Characterization of Isotropic and Anisotropic Particles Dispersed in Lubricating Automotive Greases using SEM-EDS

Jared Estevanes, BS* and Geraldine Monjardez, PhD

Department of Forensic Science
Sam Houston State University
Huntsville, TX 77340

Disclaimer

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TSM

Embracing All Forms of Microscopy

AMERICAN SOCIETY OF TRACE EVIDENCE EXAMINERS

ASTEE

Tout Contact Laisse une Trace

2009

Introduction

- According to the National Highway Traffic Safety Administration (NHTSA)[1]:
- Increase of 3.9% in pedestrian death from traffic crashes from 2019 to 2020 (6,272 to 6,516)
- Number of hit and runs increased at rate of 7.2% from 2009 to 2016[2]
- The estimated rate at which the offender is caught is around 50%

[1] NHTSA. 2020 Summary of Motor Vehicle Crashes. Washington, D.C.: NHTSA's National Center for Statistics and Analysis, 2022.
[2] Benson A, Arnold LS, Tefft BC, Horrey WJ. Hit-and-Run Crashes: Prevalence, Contributing Factors and Countermeasures. Washington, D.C.: AAA Foundation for Traffic Safety, 2018.

Connecting a Vehicle to a Crime Scene

- Substances can be left behind at the scene of an accident
  - Road
  - Victims
- We can link a vehicle by
  - Glass
  - Paint
  - Automotive Fluids?

[1] NHTSA. 2020 Summary of Motor Vehicle Crashes. Washington, D.C.: NHTSA's National Center for Statistics and Analysis, 2022.
[2] Benson A, Arnold LS, Tefft BC, Horrey WJ. Hit-and-Run Crashes: Prevalence, Contributing Factors and Countermeasures. Washington, D.C.: AAA Foundation for Traffic Safety, 2018.

Previous Research

- Automotive fluids can include
  - Motor oil
  - Transmission fluids
  - Greases
- Many studies have been conducted in the differentiation of motor oils for forensic applications[3-5]
- Few studies have been done on the differentiation of transmission fluid or automotive greases[6]

[3] I. Kaplan, S.-T. Lu, H. Alimi, J. MacMurphey, Fingerprinting of High Boiling Hydrocarbon Fuels, Asphalts and Lubricants, Environ. Forensics. 2 (2001) 231–248. https://doi.org/10.1006/enfo.2001.0053.
[4] R. Hibbard, J.V. Goodpaster, M.R. Evans, Factors Affecting the Forensic Examination of Automotive Lubricating Oils*: FACTORS AFFECTING LUBRICATING OILS, J. Forensic Sci. 56 (2011) 741–753. https://doi.org/10.1111/j.1556-4029.2011.01722.x.
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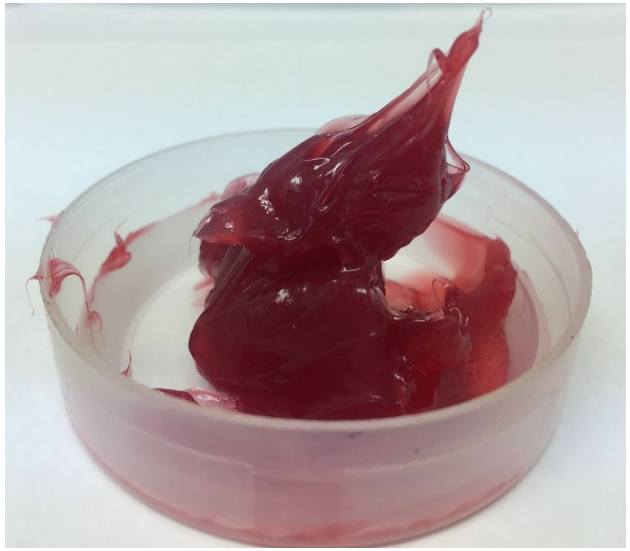
[6] J. Day, The Characterization and Discrimination of Transmission Fluids, Brake Fluids, and Vehicular Greases, 2018.

Automotive Lubricating Greases

- Lubrication compounds with a higher viscosity than motor oil
- Used in wheel bearings, chassis components, and CV joints
- Generally composed of 3 main components
  - Base oil
  - Soap thickener
  - Additives
- Grease blends are proprietary



Light Microscopy of Automotive Lubricating Greases

- Day (2018) found that many of the greases have particles imbedded in the matrix[6]
- Classified in three groups based on microscopy
  - Opaque
  - Isotropic
  - Anisotropic

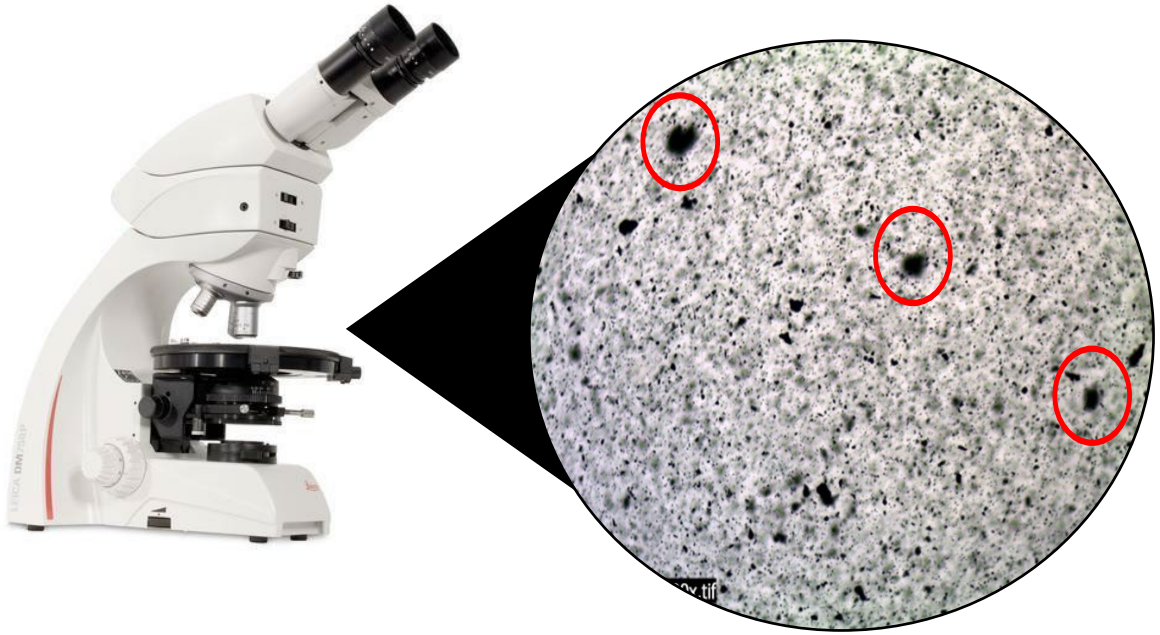
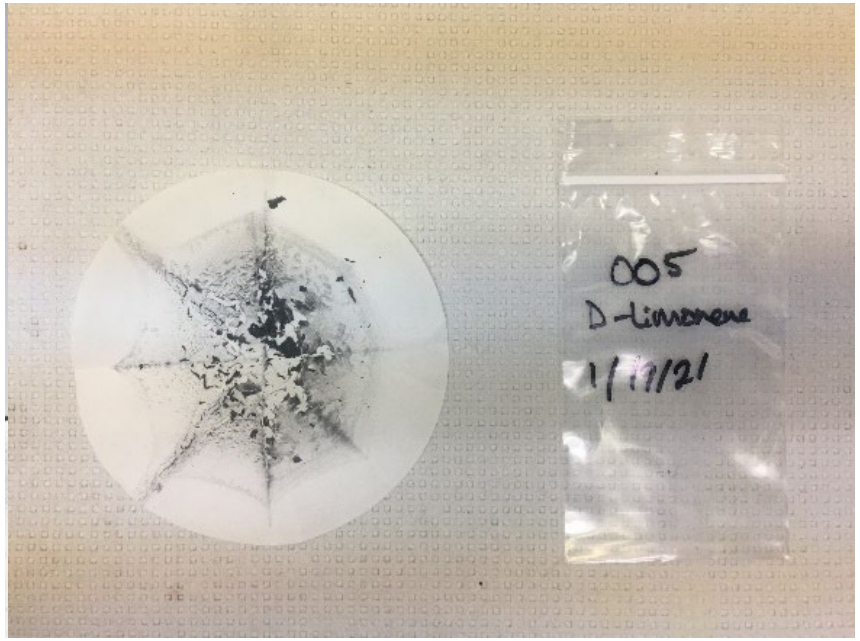


Image courtesy of Leica

[6] J. Day, The Characterization and Discrimination of Transmission Fluids, Brake Fluids, and Vehicular Greases, 2018.

Characterization of Opaque Particles Using SEM-EDS

- The full analysis scheme was conducted on greases containing opaque particles
  - Microscopy
  - Extraction
  - SEM-EDS
- SEM-EDS revealed that the opaque particles were solid lubricant additives
- Consisted mainly of heavier elements such as molybdenum, niobium, or zirconium



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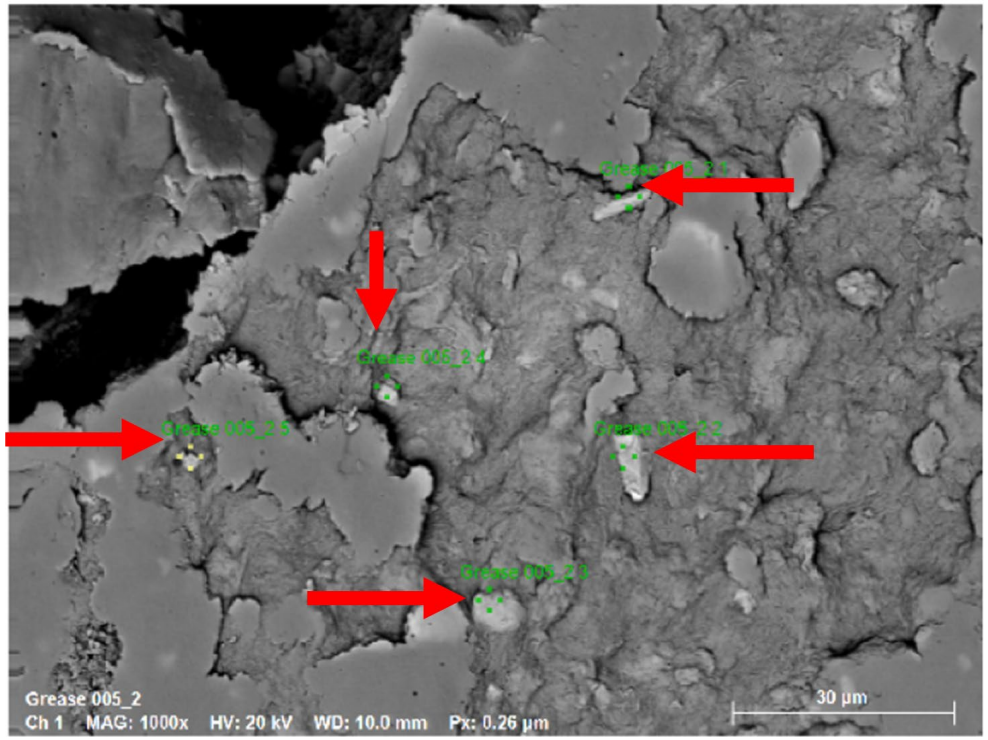
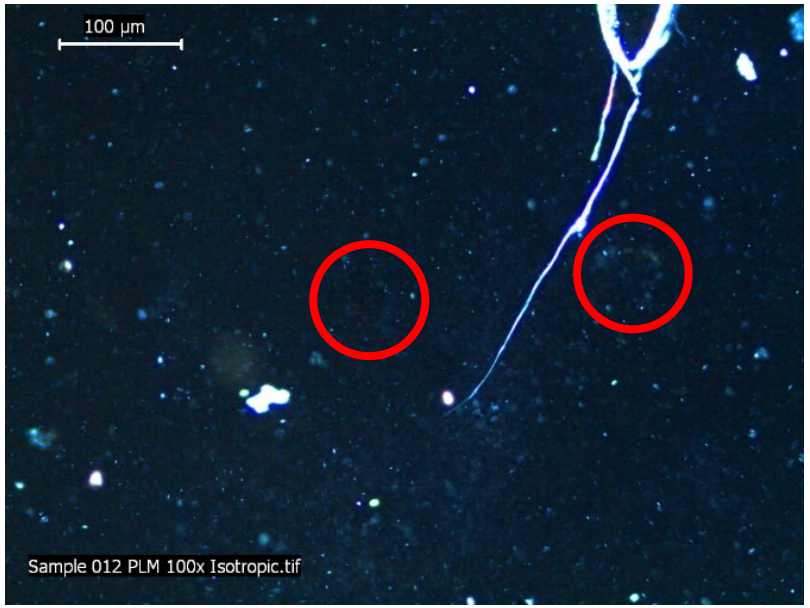


Purpose of Current Research

- The opaque particles were characterized, two types remain
  - Isotropic
  - Anisotropic

Bright Field



Polarized Light Microscopy

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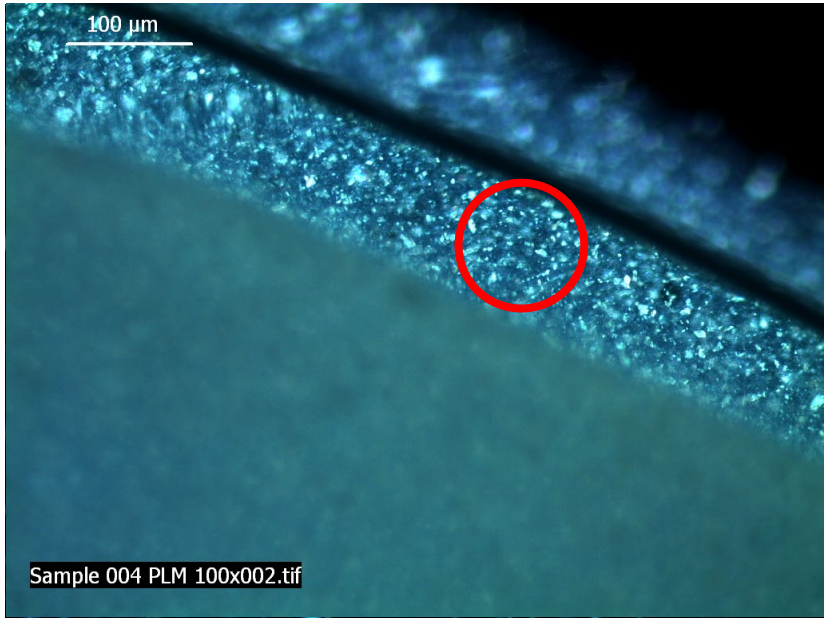


Polarized Light Microscopy

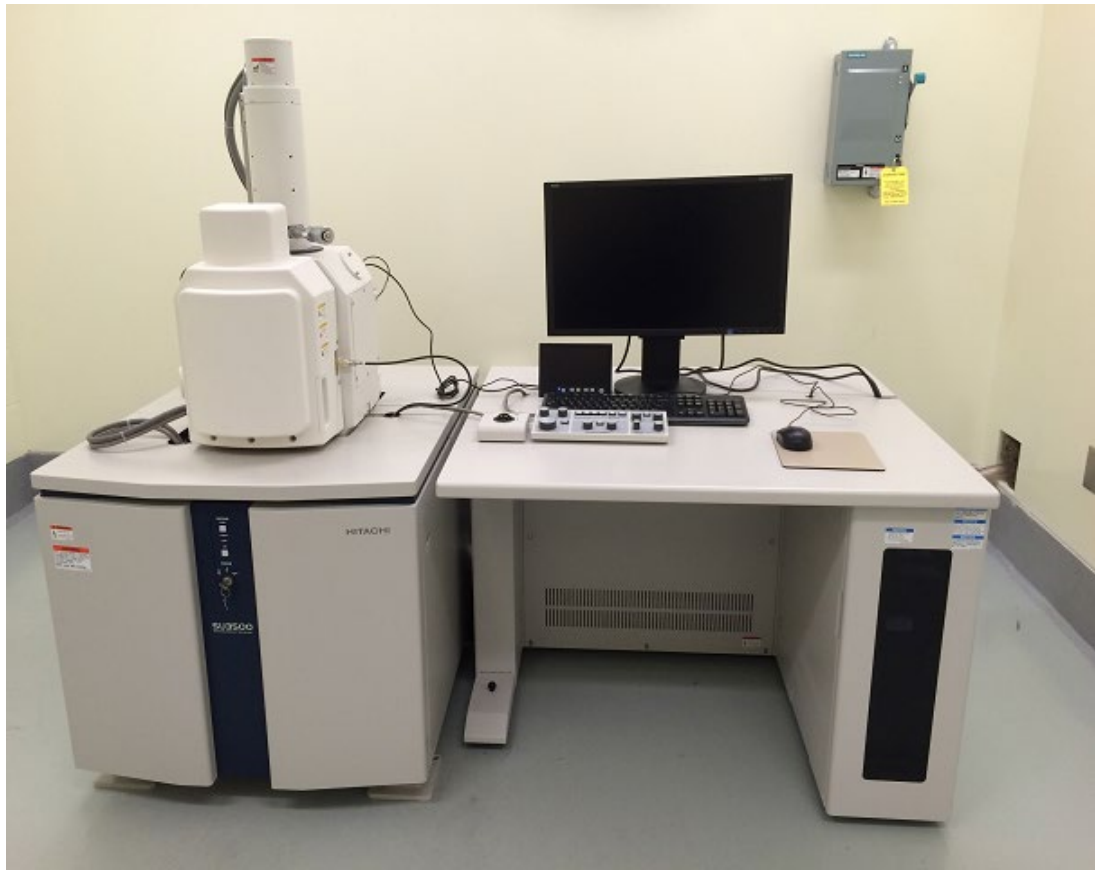
Purpose of Current Research

- The opaque particles were characterized, two types remain
  - Isotropic
  - Anisotropic

1. Apply the previously developed extraction scheme to remove **isotropic/anisotropic** particles from the grease matrix
2. Develop an SEM/EDS protocol to analyze the **isotropic/anisotropic** particles removed from the matrix and characterize their elemental composition

Instrument and Parameters

- Hitachi SU-3500 SEM in BSE mode
- Bruker Quantax XFlash® 6 EDS
  - 25 kV
  - 50% spot size
- **60 Pa in variable pressure mode**
- Calibrated to a copper tape standard
- **Auto Identified elements** using Quantax ESPRIT software

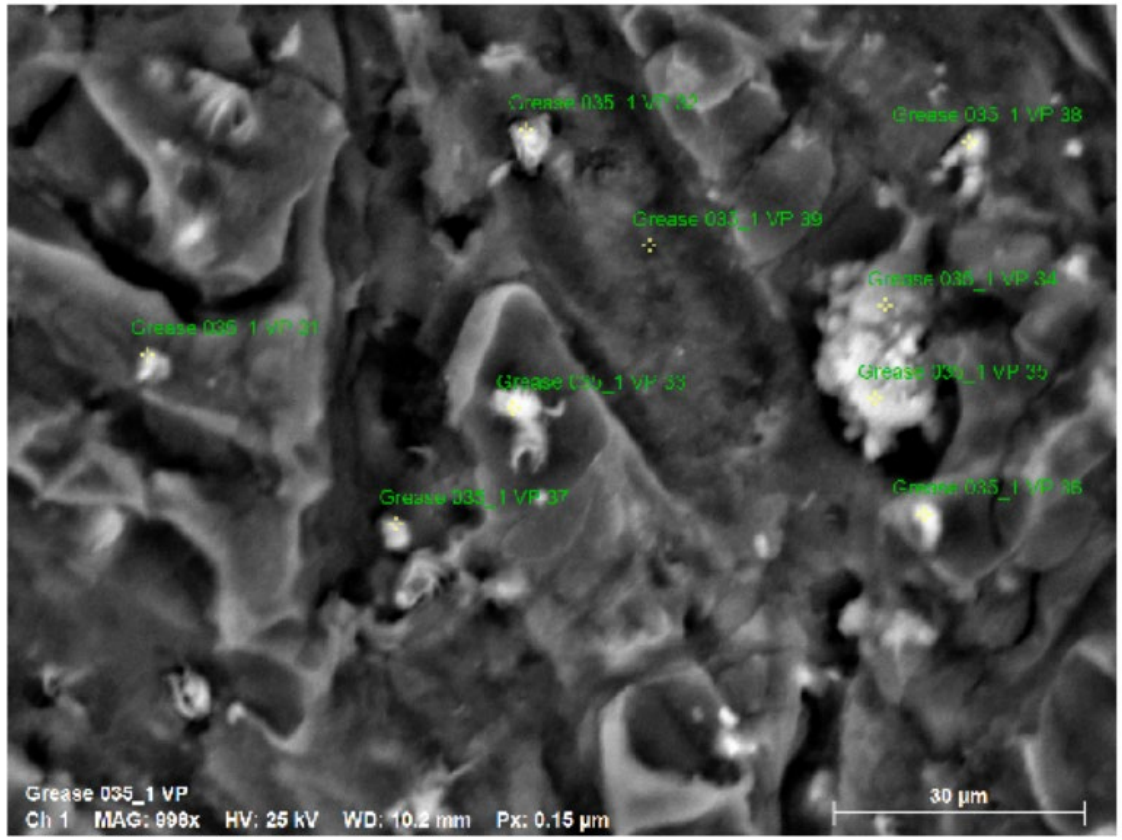


Samples

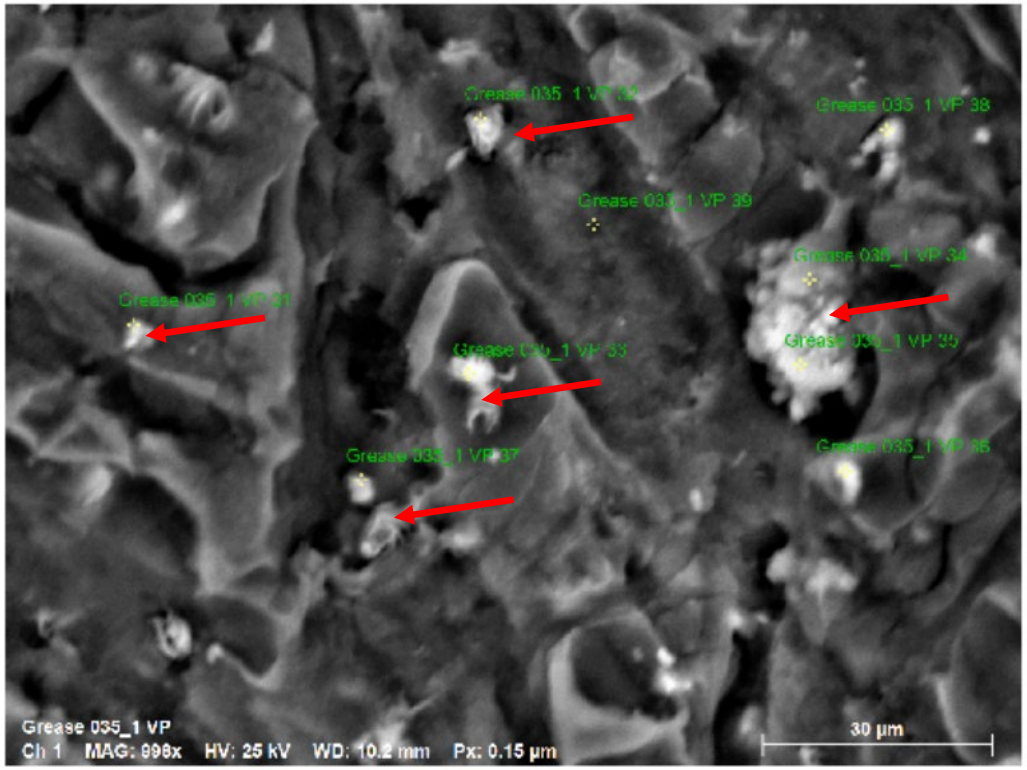
Sample #	Description
2	Lucas Marine
3	Lucas Red “N” Tacky
8	Masterpro Super White
9	Masterpro Wheel Bearing
10	Mobil1 Synthetic Grease
12	Mystik JT-6 Multipurpose
13	Nano Pro MT Hi-Temp
16	Sta-Lube Extreme Pressure Sta-Plex
17	Sta-Lube Lithium General Purpose
21	SuperTech Marine
24	Valvoline Cerulean
32	WD-40 Marine
33	WD-40 Specialist Heavy-Duty High Temp
35	Specialist Superior Performance True Multi-Purpose

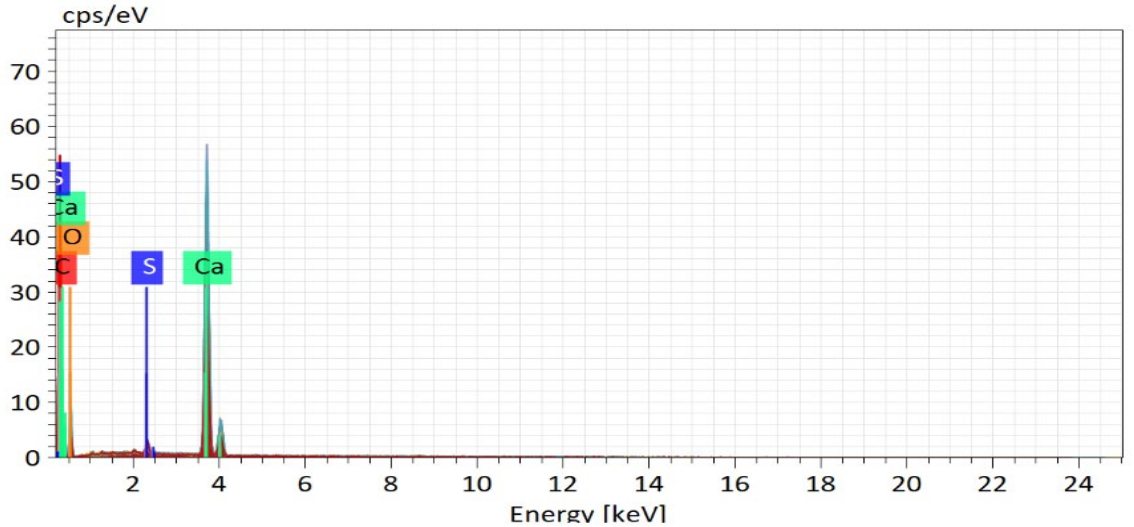
Characterization of Isotropic and Anisotropic Particles Using SEM-EDS

- Fourteen samples analyzed for isotropic and anisotropic particles
- Particles were found using the backscatter detector
- Selected targets for EDS based upon size and morphology
- These particles are presumed to be a different kind of solid lubricant additive



Characterization of Isotropic and Anisotropic Particles Using SEM-EDS





Auto ID

Normalized mass concentration [%]

Spectrum	Carbon	Oxygen	Sulfur	Calcium
Grease 035_1 VP 31	38.01	36.96	0.37	24.67
Grease 035_1 VP 32	38.88	35.45		25.67
Grease 035_1 VP 33	42.01	36.82		21.17
Grease 035_1 VP 34	43.14	35.44		21.42
Grease 035_1 VP 35	27.34	45.11		27.55
Grease 035_1 VP 36	44.86	39.61	0.22	15.32
Grease 035_1 VP 37	40.24	40.42	0.35	19.00
Grease 035_1 VP 38	31.42	34.95		33.63
Grease 035_1 VP 39	50.18	24.56	1.07	24.19
Mean	**39.56**	**36.59**	**0.50**	**23.62**
Sigma	**6.88**	**5.55**	**0.38**	**5.27**
SigmaMean	**2.29**	**1.85**	**0.13**	**1.76**

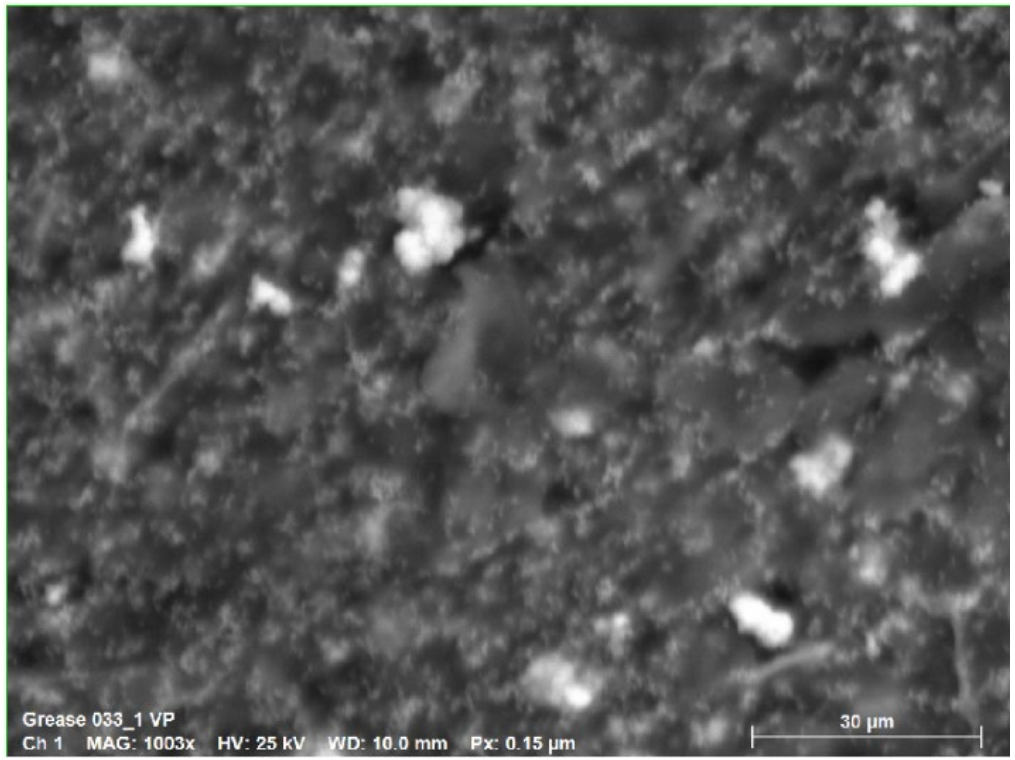
Characterization of Isotropic and Anisotropic Particles Using SEM-EDS

Average normalized mass concentration [%]

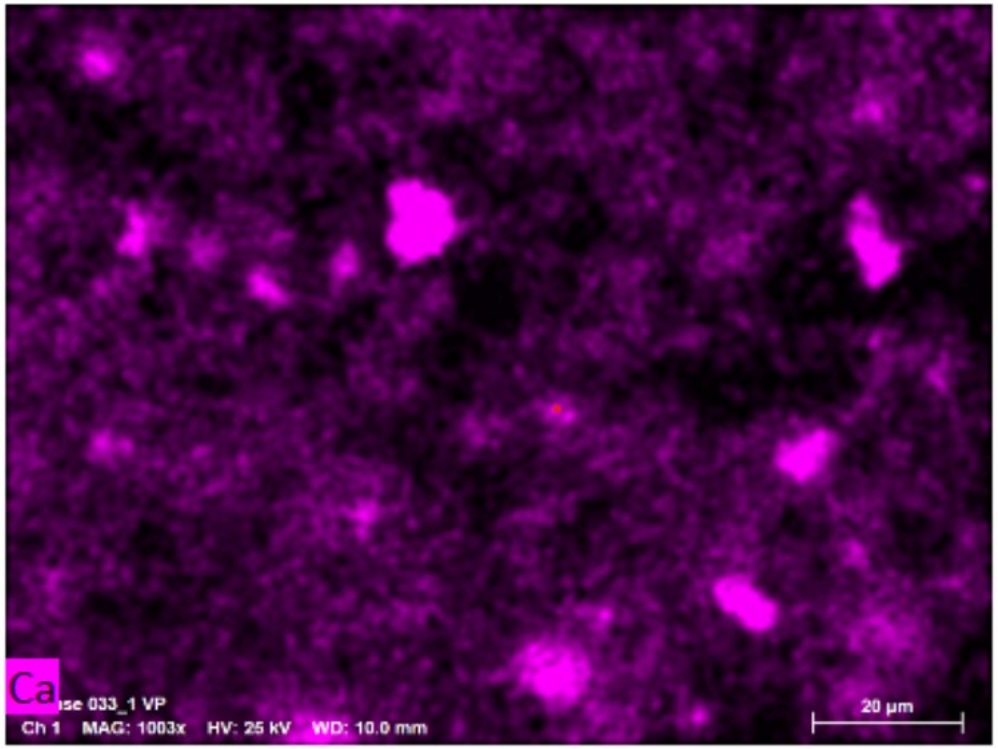
Sample	Elements											
	Na	*Al*	*Si*	*P*	*S*	*K*	*Ca*	*Zn*	*Mo*	*Sb*	*Fe*	*I*
2	0.60	0.11*					0.27*					
4							26.32					
8		0.24*					6.39	8.82				
9					.40*	1.15	1.71	0.18*				
10				0.20	0.28*			0.26*				
12			1.30		0.21*	3.76	10.80				1.06	
13	0.15*			1.34	0.12*		4.92			0.26*		
16				0.52	2.55		12.73	4.79	1.68			29.38
17			0.28*		0.67		3.13		2.24			
21					0.70		6.64			2.09		
24					1.34		7.86					
32					0.15*		20.00					
33					0.32*		13.34	0.28*				
35					0.50		23.62					
Total avg %	**0.0625**	**0.029167**	**0.143182**	**0.17166667**	**0.525769**	**0.377692**	**9.837857**	**1.179167**	**0.326666667**	**0.195833**	**0.088333**	**2.448333**

(*) indicates normal mass concentration less than 0.5%

Characterization of Isotropic and Anisotropic Particles Using SEM-EDS

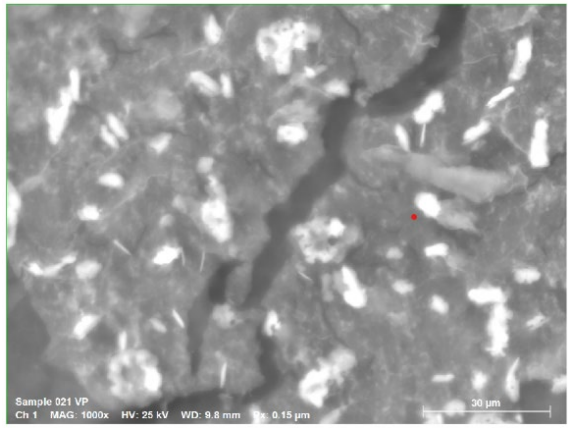


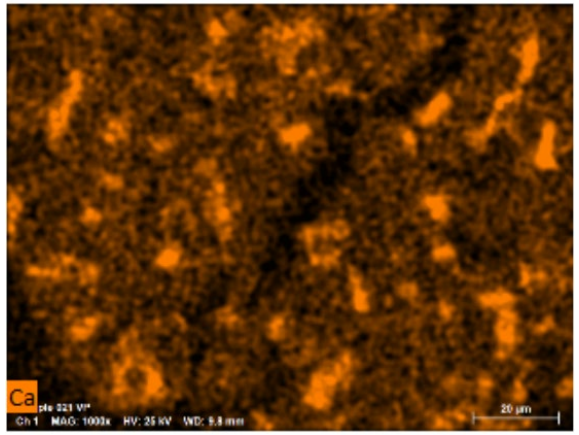
SEM BSE Image

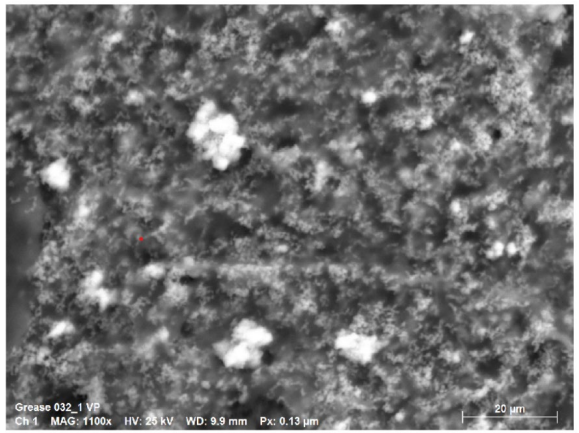


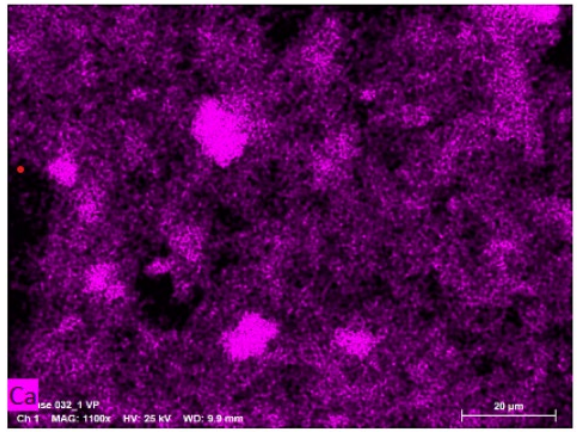
EDS Calcium Map

Characterization of Isotropic and Anisotropic Particles Using SEM-EDS









SEM BSE Image

EDS Map

Characterization of Isotropic and Anisotropic Particles Using SEM-EDS

- Most frequently detected element is calcium
- Calcium sulfonate (CS) thickeners are an alternative to lithium-based thickeners
- CS greases have many advantages over traditional lithium-based greases

Average normalized mass concentration [%]

Sample	*Elements*											
	Na	*Al*	*Si*	*P*	*S*	*K*	*Ca*	*Zn*	*Mo*	*Sb*	*Fe*	*I*
2	0.60	0.11*					0.27*					
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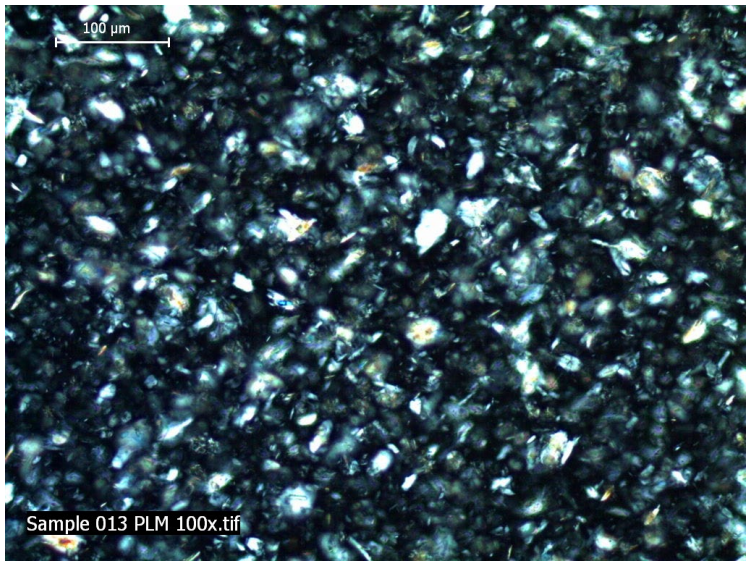
Characterization of Isotropic and Anisotropic Particles Using SEM-EDS

- Calcite is intentionally formed in calcium sulfonate greases to be a solid lubricant[7]
- Calcite acts as a solid lubricant, especially at high temperatures[8-10]
- Calcite is birefringent underneath PLM[11]



[7] Sniderman D, Mackwood W. Calcium sulfonate complex greases. Tribology and Lubrication Technology 2016.
[8] Understanding Calcium Sulfonate Thickeners. https://www.machinerylubrication.com/Read/909/calcium-sulfonate-thickeners (accessed March 15, 2023).
[9] Mackwood W, Brown KJ. Proper Grease Selection Reduces Steam Valve Maintenance. NLGI 2001;66(4).
[10] John PJ, Prasad SV, Voevodin AA, Zabinski JS. Calcium sulfate as a high temperature solid lubricant. Wear 1998;219(2):155–61. https://doi.org/10.1016/S0043-1648(98)00167-7.
[11] Calcite. https://www.science.smith.edu/geosciences/petrology/petrography/calcite/calcite.html (accessed March 15, 2023).

Image courtesy of mindat.org

Characterization of Isotropic and Anisotropic Particles Using SEM-EDS

- Other greases are “lithium complex”, “mixed”, or do not state thickener type
- **Based upon the microscopy and EDS results, these other greases could use calcium sulfonate or add calcite separately as a solid lubricant**

Average normalized mass concentration [%]

Sample	*Elements*											
	Na	*Al*	*Si*	*P*	*S*	*K*	*Ca*	*Zn*	*Mo*	*Sb*	*Fe*	*I*
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CS

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Characterization of Isotropic and Anisotropic Particles Using SEM-EDS

- Next most detected element is sulfur, followed by zinc
- Zinc and sulfur are not always localized
- Zinc and sulfur are "performance additives" and this signal can be coming from a variety of places such as grease additives or thickeners[12]

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[12] S. Rawat, A.P. Harsha, Chapter 9: Current and Future Trends in Grease Lubrication, in: Automotive Tribology, Springer, 2019: pp. 147–182. https://doi.org/10.1007/978-981-15-0434-1_13.

Conclusions

- The proprietary nature of greases makes analysis of greases difficult
- No trends seen between EDS results or microscopy linking to grease purpose or type
- **Elemental composition and microscopy indicates the identity of the anisotropic particles are solid lubricants**
  - **Calcite ($CaCO_3$)**
- **SEM-EDS analysis of isotropic particles is still challenging due to particle size (<5 μm) and interferences**

Future Work

- Quantitative analysis with ICP-OES could prove beneficial
- Forensically, a suggested examination scheme for pure greases would be:
  1. Microscopy
  2. Extraction
  3. SEM-EDS
  4. ICP-OES
- Examination of greases is comparative in nature
- Future work will evaluate how greases change over time and with use

Questions?

Jared Estevanes

jae031@shsu.edu

References

[1] NHTSA. 2020 Summary of Motor Vehicle Crashes. Washington, D.C.: NHTSA's National Center for Statistics and Analysis, 2022.

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