO NANODIAMOND'S POTENTIAL = DE-AGGREGATION



- Stirred media milling
- Zirconia Beads

Krueger et al., *physica status solida*, 2007, 204 (9), 2881-2887

FIRST KEY TO NANODIAMOND'S POTENTIAL = DE-AGGREGATION

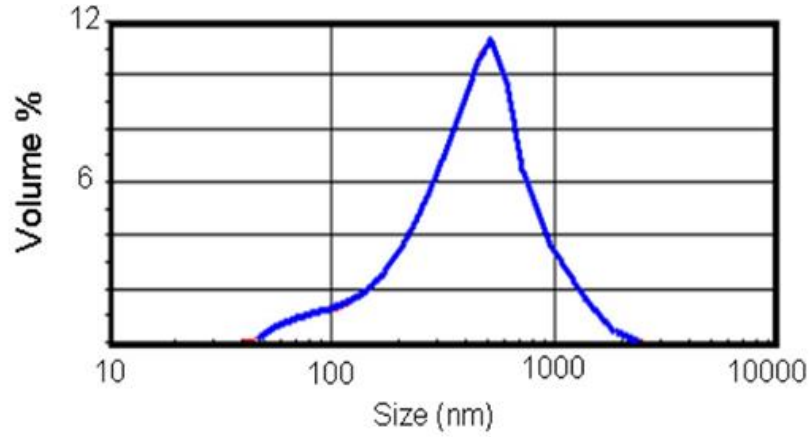


Branson, B., FLUIDS AND POLYMER COMPOSITES COMPRISING DETONATION NANODIAMOND, 2010

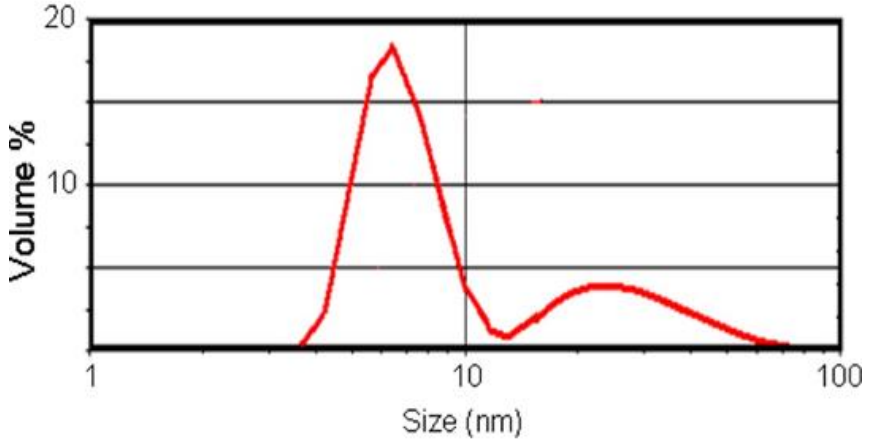
- Colliding zirconia beads break-up nanodiamond

DE-AGGREGATION IN DMSO

Particle Size Distribution Before Disaggregation

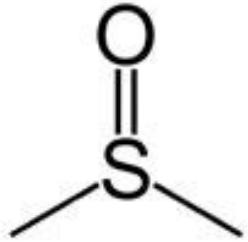


Particle Size Distribution After Disaggregation



Branson et al, *ACS NANO*, 2013, 7, (4).

DMSO
(Strong Hydrogen Bond Acceptor)



Before/After Pictures

WHAT ABOUT OTHER SOLVENTS, I.E. WATER OR OILS, ETC.?

DMSO

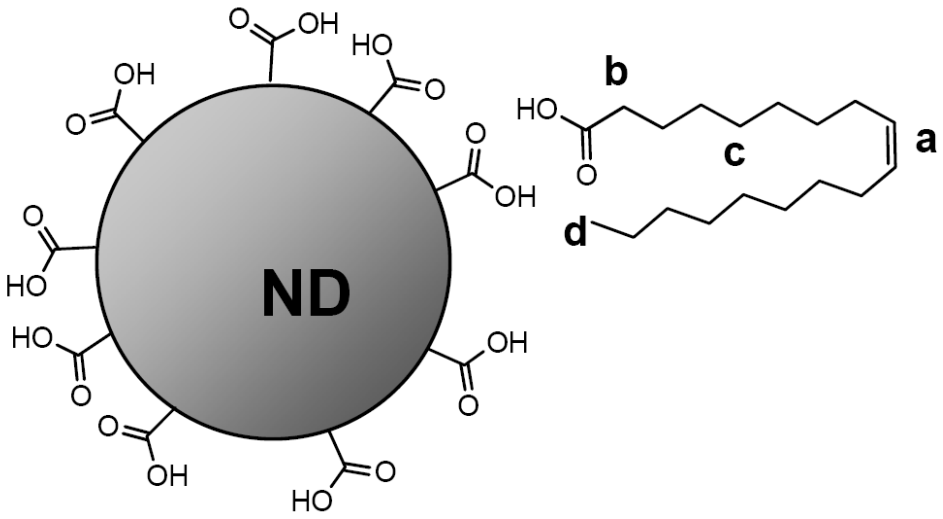
Synthetic Oil

Water

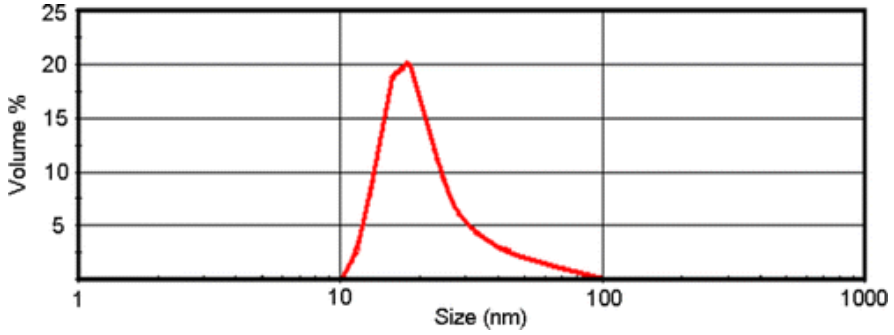
MOST MAKE NANODIAMOND COMPATIBLE WITH MORE FLUIDS FOR COMMERCIAL APPLICATIONS

SECOND KEY TO NANODIAMOND'S POTENTIAL = SURFACE FUNCTIONALIZATION

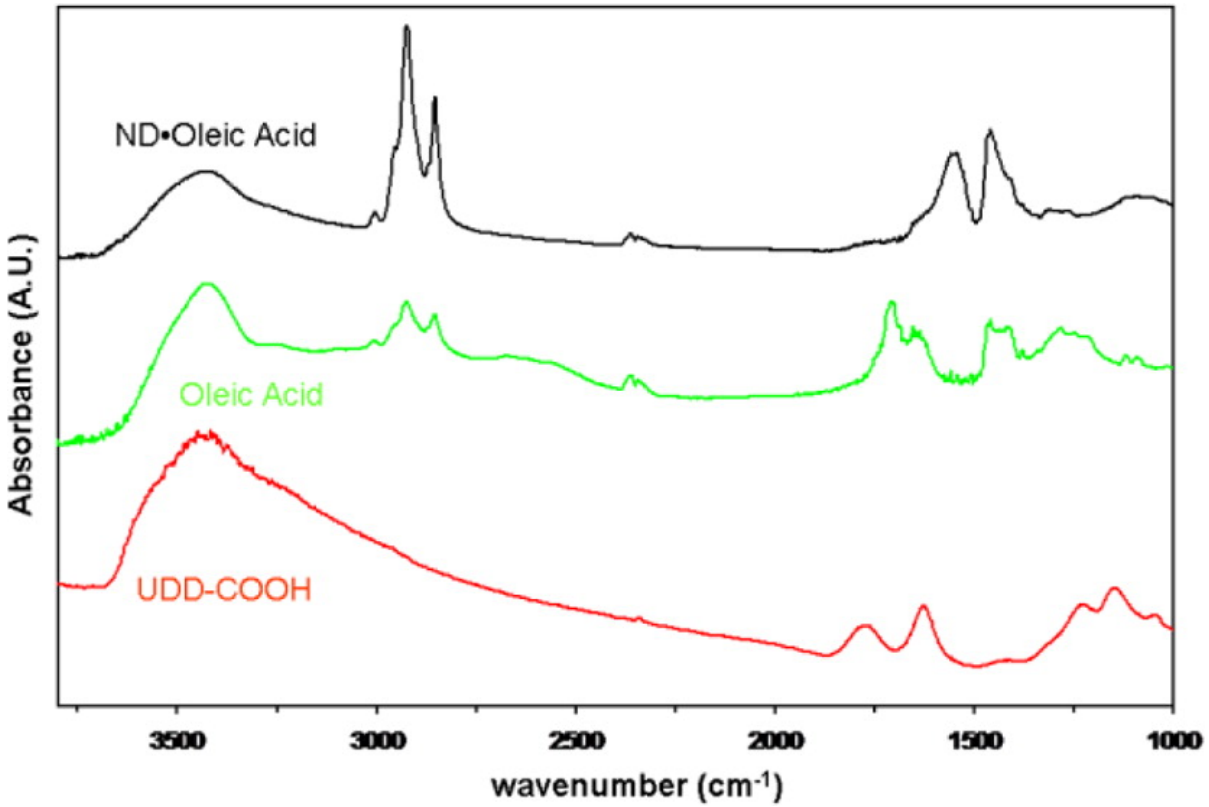
FUNCTIONALIZATION FOR HYDROCARBON SOLVENTS



Particle Size Distribution in toluene



FTIR

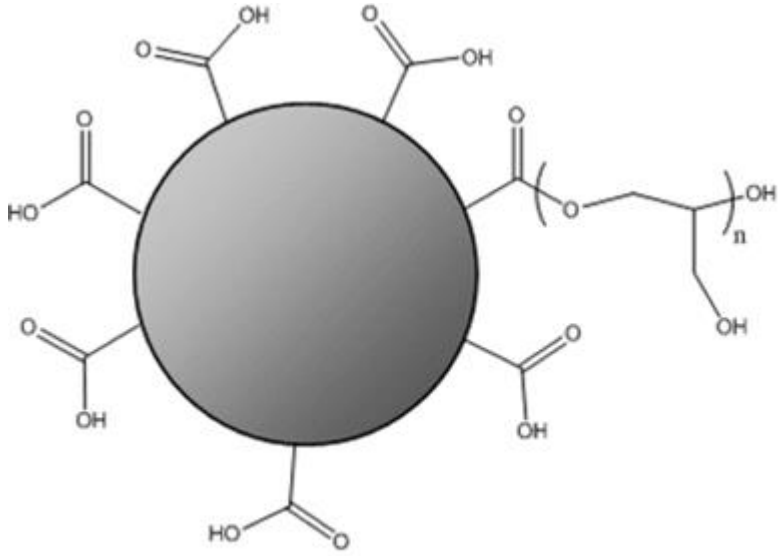


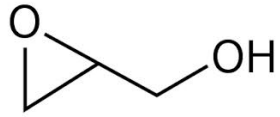
Branson et al, *ACS NANO*, 2013, 7, (4).

SECOND KEY TO NANODIAMOND'S POTENTIAL = SURFACE FUNCTIONALIZATION

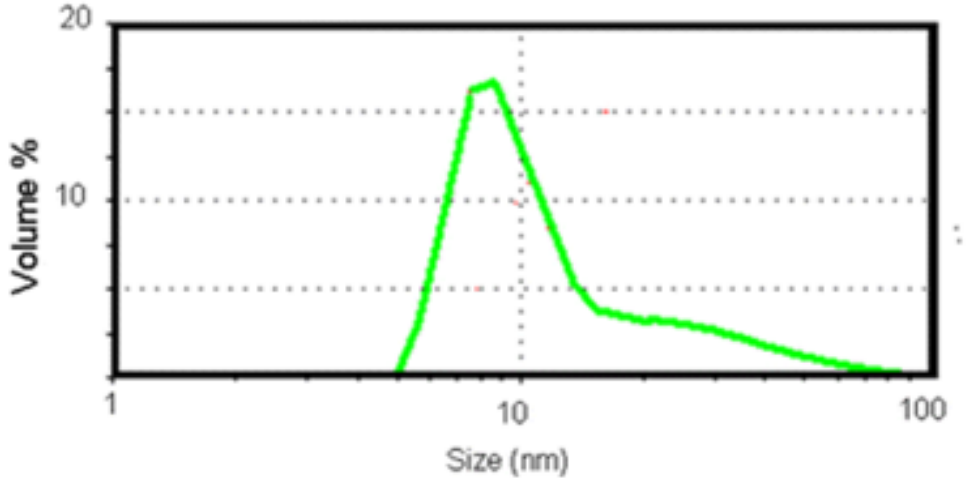
FUNCTIONALIZATION FOR POLAR SOLVENTS

Reaction with glycidol



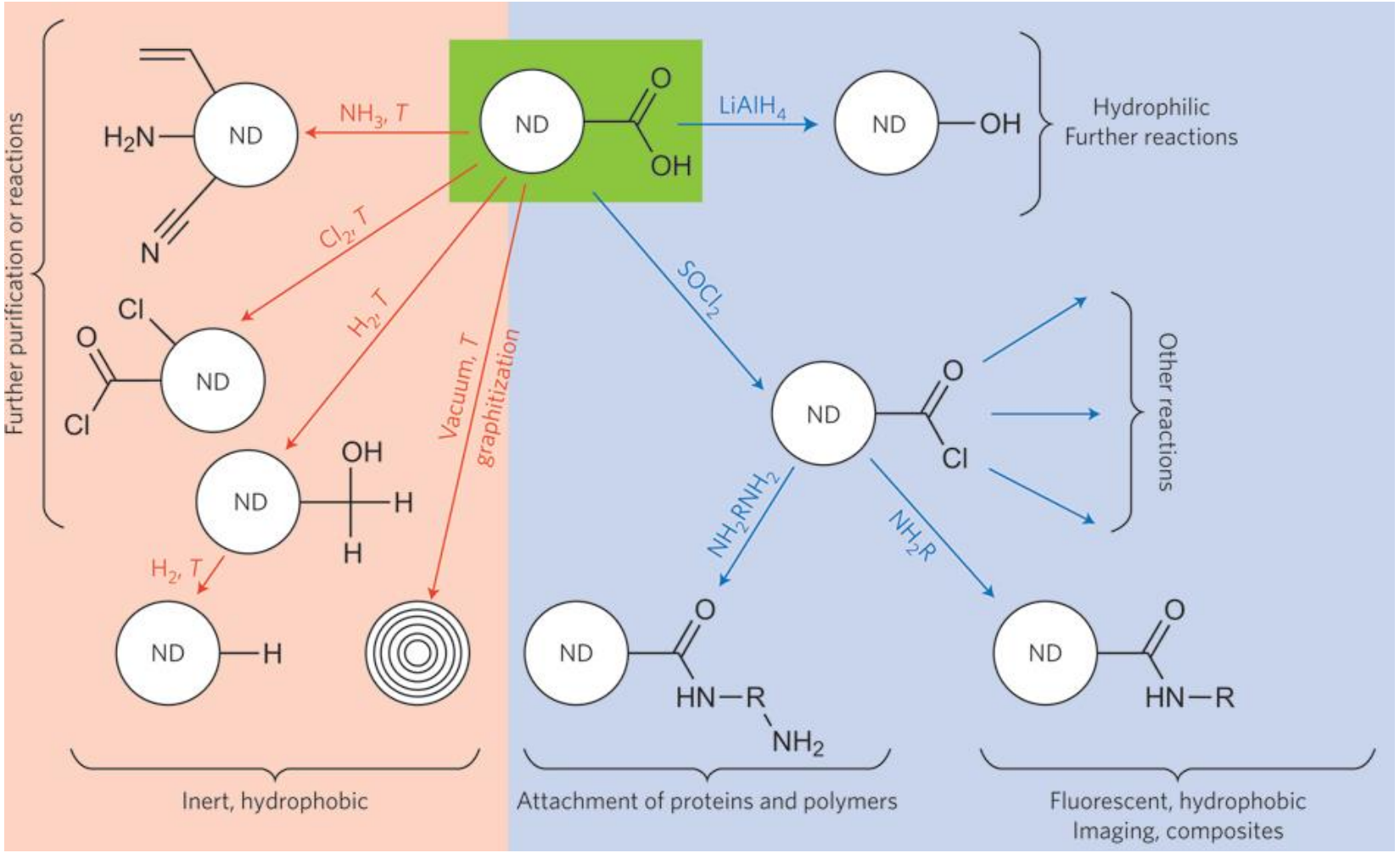


Particle Size Distribution in Water



Branson et al, *ACS NANO*, 2013, 7, (4).

OTHER FUNCTIONALIZATION ROUTES



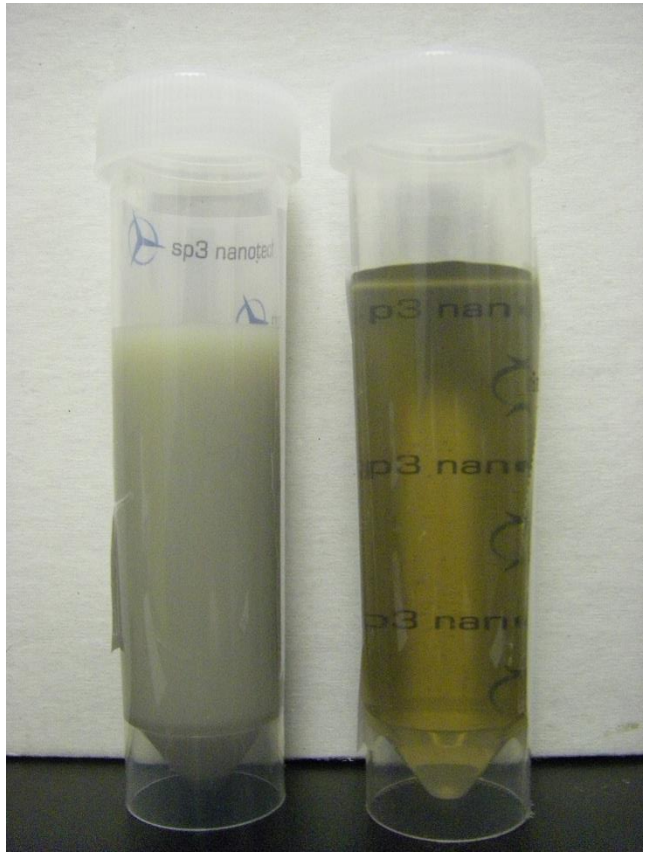
Mochalin et al, *Nature Nanotechnology*, 2012, 7.

CAN NOW DISPERSE IN A WIDE VARIETY OF FLUIDS

DMSO

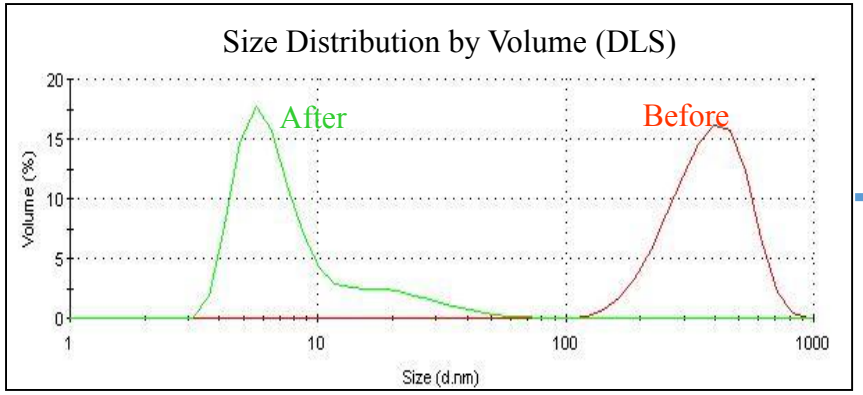
Synthetic Oil

Water

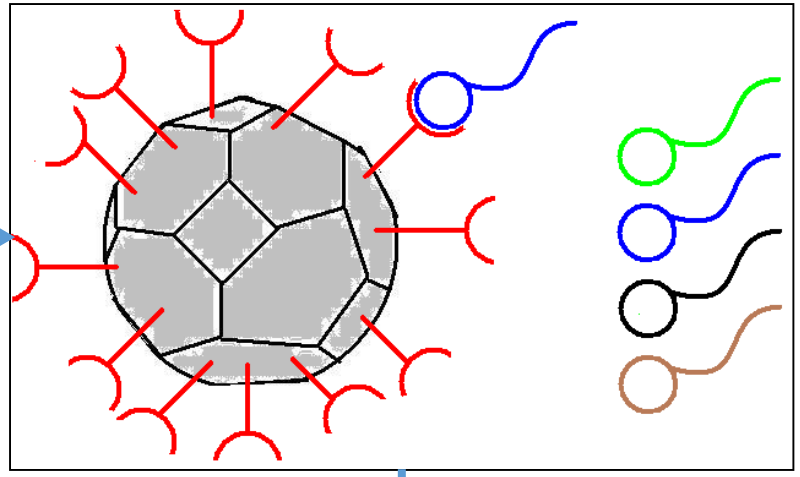


SUMMARY: SP3'S THREE-STEP PROCESS TO PREPARE NANODIAMOND

Step 1: Disaggregation



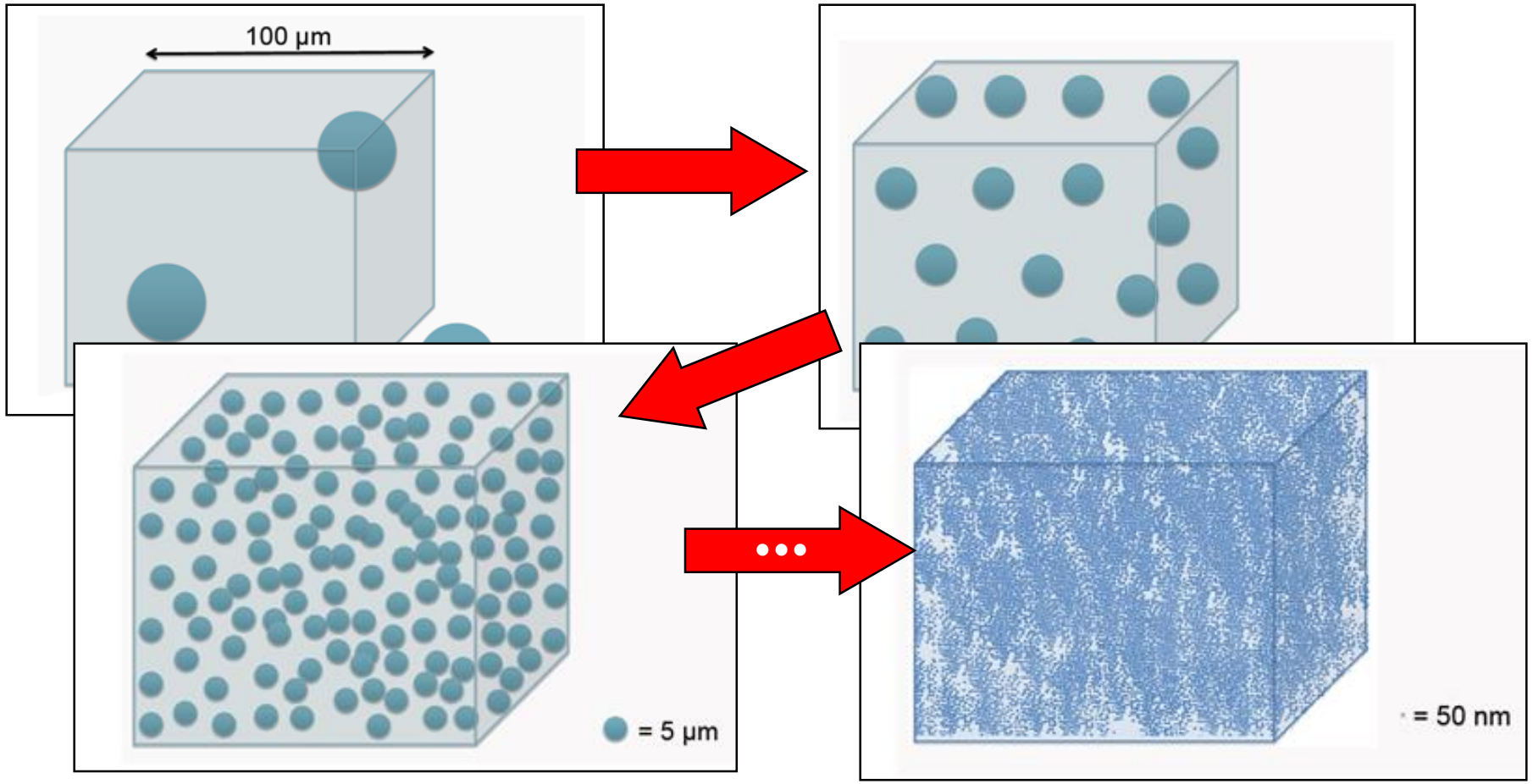
Step 2: Functionalization



Step 3: Incorporation

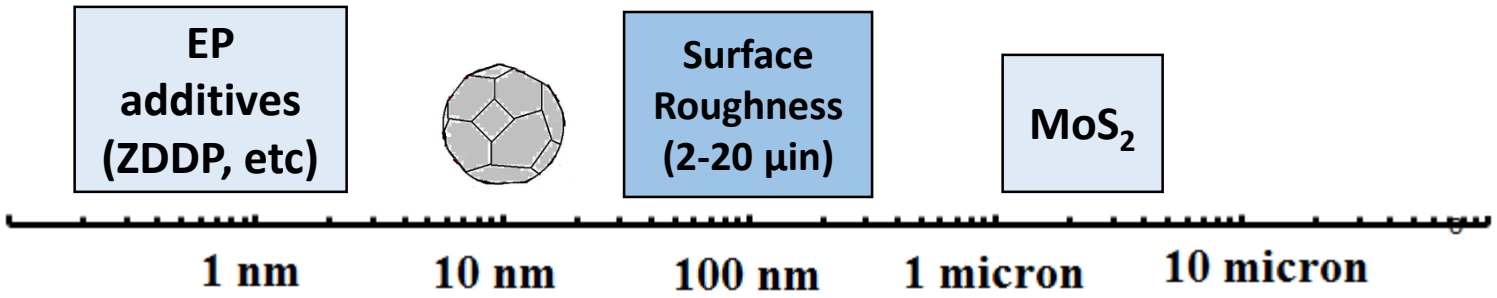
WHY “NANO”?

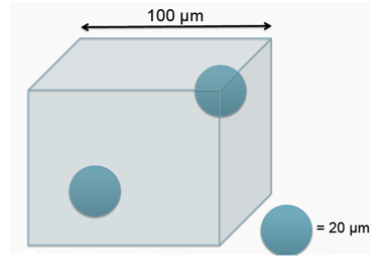
- Specific number density is very high

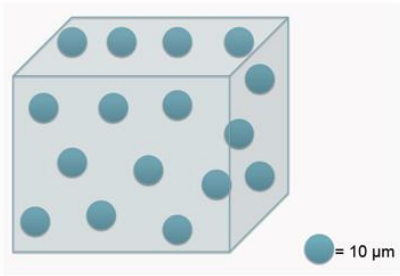


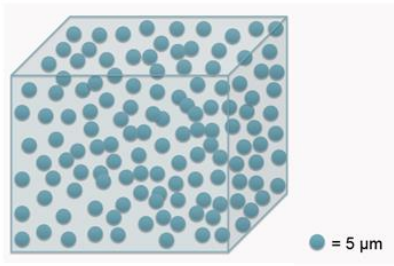
WHY “NANO”?

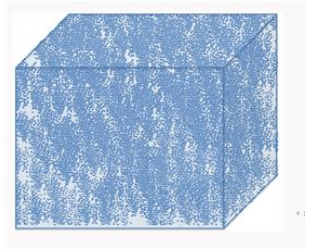
- Nanodiamond (ND) Is The Right Size-scale To Best Match Surface Roughness
  - ND Is Larger Than Extreme Presure (EP) Additives such as Molecular Zinc-, Sulfur- Compounds
  - Smaller Than AF Additives such as Moly Disulfides
  - Small Doses = Enormous Numbers of Particles
    - @0.01 wt% (100 ppm), ~100 Trillion NDs/mL of Lube









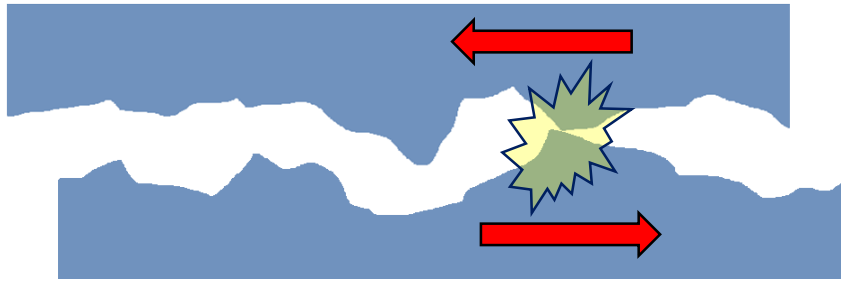


- Nanodiamond Is Not Consumed During Use

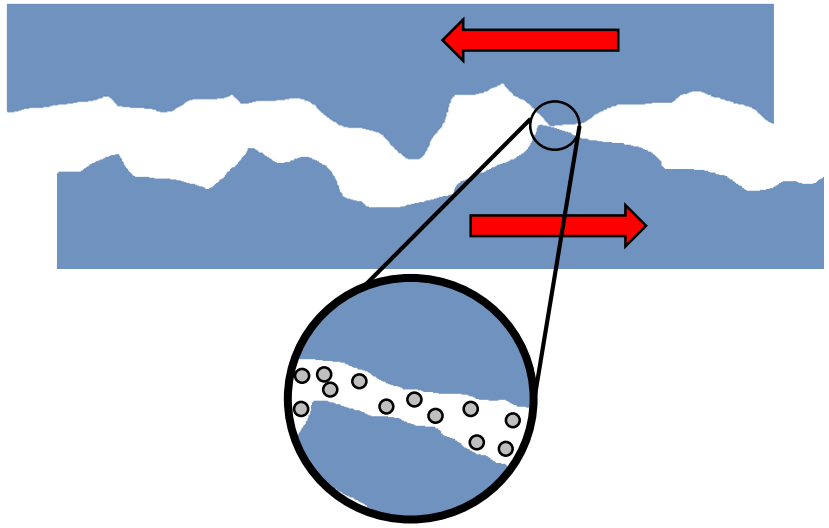
- Nanodiamond Does Not Change Bulk Fluid Viscosity at recommended concentrations (<100ppm)

HOW NANODIAMOND ENHANCES LUBRICATION

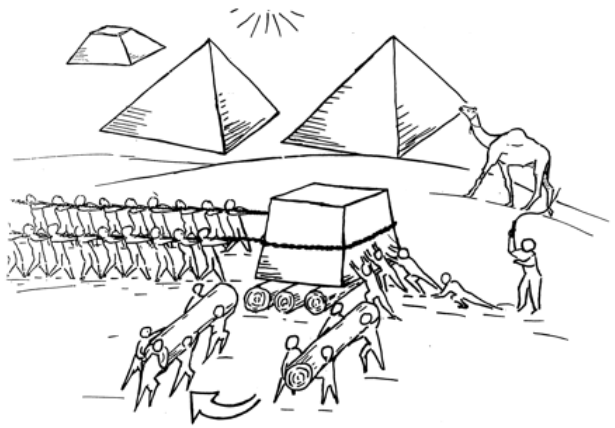
Traditional Boundary Contact



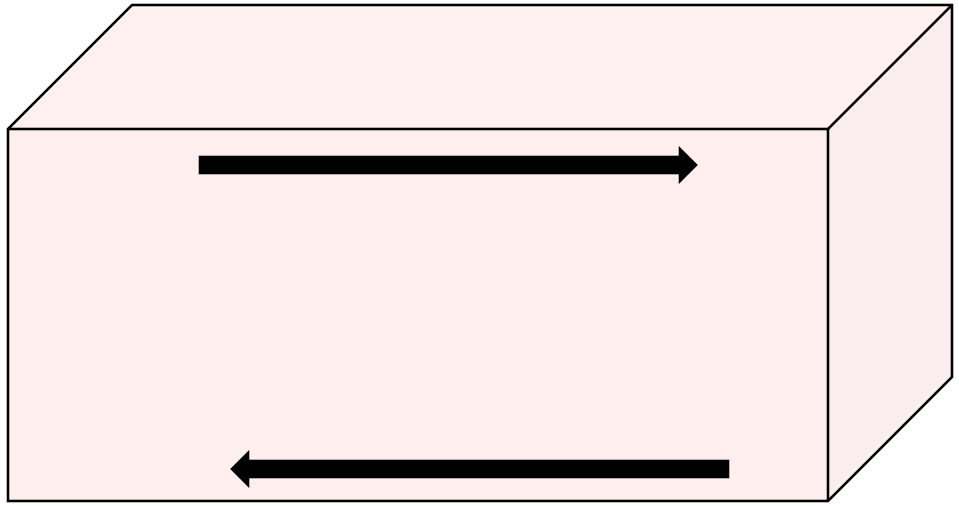
Lubricant with Nanodiamond

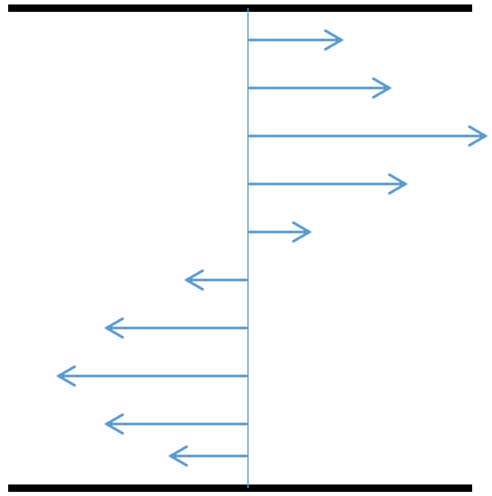


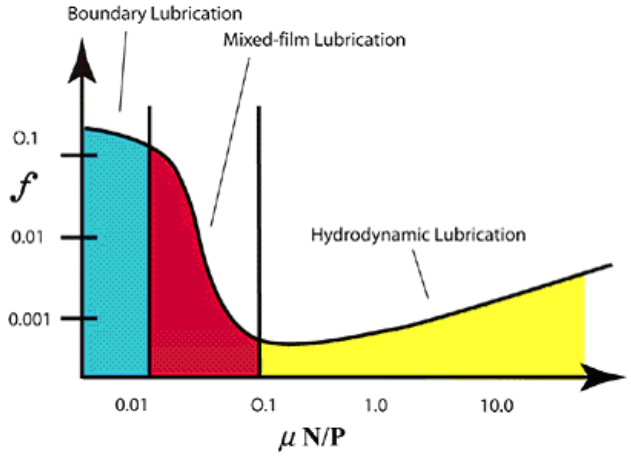
- Many, Many Particles Trapped Between Approaching Surfaces
  - Acts Like Nanoscale Ball-bearings
  - Transfers Sliding Friction to Rolling Friction
- Prevents Asperity-Asperity Contact



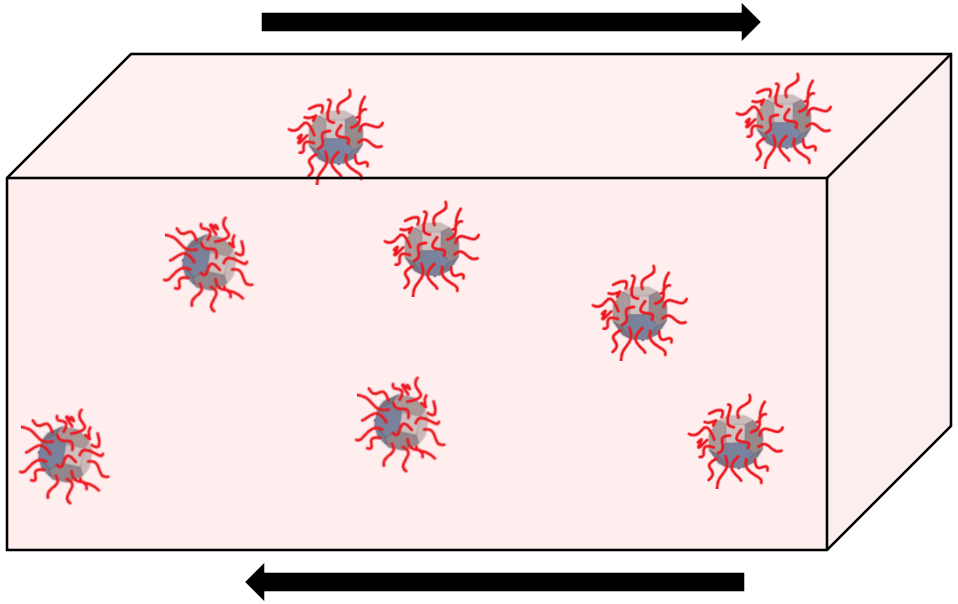
MECHANISM FOR ENHANCEMENT – HYDRODYNAMIC LUBRICATION REGIME

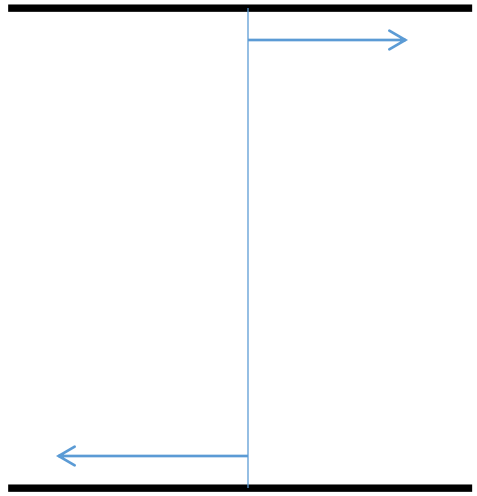






MECHANISM FOR ENHANCEMENT – HYDRODYNAMIC LUBRICATION REGIME

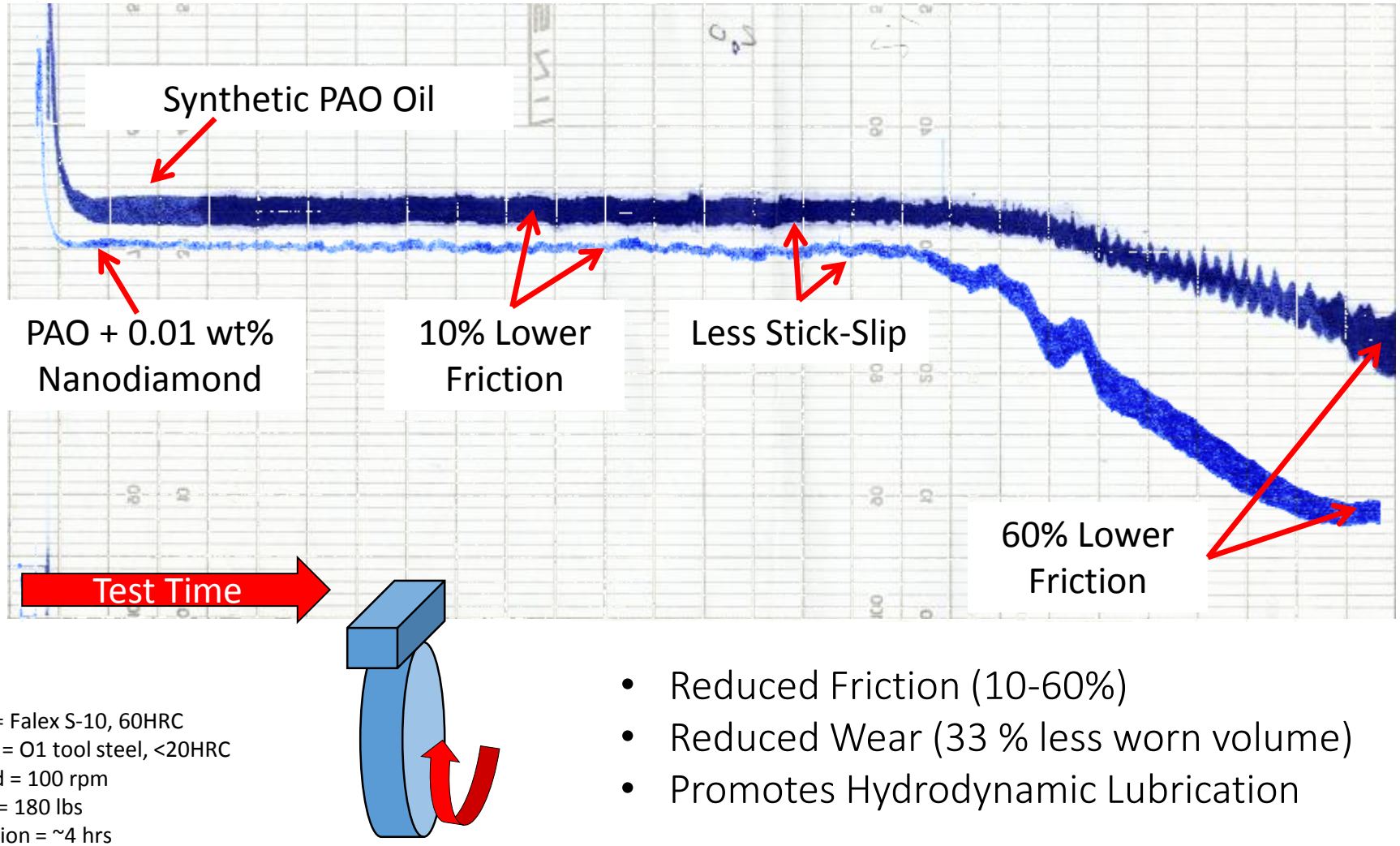




- Nanoparticles impede lubricant molecules
- Lubricant molecules “trapped” – localized viscosity increase
- Shear only occurs at edges

POLYALPHAOLEFIN (PAO) AND NANODIAMOND FRICTION TESTS

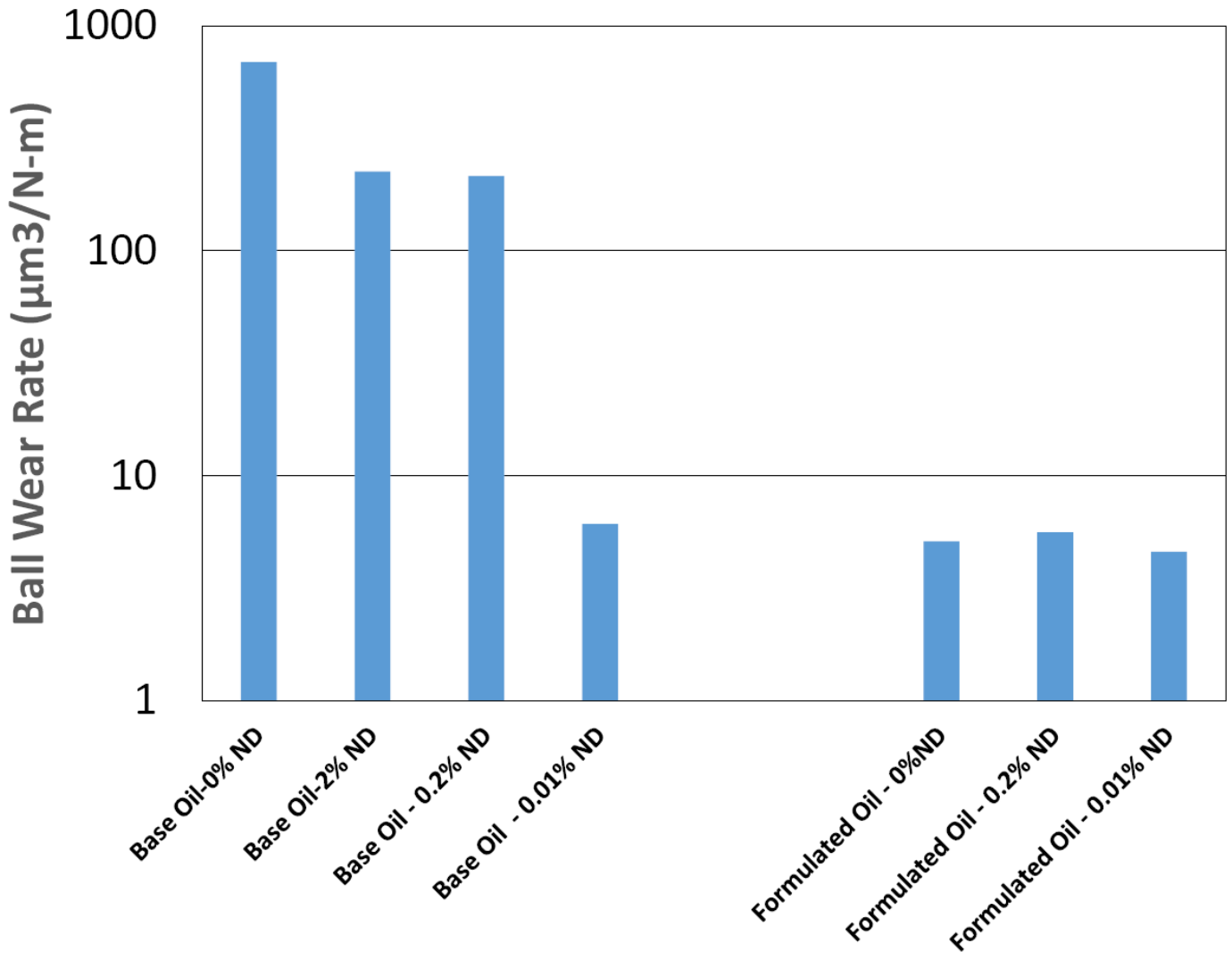
Block-on-Ring Testing (ASTM G77) – SpectraSyn™ 5 PAO

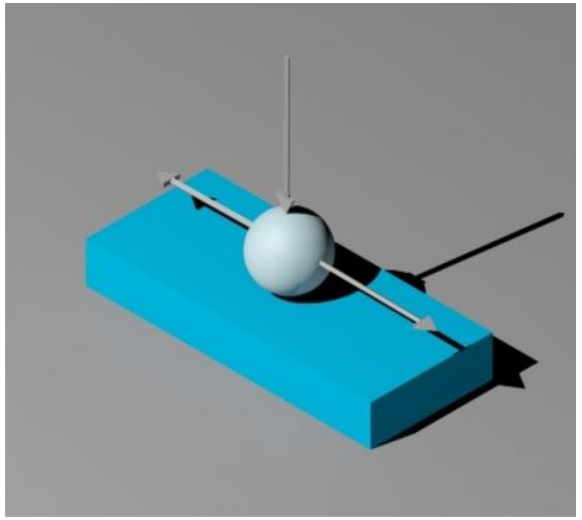


Ring = Falex S-10, 60HRC
Block = O1 tool steel, <20HRC
Speed = 100 rpm
Load = 180 lbs
Duration = ~4 hrs

- Reduced Friction (10-60%)
- Reduced Wear (33 % less worn volume)
- Promotes Hydrodynamic Lubrication

TESTING IN FULLY FORMULATED OILS CAN BY TRICKY, EXAMPLE: A DIESEL ENGINE OIL

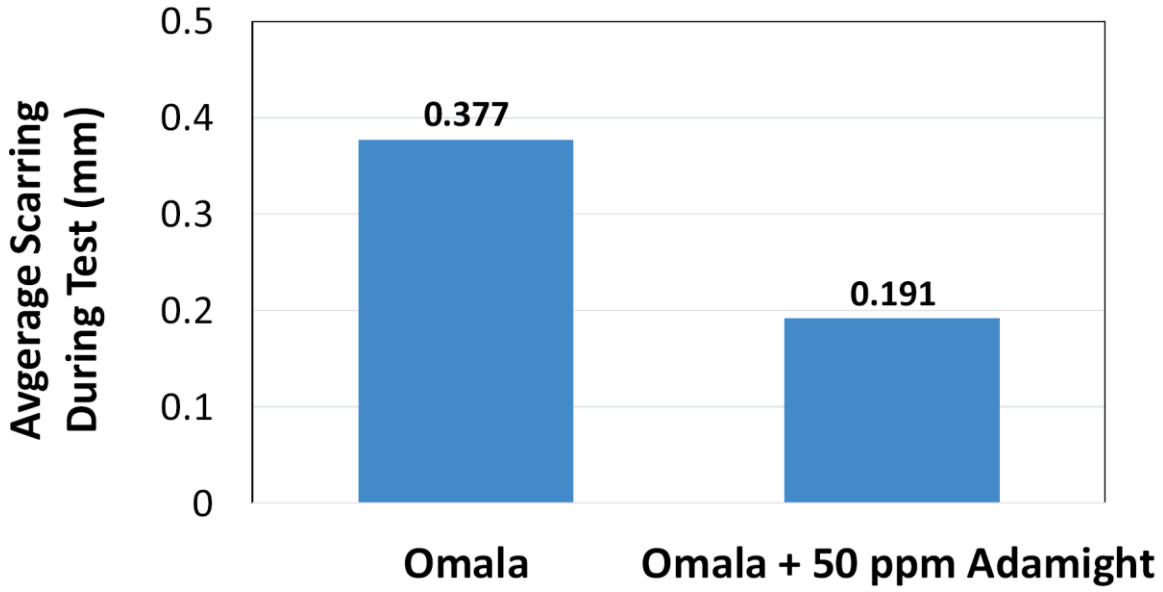




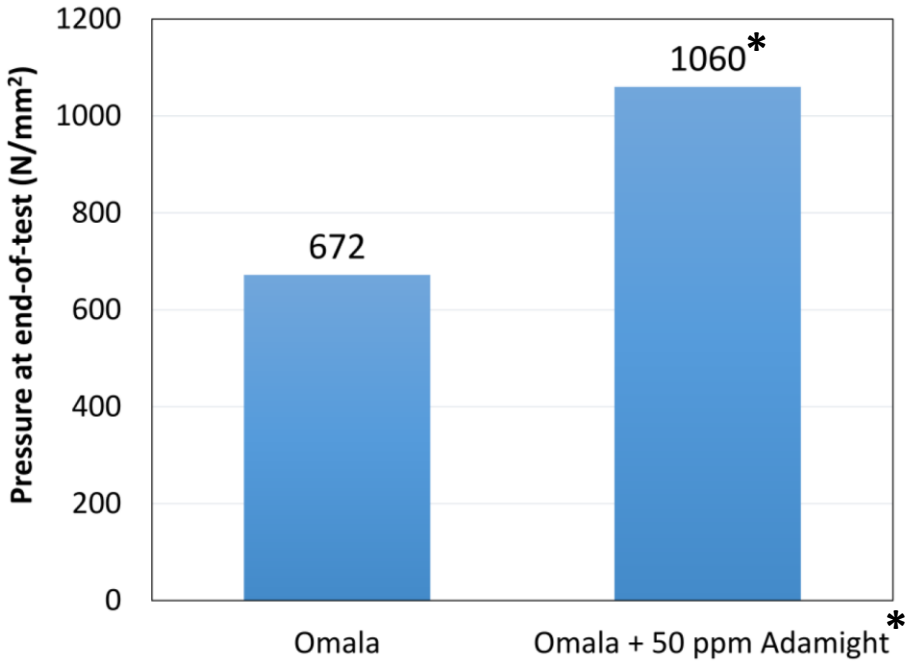
Flat: hardened 52100 mirror polished, 1.5” x 2”
Ball: hardened ½” dia 52100 ball
Load: 15.6 N
Peak contact pressure: 1 GPa
Temperature: 100°C
Drops of oil: 10

TESTING IN FULLY FORMULATED OILS – A GEAR OIL

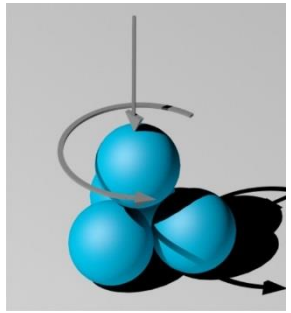
POST-TEST WEAR



PRESSURE AT FAILURE



***Omala with Nanodiamond (nanodiamond) did not fail, it exceeded the bonds of the test**



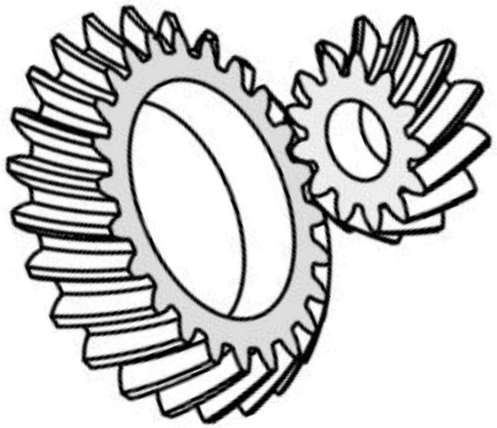
Ball = AISI-E52100, Hardness (64-66)
Speed = 600 rpm
Load = Increased 10 kg every 10 min.
Temp. = 75°C

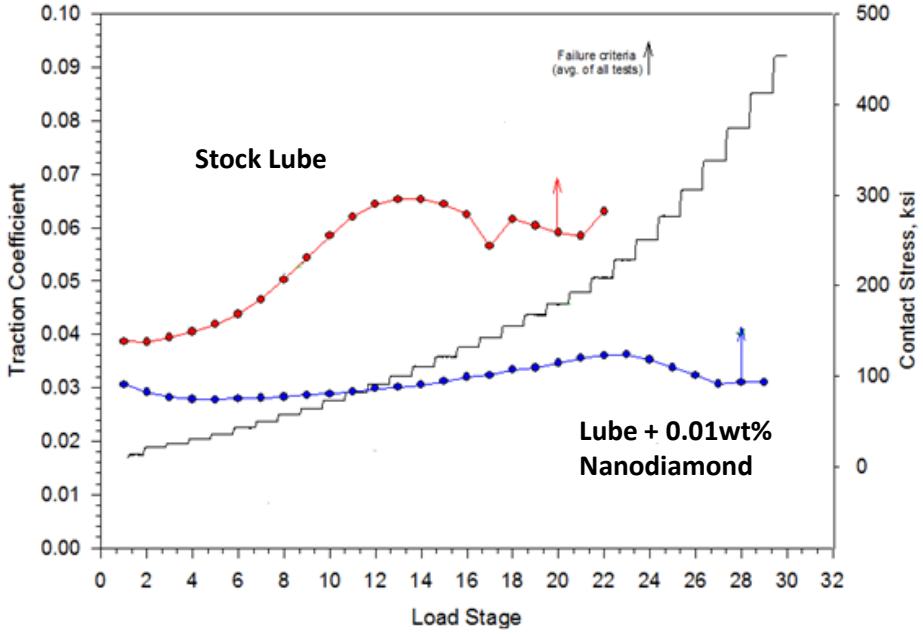
ttzh.de/products/tribometers,en

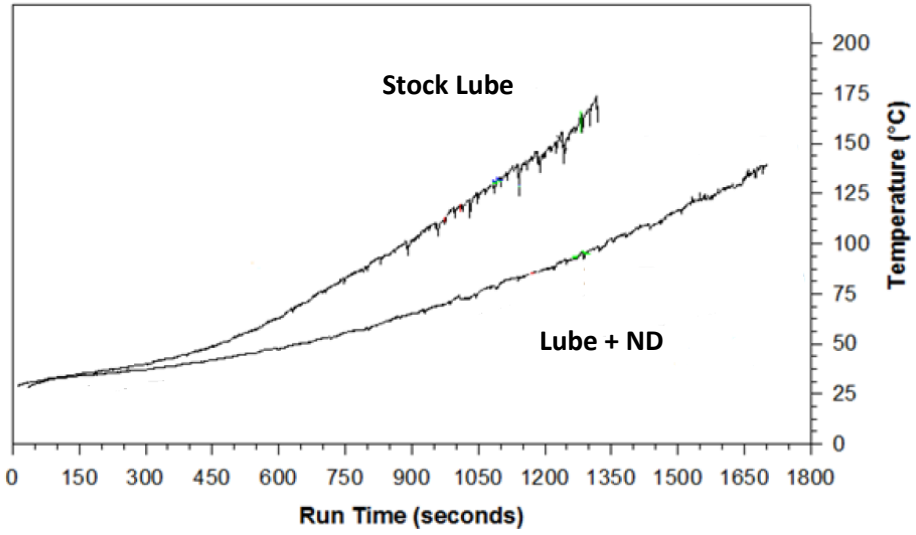
- Nanodiamond reduced wear and increased seizure load in Omala Gear Oil

APPLICATION – GEARBOX LUBRICANT

- Helicopter gearbox lubricant
- WAM Tests:
  - > 50% Reduction in Friction
  - > 70°C Lower Surface Temperatures
  - >100% Increase in Scuffing Stress







SOUTHWEST RESEARCH INSTITUTE'S FUEL EFFICIENCY TEST

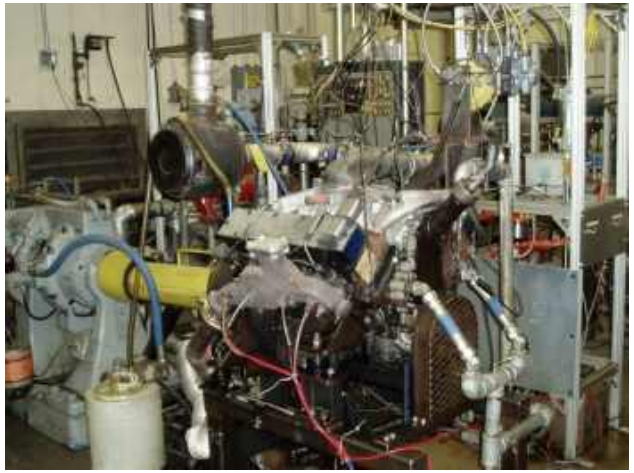
SwRI FE Test Results:

Operating Targets

Stage #	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Speed, rpm	2000	2000	1500	695	695	695
Power, kw	22	22	16.5	1.5	1.5	2.9
Oil temp, °C	115	65	115	115	35	115
Coolant in temp, °C	109	65	109	109	35	109

FEI1 Final 1.05%

- GF-5/VID Test Stand
- Improved Fuel Efficiency by 1.05 %
  - Control lubricant is SpectraSyn™ 4
  - >8 standard deviations above control (σ = 0.12%)



APPLICATIONS AREAS FOR NANODIAMOND

$3.33	=	1%	=	2.5 gal	=	$8.66
Cost of Nanodiamond/ Vehicle		Fuel Efficiency Improvement		Fuel Savings/ OCI		ROI = 250% +

4.5 qt oil capacity, 7.5K mi OCI, 30 mpg, $3.50/gal

APPLICATIONS AREAS FOR NANODIAMOND

$6 = 1% = 5 gal = $20 to $2000

Cost of Nanodiamond/ Vehicle

Fuel Efficiency Improvement

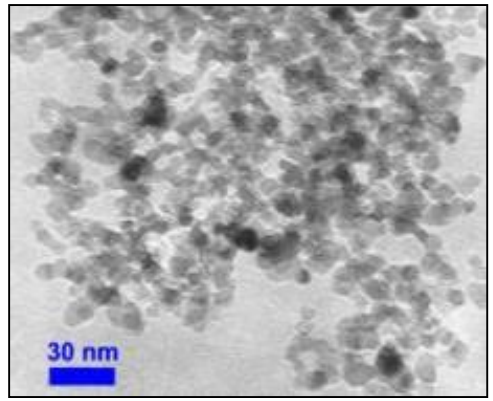
Fuel Savings/ OCI

ROI = 300% +++

8 qt oil capacity, 3K mi OCI, 6 mpg, $4-$400/gal

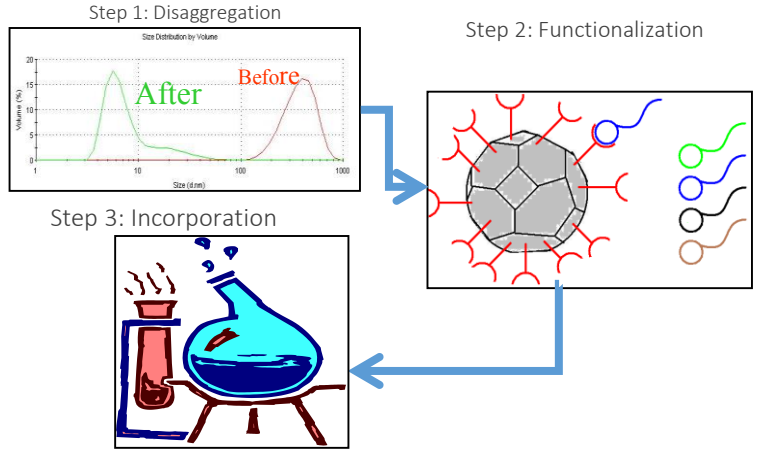
SUMMARY - NANODIAMOND ADDITIVE FOR LUBRICANTS

- Improves Performance Of Oils
  - Reduces Friction 10-60%
  - Maintains Lubricant Film Integrity
  - Reduces Lubricant/Machinery Temperatures Up To 70°C



- Is Made From Nanodiamond (ND)
  - 4-6 nm Spherical Diamond Particles – Hard and Strong
  - Raw Material Is Strongly Aggregated and Hydrophillic

- Is Processed by sp3 Into Oil Additive
  - Functionalize Surface With Tailored Chemistries
  - Disaggregate ND Clusters (~1µm To ~5 nm)
  - Highly Dispersed, Stable Suspensions
  - Easily Blended into Target Fluid

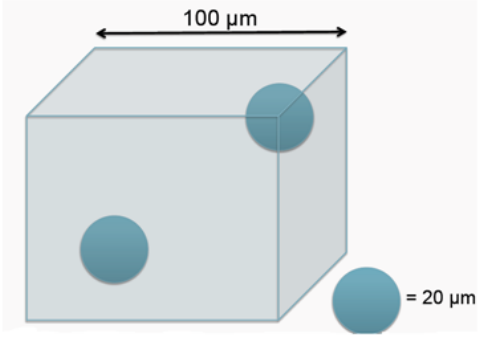


OUTLINE

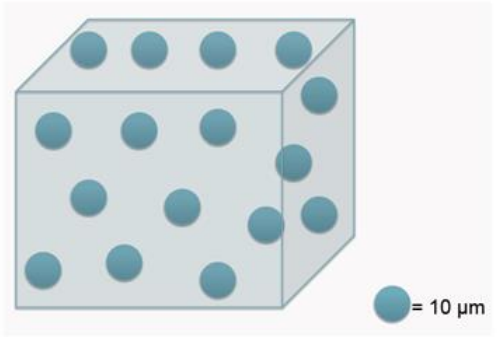
- Lubrication/Tribology Basics
- Overview of Nanodiamond
- Application of Nanodiamond to Tribology/Lubrication
- **Application of Nanodiamond to Polymer Composites**

WHY “NANO”?

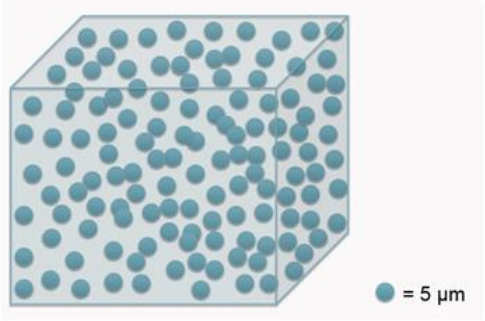
- Enhanced surface area for interaction with polymer matrix phase
- Transparency



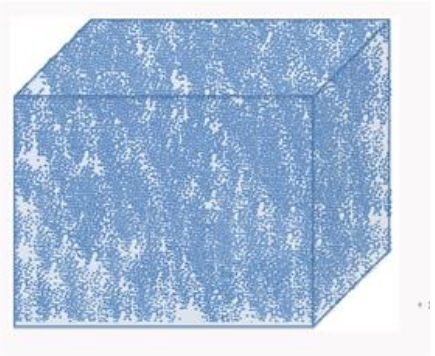
(a)



(b)



(c)

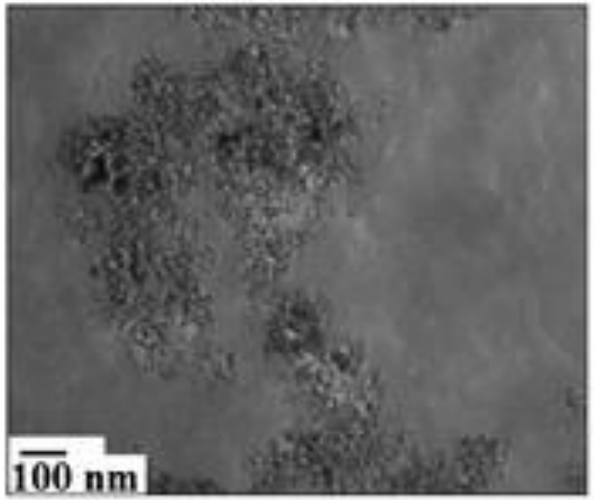


NANODIAMOND IN POLYACRYLONITRILE (PAN)

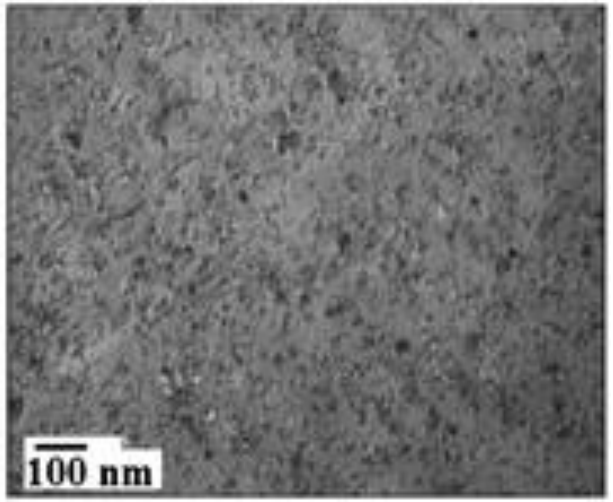
- Disperse nanodiamond in DMSO
- Co-dissolve nanodiamond and PAN in DMSO
- Solution-cast a film of nanodiamond-reinforced PAN
- Anneal at 240^{o}C

TEM Images of PAN with Nanodiamond

Detonation Nanodiamond



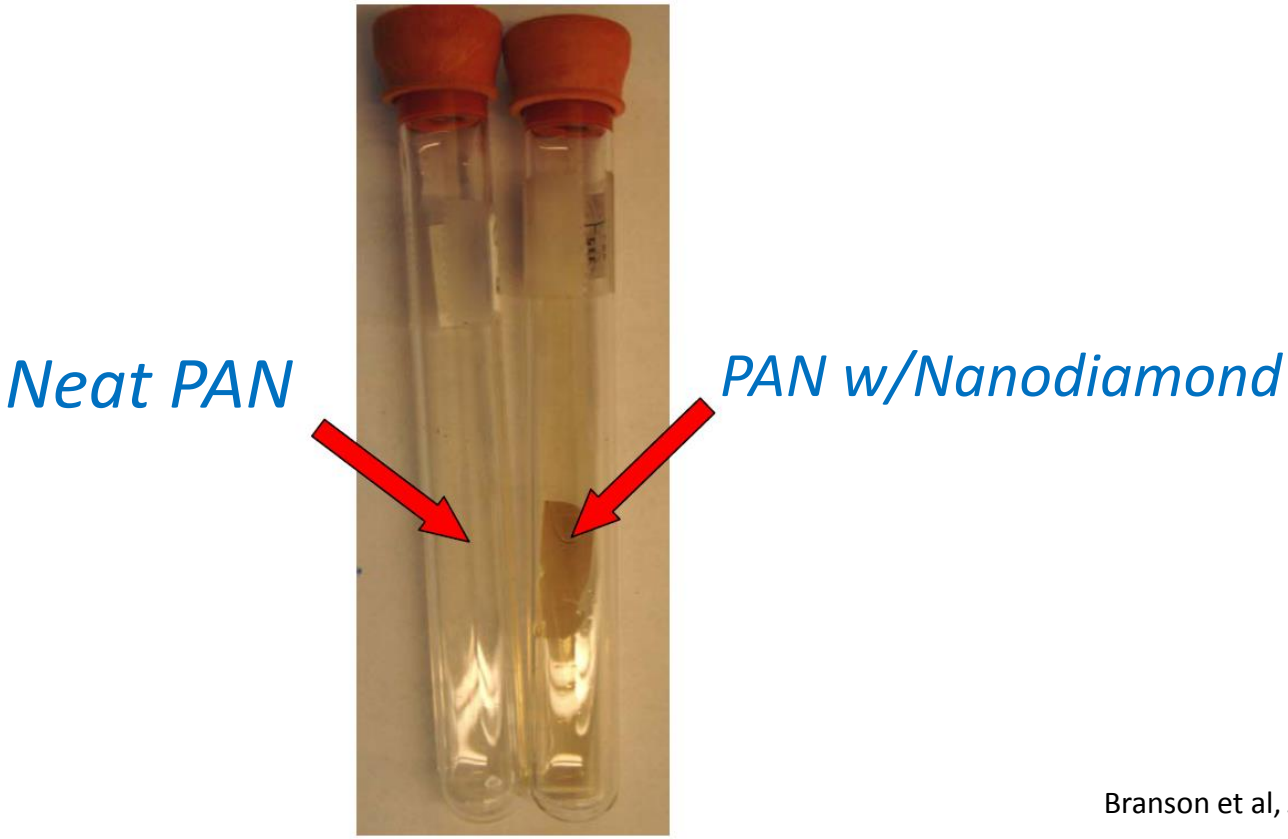
Deaggregated Nanodiamond



Branson et al, *Journal of Materials Chemistry,* 2011, 21, (46).

NANODIAMOND'S EFFECT ON FILM SOLUBILITY

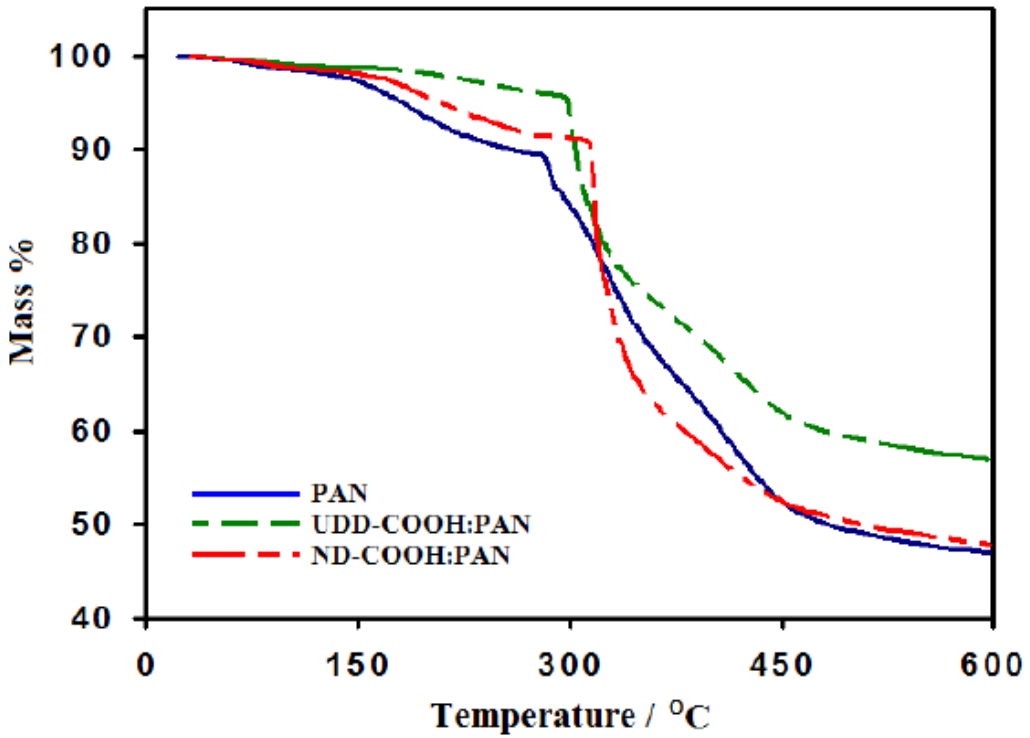
- Neat PAN dissolves in DMSO within one hour
- PAN with Nanodiamond (7 wt%) remains undissolved after several weeks in DMSO



Branson et al, *Journal of Materials Chemistry,* 2011, 21, (46).

ENHANCED THERMAL STABILITY

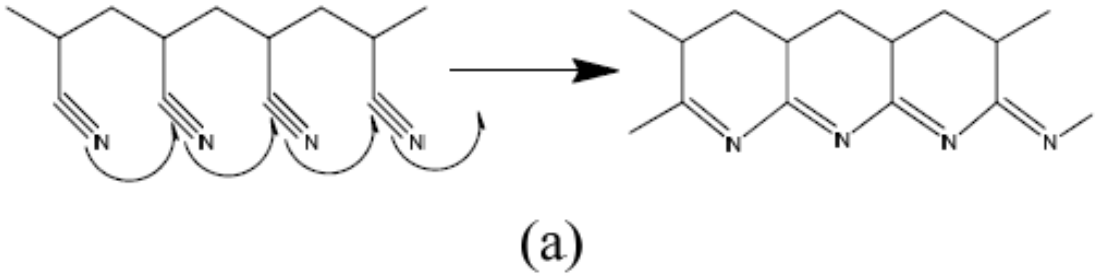
TGA



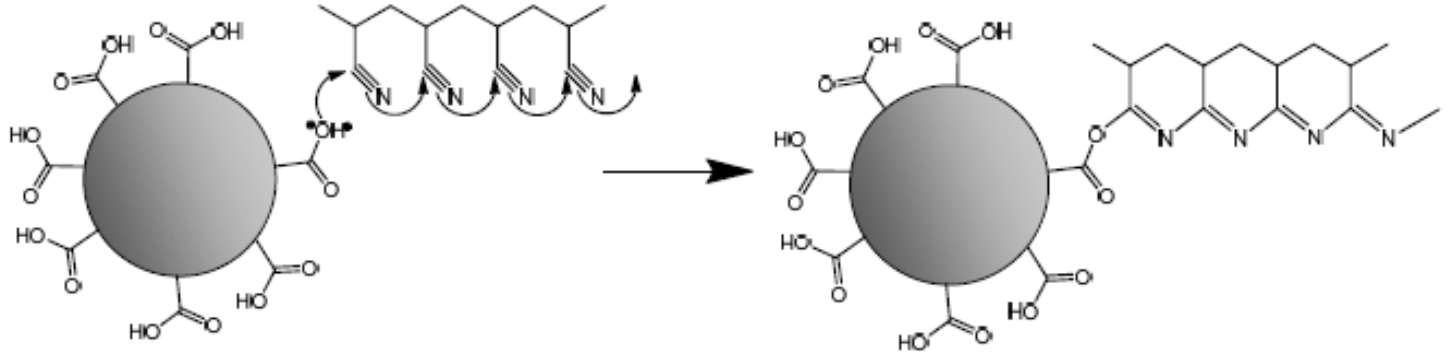
- Addition of diamond increases the degradation temperature
  - 15°C for aggregated diamond (UDD)
  - 30°C for dispersed diamond

Branson et al, *Journal of Materials Chemistry,* 2011, 21, (46).

POSSIBLE CYCLIZATION REACTIONS



(a)



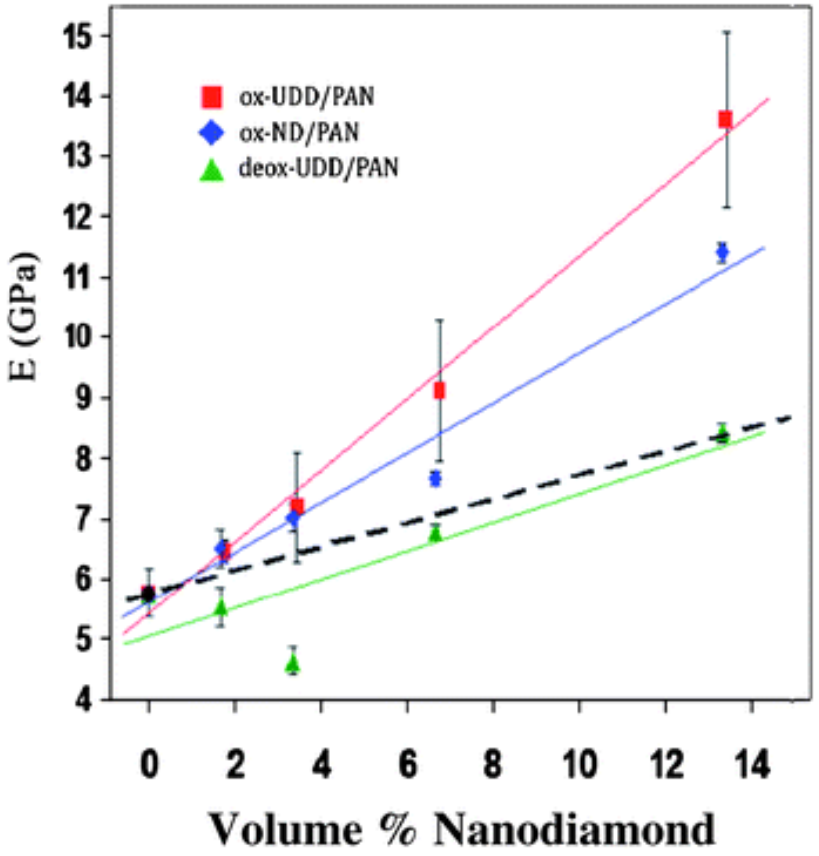
(b)

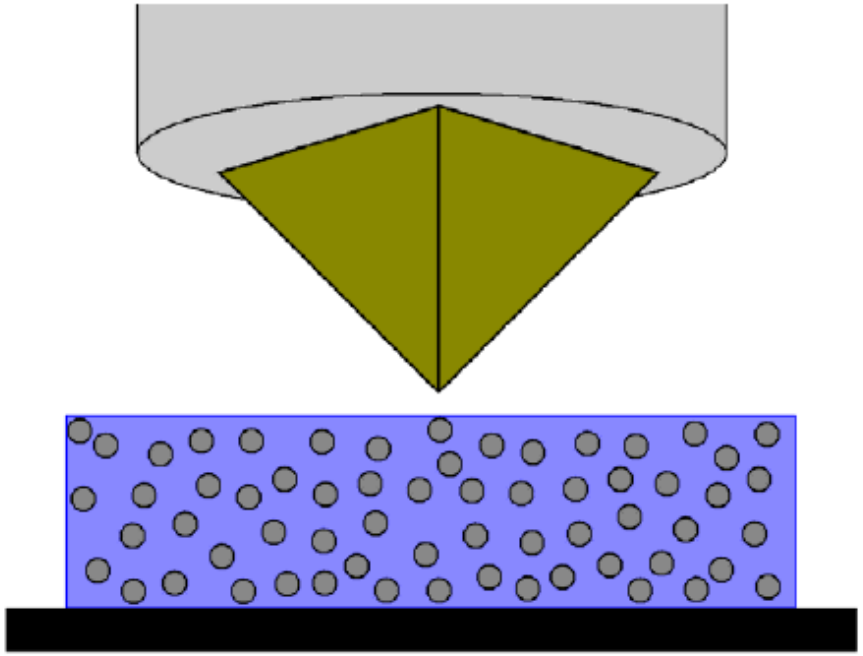
- Upon heating, nanodiamond becomes covalently bond to the polymer matrix
- Chemical and thermal stability increases (upon nanodiamond addition) could be due to steric hindrances as well

Branson et al, *Journal of Materials Chemistry,* 2011, 21, (46).

MECHANICAL PERFORMANCE IMPROVEMENT (NANODINDENTATION)

Elastic hardness (*E*) *versus* additive loading



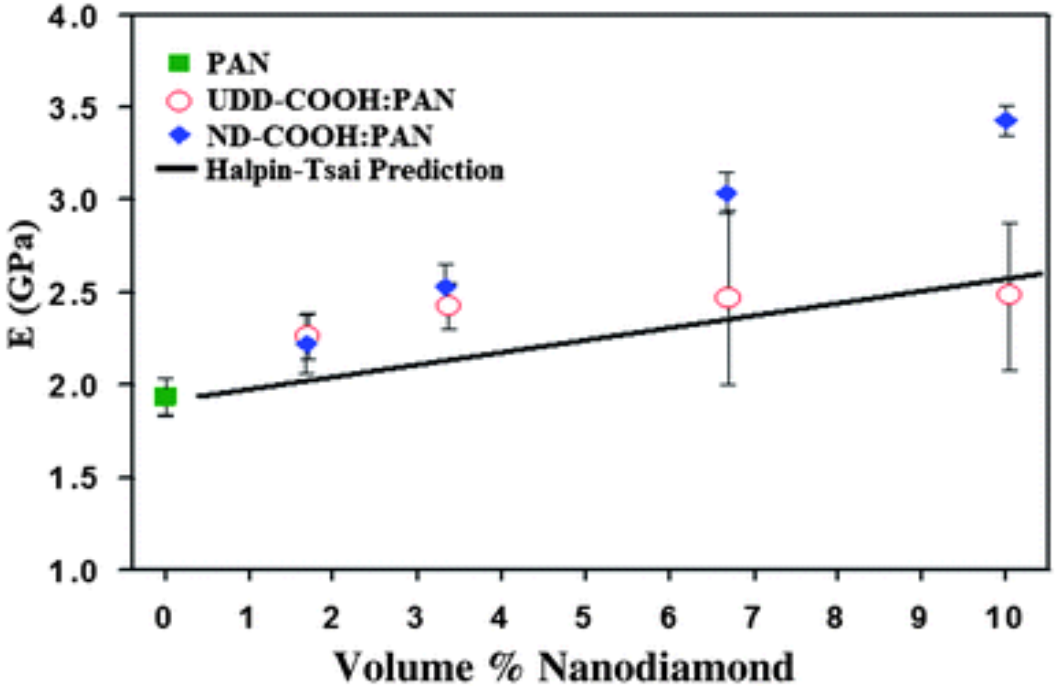


Dashed black line is calculated using the Halpin-Tsai equations.

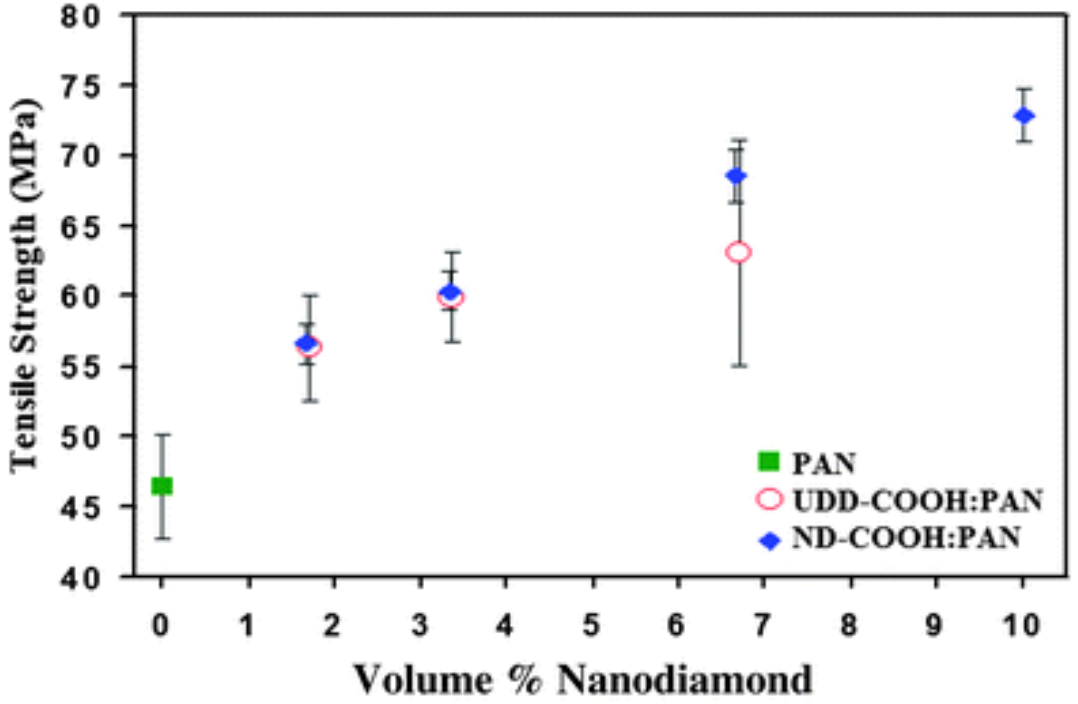
Branson et al, *Journal of Materials Chemistry,* 2011, 21, (46).

MECHANICAL PERFORMANCE IMPROVEMENTS (TENSILE TESTS)

Elastic Modulus



Tensile strength

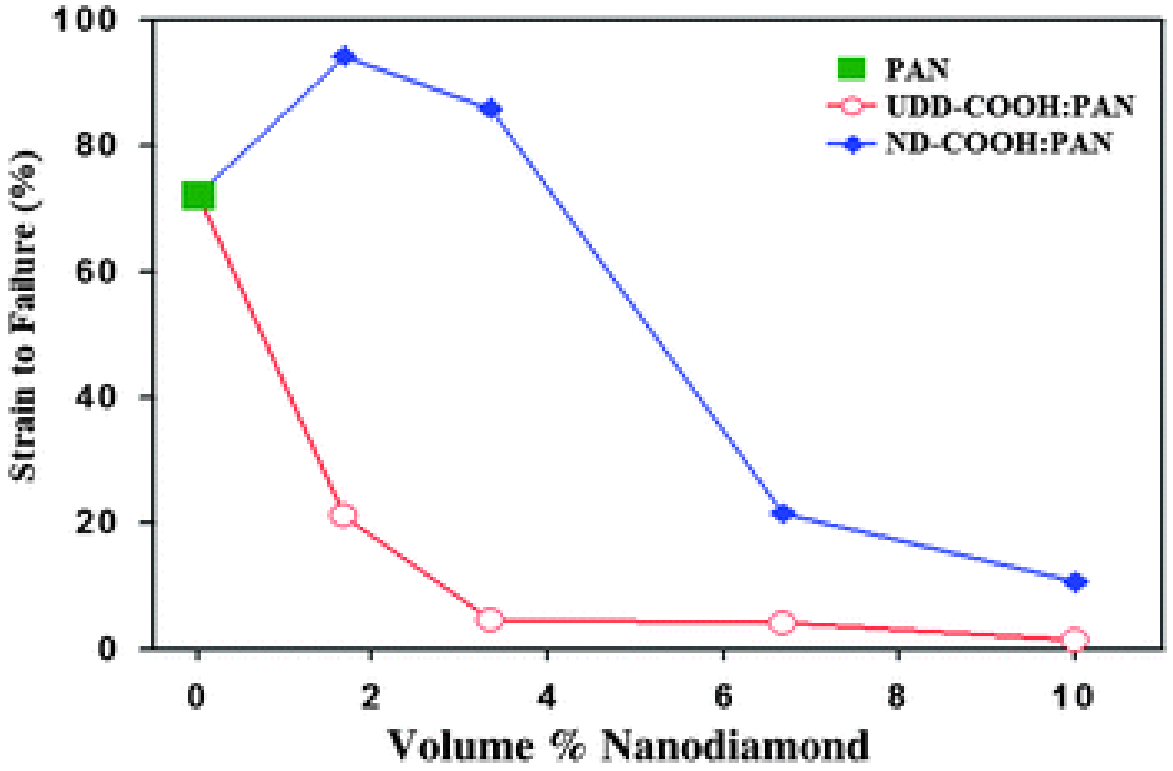


- In “bulk” mechanical testing, de-aggregated/dispersed nanodiamond (ND) outperforms aggregated diamond (UDD)
- At 10 wt% nanodiamond, a ~75% increase in stiffness and ~55% increase in strength

Branson et al, *Journal of Materials Chemistry,* 2011, 21, (46).

MECHANICAL PERFORMANCE IMPROVEMENTS (TENSILE TESTS)

Elongation at Break



- Dispersed nanodiamond (ND) is much more ductile than aggregated diamond (UDD)
- Dispersed ND better allows polymer chains to reconfigure before covalent bond breakage

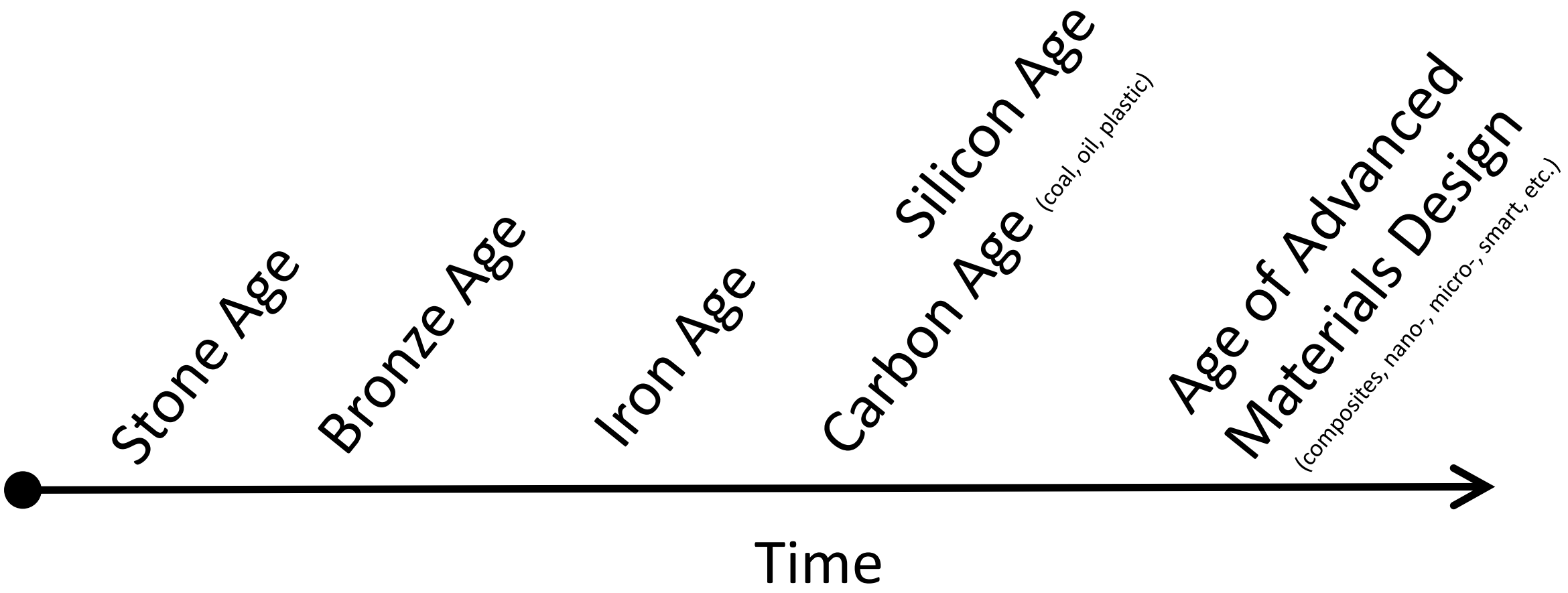
Branson et al, *Journal of Materials Chemistry,* 2011, 21, (46).

CONCLUSIONS

- Nanodiamond improves the performance of lubricants
  - Lower Friction
  - Lower Wear
  - Better Fuel Efficiency

- Nanodiamond improves the mechanical properties of polymers
  - Higher stiffness
  - Higher Strength

HUMAN HISTORY



Questions?