The Three Categories of Lubricating Grease Formulation Work: A Forty-Six Year Perspective

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FORMULATION CATEGORY 1: *Using only existing componentry (base oils, thickeners/thickener reactants, additives), and using them in the manner that is well-known to achieve results that are also well-known and expected, based on information available in the open literature.*

The Quintessential Category 1 Formulation Work: SAE and ILSAC Licensed Motor Oils

- Performance additive supplier does Level 2 (Engine Tests)
- Performance additive concentration set by Level 2 passes
- Allowable base oils determined by Level 2 passes and API 1509 Annex E
- VI Improver and Pour Point Depressant (if needed) also determined
- Only thing left is to adjust base oils and VI Improver concentrations so as to pass Level 1 (laboratory tests)

Category 1: Strategic Cruise Missile Engine Thrust Bearing Grease (Circa 1990)

- ***The problem:*** U.S. Air Force noted that these bearings were exhibiting corrosion during long-term storage.
- ***The cause:*** insufficient corrosion (rust) protection provided by the grease
- ***The task:*** develop a new grease that would provide the needed corrosion protection while also providing the other performance requirements.
  - EP/AW
  - Passivity to Fe, Cu
  - Oil bleed
  - Shear stability
  - Usable from -54 C (-65 F) to 135 C (275 F)

Cruise Missile Engine Thrust Bearing Grease Formulation	
	wt%
PAO (40 cSt at 100 C)	47.0
PAO (6 cSt at 100 C)	31.3
Lithium 12-Hydroxystearate	12.0
Ashless Dithiocarbamate	3.0
Tri-Aryl Phosphate Ester	3.0
Barium Dinonyl Naphthylene Sulfonate (in PAO)	1.5
Borated Alkenyl Amide	1.5
Phenyl Alpha-Naphthylamine (PANA)	0.5
Alkyl Tolutriazole	0.1
Excess Lithium Hydroxide	0.1

Cruise Missile Engine Thrust Bearing Grease Test Results

Worked 60 Stroke Penetration, ASTM D217, 0.1 mm	307
Worked 100,000 Stroke Penetration, ASTM D217	
Final Value, 0.1 mm	329
% Change from Worked 60 Stroke Value	7.2
Dropping Point, ASTM D2265, C (F)	206 (403)
Oil Separation, FTM 791-321, % Loss	
24 hr, 100 C	2.5
100 hr, 100 C	5.9
Copper Corrosion Protection, ASTM D4048, 24 hr, 100 C	1B
Four Ball Wear, ASTM D2266, mm	0.4
Four Ball EP Load Wear Index, ASTM D2596	40.6
Optimol SRV Stepload Test, GM Procedure, Maximum Pass, N	1000
Corrosion Prevention, ASTM D1743, 5% Synthetic Sea Water	Pass, Pass
Water Washout at 38 C (100 F), ASTM D1264, % Loss	2.5
Low Temperature Torque at -40 C (-40 F)	
Starting, N-m	0.320
Running, N-m	0.058
Low Temperature Torque at -54 C (-65 F)	
Starting, N-m	1.06
Running, N-m	0.23

The Final Result

- U.S. Air Force evaluated the grease using a jet engine test rig
- Tests run to simulate cruise missile start up and flight conditions
- Used actual cruise missile ball bearings with grease
  - New
  - After prolonged storage at 100% relative humidity
- Grease was approved for use
- A new specification, MIL-PRF-32014, was created specifically for this grease formulation.
- Subsequently shown to work in another U.S. Air Force application
- U.S. Patent No. 5,133,888 (July 28, 1992)

FORMULATION CATEGORY 2: *Using only existing componentry, but using at least one existing component in a novel way that achieves a beneficial result that has not been previously documented in the open literature.*

Category 2: CV Joint Grease - Restricting Oil Bleed (Circa 1986)

Polyurea Grease Formulation For CV Joints

	wt%
Paraffinic Base Oil (850 SUS Oil at 100 F)	47.6
Paraffinic Severely Hydrotreated (White) Base Oil (350 SUS at 100 F)	31.2
Polyurea Thickener	9.5
Tri-Basic Calcium Phosphate	5.0
Calcium Carbonate	5.0
Barium Dinonyl Naphthalene Sulfonate (Neutral)	1.0
Borated Alkenyl Amide	0.5
Mixed Aryl Amine Antioxidant	0.2
Dye	0.02

Restricting Oil Bleed in Polyurea Grease by Using Borated Chemistry

Grease No.	1	2	3	4
Polyurea Thickener, wt%	9.6	9.6	6.0	6.0
% Borated Alkenyl Amide	0.0	0.5	0.0	0.5
Worked 60 Stroke Penetration, ASTM D217, 0.1 mm	312	315	383	384
Dropping Point, ASTM D2265, C (F)	255 (491)	258 (497)	ND	ND
Oil Separation, SDM 433, % Loss				
6 hr, 100 C	5.5	3.3	ND	ND
24 hr, 100 C	8.7	6.0	9.6	6.9
24 hr, 149 C	9.7	7.9	12.1	5.6
24 hr, 178 C	15.7	8.1	34.3	30.0

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Dye	0.02

Category 2: Using a Base Oil to Solve a Dropping Point Problem (Circa 1986)

- Early formulation used a comparable viscosity lightly hydrotreated paraffinic base oil instead of the white oil
- Dropping points ranged from 104 C (220 F) to 161 C (321 F)
- Dropping point for polyurea grease should be at least 260 C (500 F)
- Entire grease slid out the bottom of the dropping point cup
- No visible oil separation

Polyurea Formation Chemistry

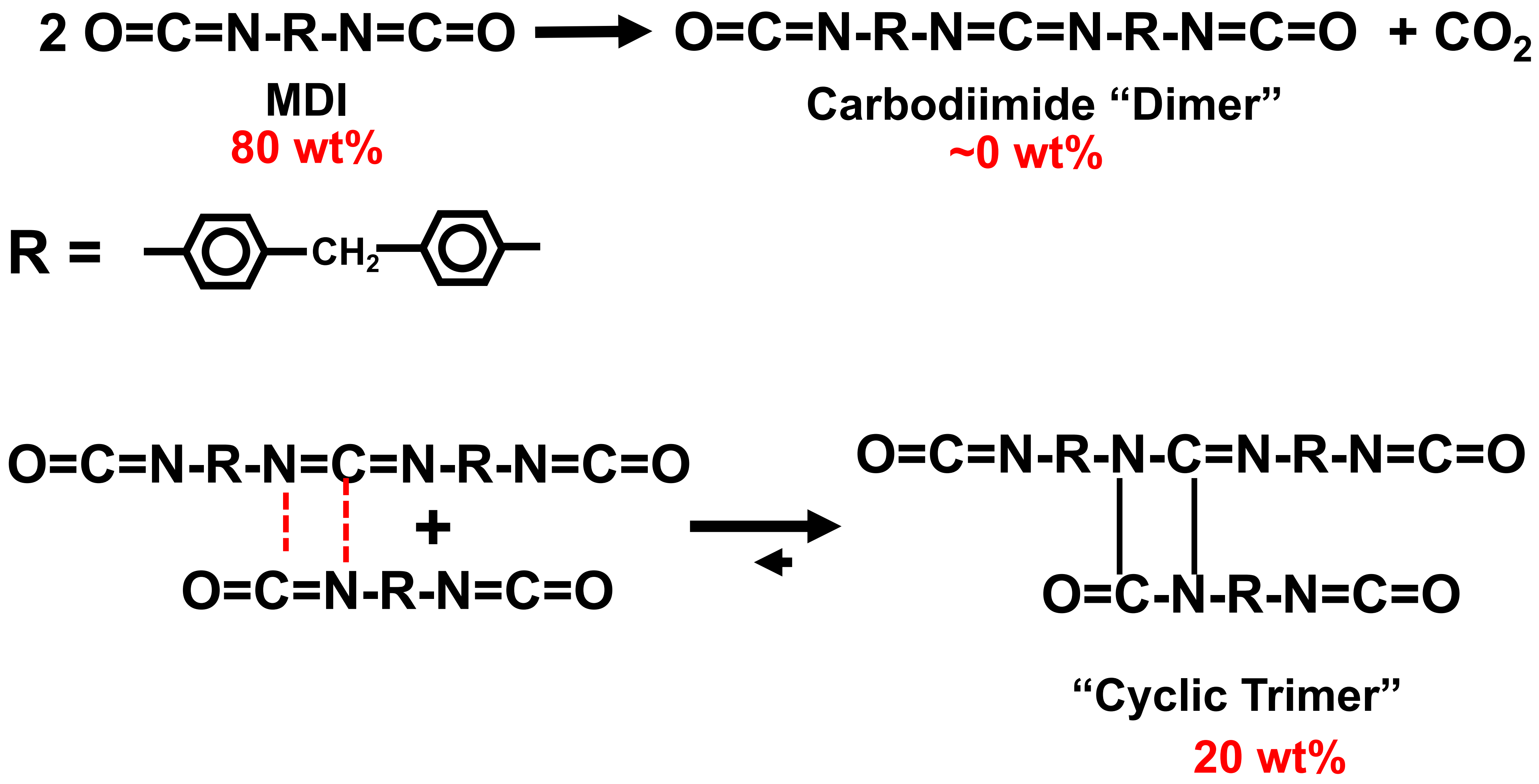
Typical for 1980's

Di-isocyanate + Di-amine + alkyl amine ⟶ polyurea

The Method Used For My Grease Development

Di-isocyanate + Water + alkyl amine ⟶ polyurea

- The water reacts with the di-isocyanate to form the corresponding di-amine in-situ.
- This method requires certain conditions to achieve the proper balance.
- Di-isocyanate used was MDI.
- MDI is solid at 25 C. (M.P. is 40 C)
- **Bulk molten storage of MDI to make 10MM lb grease/year NOT DESIRABLE**


2 O=C=N-R-N=C=O
O=C=N-R-N=C=N-R-N=C=O + CO2
MDI
80 wt%
Carbodiimide "Dimer"
~0 wt%
R =
CH2
O=C=N-R-N=C=N-R-N=C=O
+
O=C=N-R-N=C=O
O=C=N-R-N-C=N-R-N=C=O
O=C-N-R-N=C=O
"Cyclic Trimer"
20 wt%

Important Additional Information

- When the eutectic MDI-based liquid was used, the “dropping point sliding problem” occurred.
- When pure MDI was used, dropping point was 260 C or higher.
- Therefore, the non-polyurea compounds must be the culprit
- When eutectic MDI-based liquid was used with naphthenic base oil, the problem got even worse.
- Therefore, aromatic content of base oil may also be contributing.
- Non-polyurea compounds might be interacting with the aromatic moieties of the base oil blend – “like dissolves like”.
- Try drastically reducing the aromatic content of the base oil blend.
- PROBLEM SOLVED!!!

Category 2: Extremely Long-Life, High-Temperature Bearing Grease (Circa 1991; Yes, More Polyurea)

- In the 1980’s, ASTM D3336 run at 178 C was the gold standard test for determining bearing grease performance at high speeds and high temperature.
- Two polyurea greases dominated for such applications.
- Technical data sheets reported D3336 bearing lives of 500 and 800 hours when the test was run at 178 C.
- Development work was done to determine if superior D3336 performance could be achieved.

Extremely Long-Life Sealed-For-Life Wheel Bearing Grease

Grease No.	1	2	3	4
Paraffinic Base Oil (850 SUS Oil at 100 F)	51.4	50.8	49.3	50.8
Paraffinic White Base Oil (350 SUS at 100 F)	34.2	33.9	32.9	33.9
Polyurea Thickener	9.5	9.5	11.0	11.0
Tri-Basic Calcium Phosphate	0.5	0.5	0.8	0.8
Calcium Carbonate	0.5	0.5	0.8	0.8
Styrene-Alkylene Copolymer	1.0	1.0	0.0	0.0
Barium Dinonyl Naphthylene Sulfonate/Polyalkenylene Succinate	1.5	1.5	2.5	0.0
Micronized Sodium Nitrite	0.0	1.0	0.2	0.2
Borated Alkenyl Amide	0.0	0.0	0.1	0.1
Alkylated Aryl Amine	1.5	1.5	2.5	2.5
Worked Penetration, ASTM D217, 0.1 mm	315	304	306	303
Dropping Point, ASTM D2265, C (F)	271 (520)	258 (496)	262 (503)	263 (505)
Bearing Life, ASTM D3336 at 178 C, hr	518, 781	875, 1,100+	1,049, 1,237	614, 742

It Doesn't Just Work For Barium

Metal Sulfonate/Succinate Used	Mg	Ca
Bearing Life, ASTM D3336 at 178 C, hr	1,640 1,464	1,594 1,864

The Final Result

- One of these greases was tested by a U.S. automobile OEM.
- Test Track
- Wheel bearings using fresh grease
- Wheel bearings using grease after storage in “hot box”
- “Torture Test”
- Performance of grease exceeded anything previously documented using that test protcol.
- U.S. Patent No. 5,207,935 (May 4, 1993)

Category 2: Calcium/Magnesium Sulfonate Complex Grease (Circa 2017 – Present)

- Covers a wide range of products based on both composition and manufacturing process
- Properties cover a very wide range
- Brief overview of only one type of Ca/Mg Sulf-X grease covered here

Calcium/Magnesium Sulfonate Complex Grease	
Chemical Component Name	%(wt)
Solvent Neutral Group I Base Oil (113 cSt @ 40 C)	47.6
Overbased Calcium Sulfonate (400 TBN)	32.0
Overbased Magnesium Sulfonate (400 TBN)	3.3
Dodecylbenzene Sulfonic Acid (DDBSA)	3.2
Powdered Calcium Carbonate	7.7
Alkylene Glycol	1.6
12-Hydroxystearic acid (12HSA)	2.5
Glacial Acetic Acid (HOAc)	0.4
Phosphoric acid (75 wt% aqueous solution)	1.7

How These Greases Were Made

1. Add 70.0 wt% of the base oil, all the OCaS and OMgS to the mixer. Mix for about 20 minutes.

2. Add all the DDBSA. Mix for at least 20 minutes.

3. Add all the powdered calcium carbonate. Mix for at least 20 minutes.

4. Add 33% of the 12HSA and 35% of the HOAc. Mix for at least 20 minutes.

5. Add 4.0% water based on the final weight of the batch.

6. Begin heating to 88 C (190 F). Adjust the rheostat controlling the heating mantle so that it takes about 1 hour to reach 88 C.

7. Hold at that temperature for 30 minutes. Then add all the alkylene glycol.

How These Greases Were Made (Continued)

8. Once FTIR confirms that the conversion process has finished, add the remaining 12HSA and HOAc. Allow the grease to mix for at least 20 minutes.

9. Slowly add the phosphoric acid. Once visible reaction has ceased, begin heating to 199 C (390 F). Adjust the rheostat controlling the heating mantle so that it takes about 2 hours to reach 199 C.

10. Once 199 C is reached, remove the heating mantle and continue mixing while the batch cools.

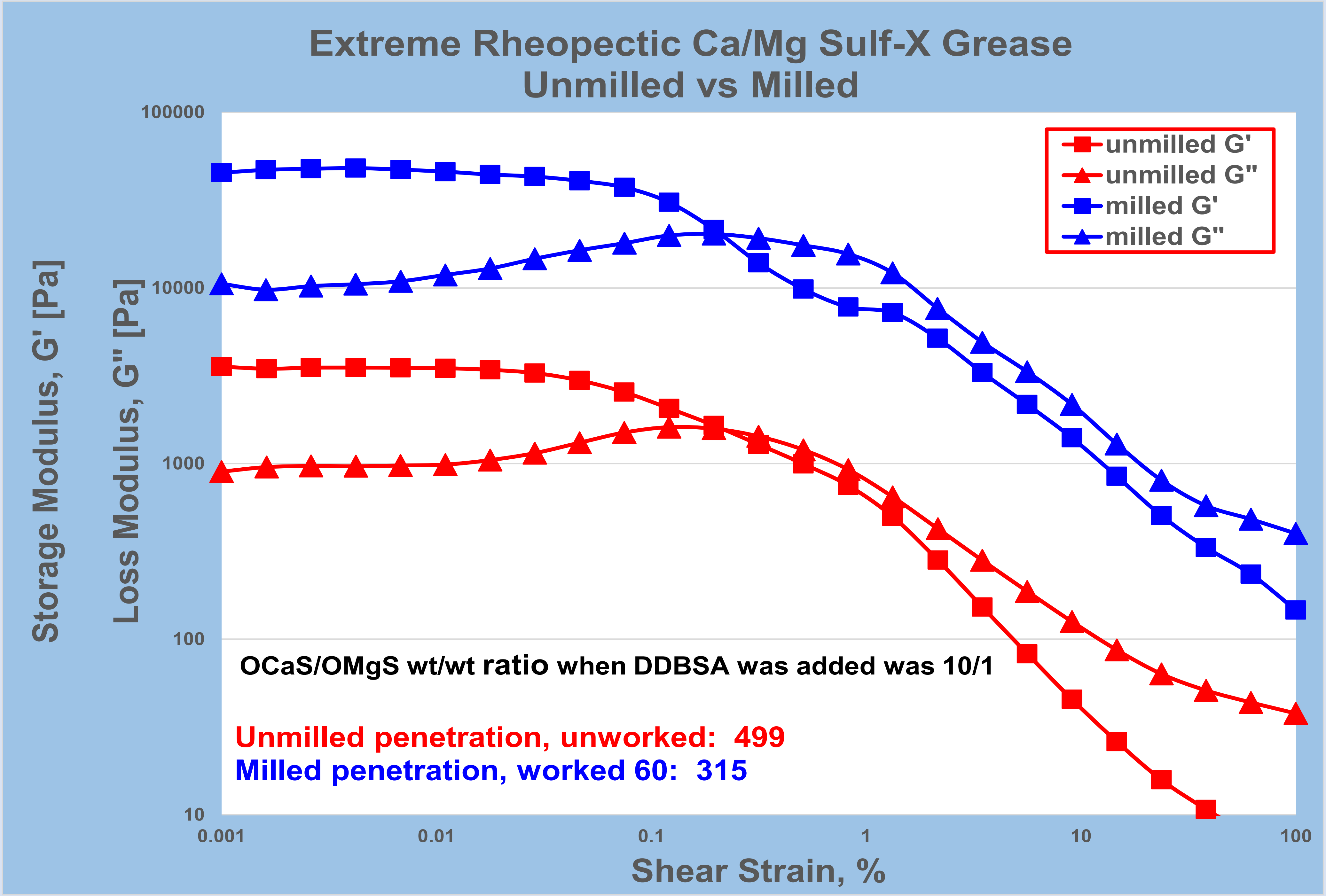
11. Once the batch reaches 77 C (170 F), remove a small portion of it, and give it three passes through a three roll mill with both gaps set at 0.03 mm (0.001 inch).

12. Record the unworked penetration (ASTM D1403) of the milled portion as an estimate of the consistency of the grease before addition of the remaining base oil.

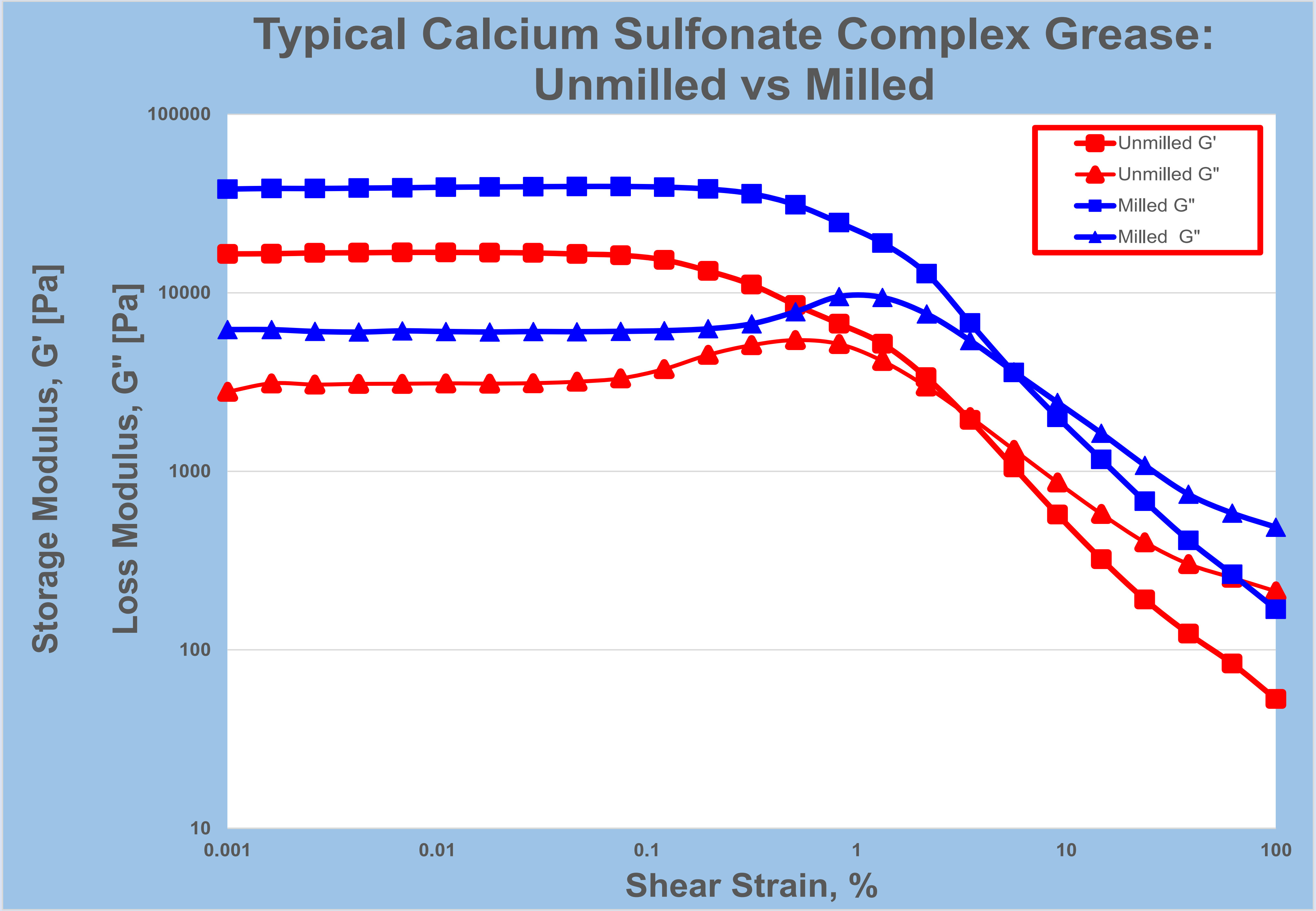
13. Return all the milled grease to the mixer, add remaining base oil, mix at 77 C for 20 minutes. Then mill the entire batch by the same procedure as in step 11.

The First Grease Made That Way

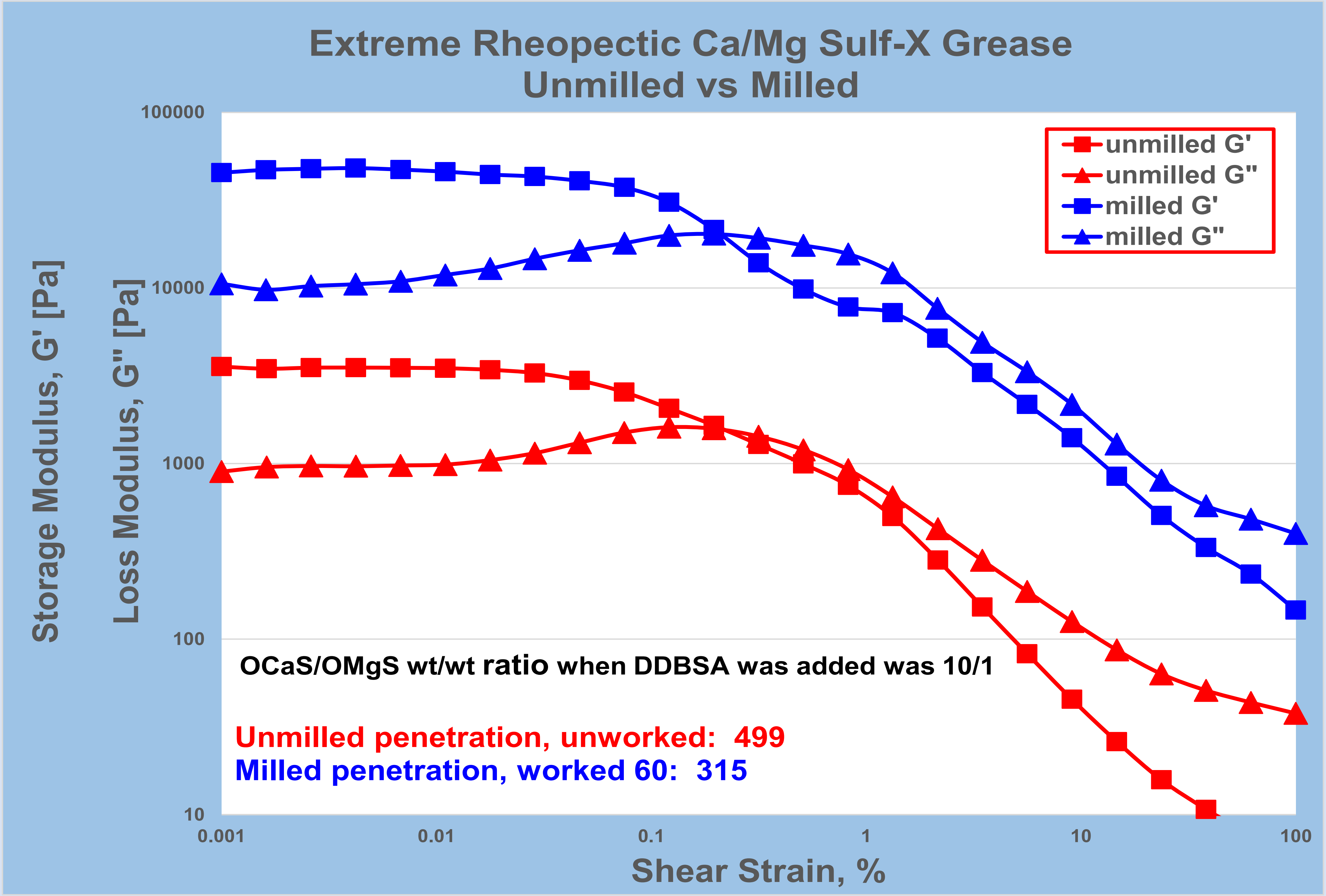
Here's where things got weird!!!



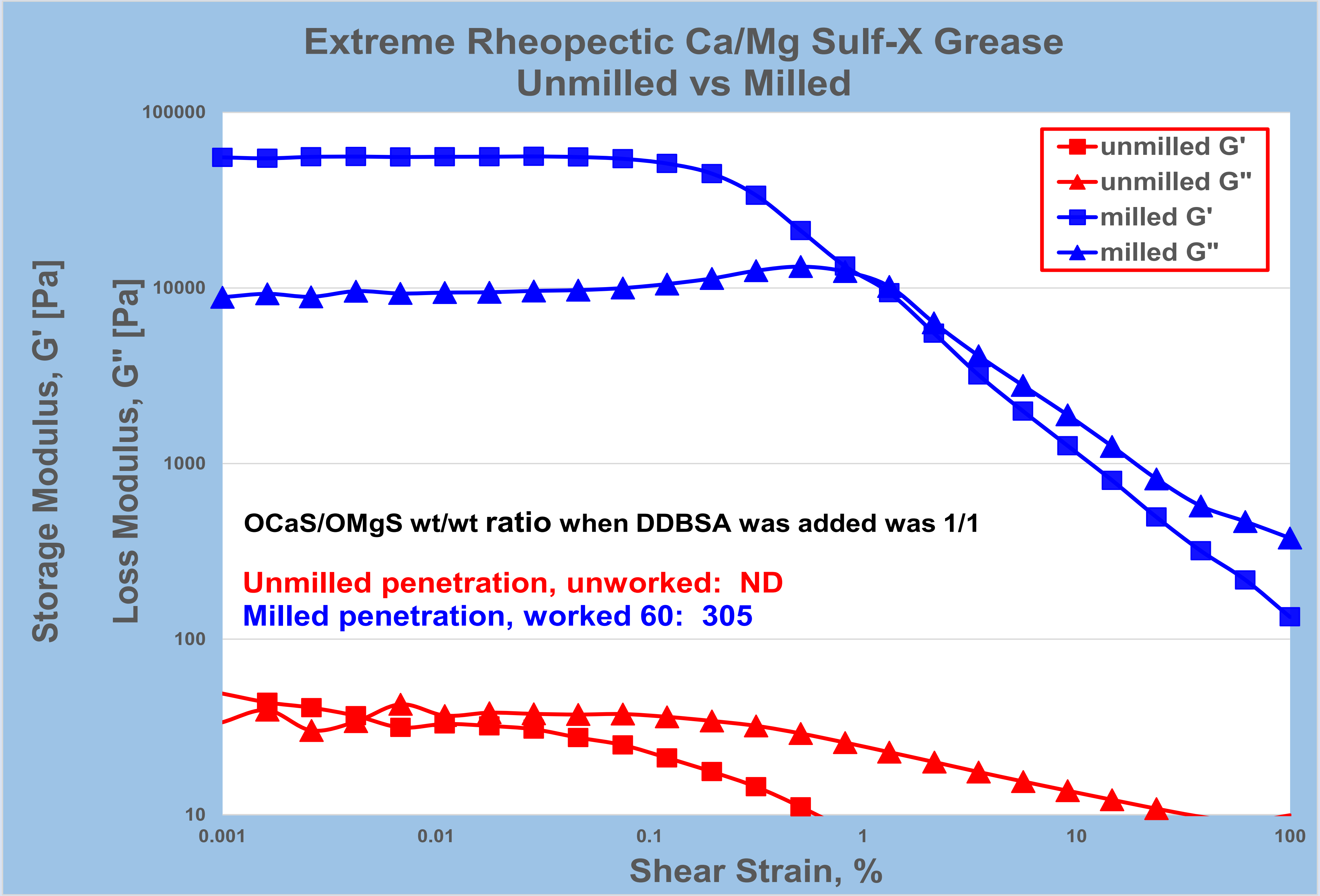
Extreme Rheopectic Ca/Mg Sulf-X Grease
Unmilled vs Milled
unmilled G'
unmilled G"
milled G'
milled G"
Storage Modulus, G' [Pa]
Loss Modulus, G" [Pa]
100000
10000
1000
100
10
0.001
0.01
0.1
1
10
100
Shear Strain, %
OCaS/OMgS wt/wt ratio when DDBSA was added was 10/1
Unmilled penetration, unworked: 499
Milled penetration, worked 60: 315



Typical Calcium Sulfonate Complex Grease:
Unmilled vs Milled
100000
10000
1000
100
10
Storage Modulus, G' [Pa]
Loss Modulus, G" [Pa]
0.001
0.01
0.1
1
10
100
Shear Strain, %
Unmilled G'
Unmilled G"
Milled G"
Milled G"



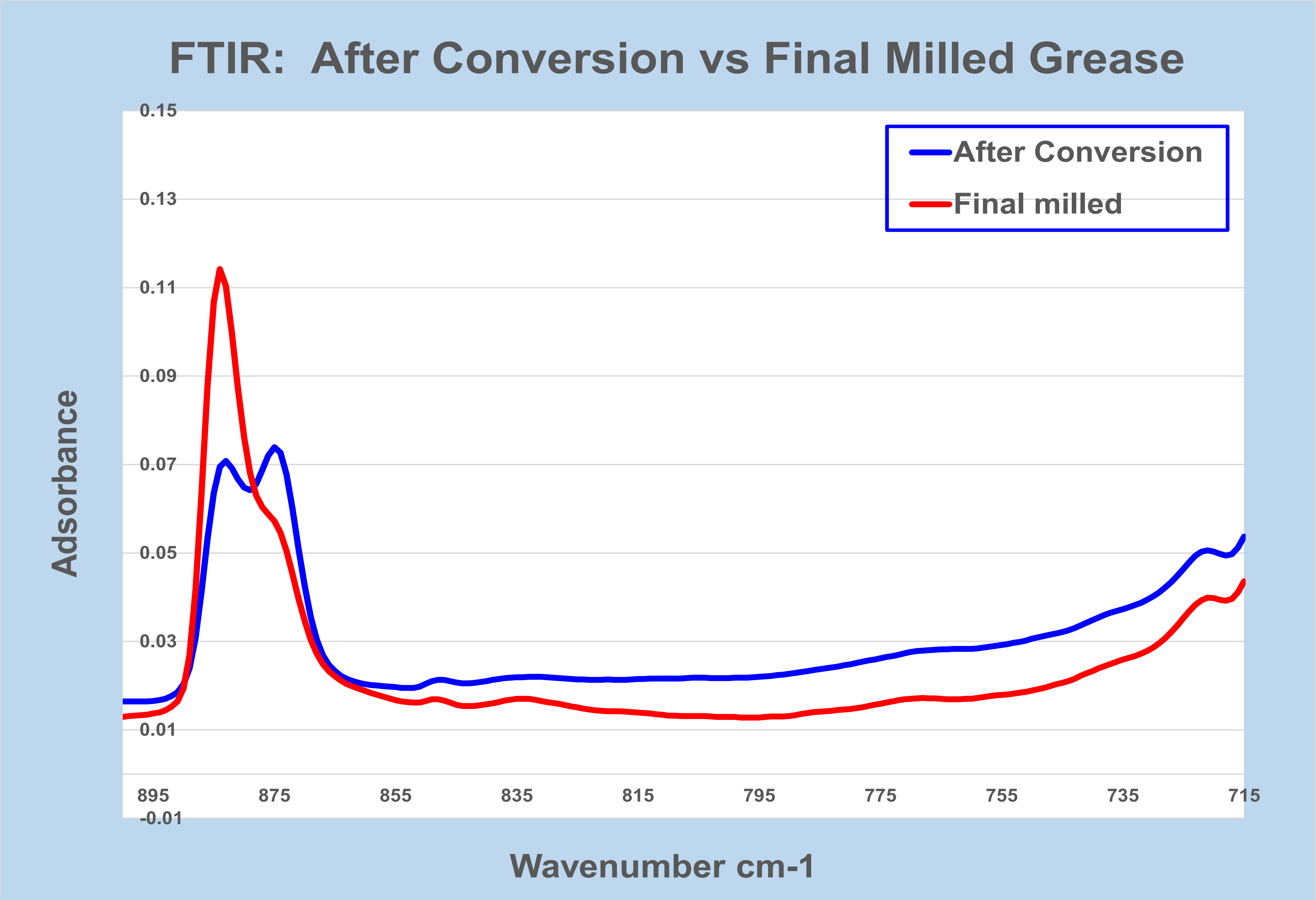
Extreme Rheopectic Ca/Mg Sulf-X Grease
Unmilled vs Milled
unmilled G'
unmilled G"
milled G'
milled G"
Storage Modulus, G' [Pa]
Loss Modulus, G" [Pa]
100000
10000
1000
100
10
0.001
0.01
0.1
1
10
100
Shear Strain, %
OCaS/OMgS wt/wt ratio when DDBSA was added was 10/1
Unmilled penetration, unworked: 499
Milled penetration, worked 60: 315



Extreme Rheopectic Ca/Mg Sulf-X Grease
Unmilled vs Milled
Storage Modulus, G' [Pa]
Loss Modulus, G" [Pa]
100000
10000
1000
100
10
0.001
0.01
0.1
1
10
100
Shear Strain, %
unmilled G'
unmilled G"
milled G'
milled G"
OCaS/OMgS wt/wt ratio when DDBSA was added was 1/1
Unmilled penetration, unworked: ND
Milled penetration, worked 60: 305

Kettle Batches of Ca/Mg Sulf-X Grease

Kettle Batch Number	1	2	3
Unmilled Grease			
Unworked Penetration, ASTM D217, 0.1 mm	ND	557	445
Milled Grease			
Unworked Penetration, ASTM D217, 0.1 mm	293	305	286
Worked 60 Stroke Penetration, ASTM D 217, 0.1 mm	303	307	294
P0 (Unmilled) - P60 (Milled)	ND	250	151


FTIR: After Conversion vs Final Milled Grease
After Conversion
Final milled
Adsorbance
Wavenumber cm-1
0.15
0.13
0.11
0.09
0.07
0.05
0.03
0.01
-0.01
895
875
855
835
815
795
775
755
735
715

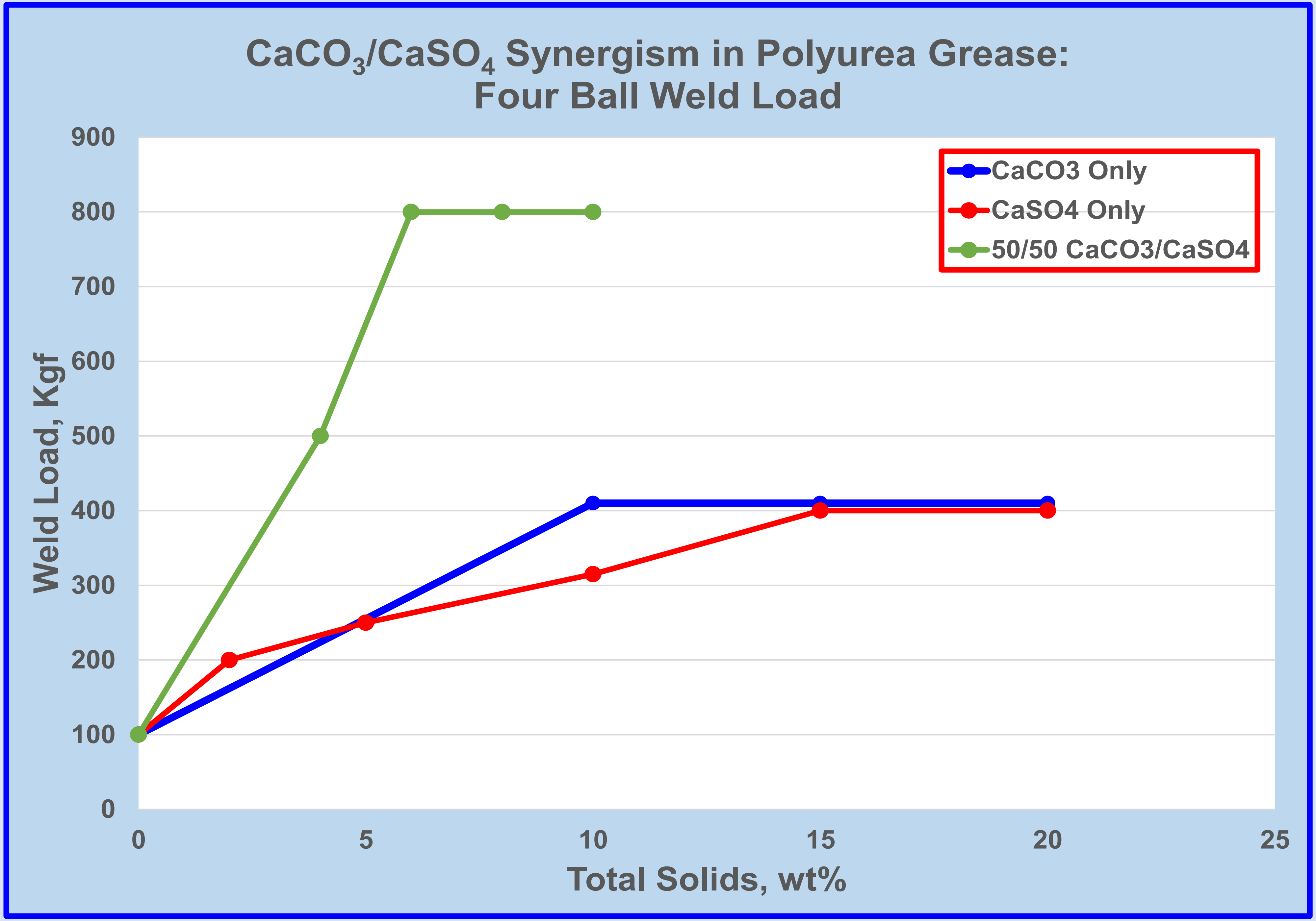
The Final Result

- Ca/Mg Sulf-X greases can cover a wide range of rheology, not documented anywhere in the open literature before this discovery.
- Extremely rheopectic Ca/Mg Sulf-X greases have a conversion FTIR spectra much different from prior-art Ca Sulf-X greases
- Ca/Mg Sulf-X greases comprise a new thickener category.
- Ca/Mg Sulf-X grease compositions and manufacturing processes covered by U.S. Patents and patents issued in other countries.

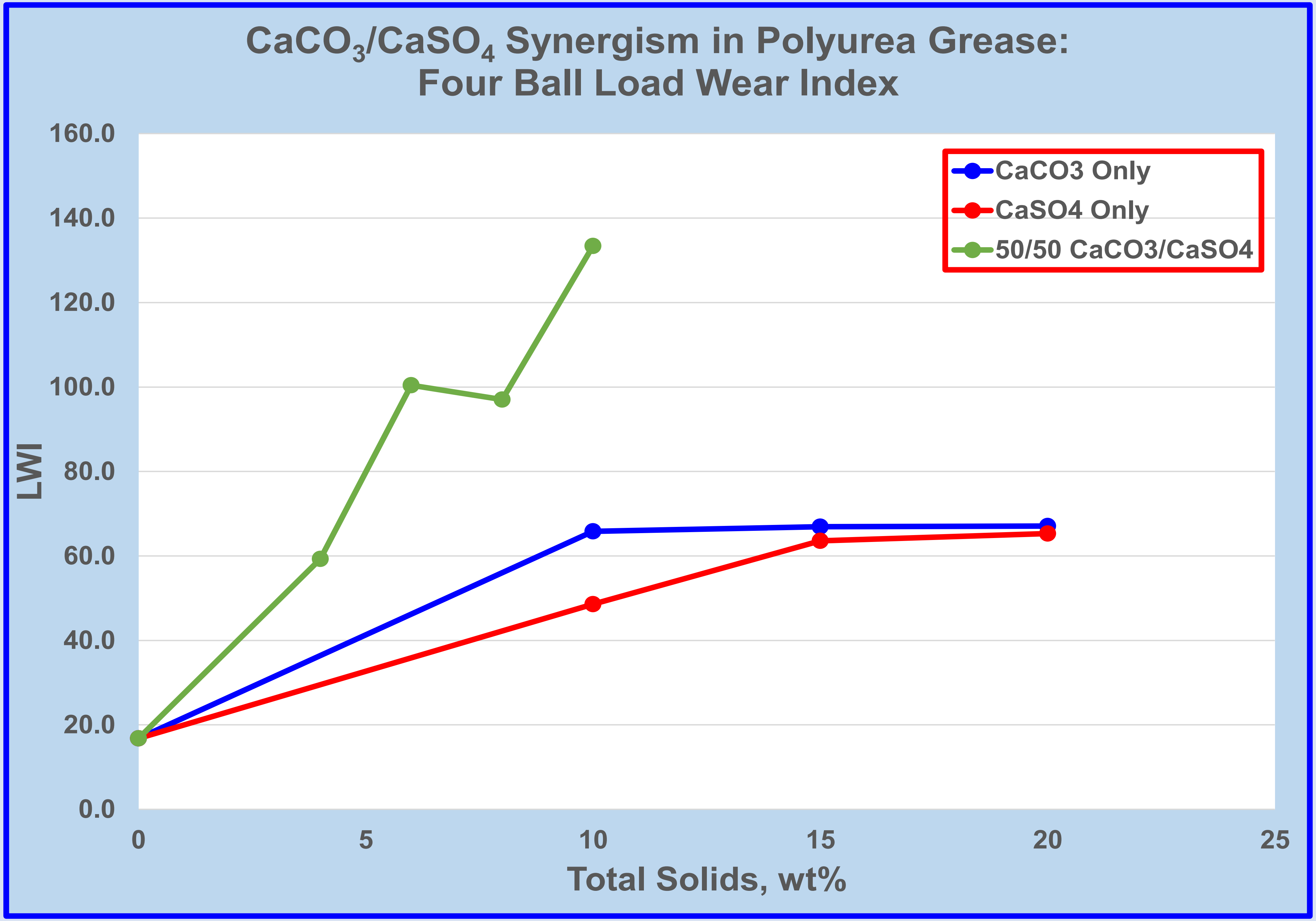
FORMULATION CATEGORY 3: *Using at least one component that has not been previously used in lubricating greases, but that nonetheless provides a beneficial result, either by itself or in combination with other components.*

Category 3: Highly Synergist Combination of Calcium Carbonate and Anhydrous Calcium Sulfate (Circa 1988)

$$CaCO_3 + CaSO_4 \xrightarrow[\text{Polyurea Grease}]{\text{Pressure, Heat, Fe Surface}} ???????$$



$CaCO_3/CaSO_4$ Synergism in Polyurea Grease:
Four Ball Weld Load
CaCO3 Only
CaSO4 Only
50/50 CaCO3/CaSO4
Weld Load, Kgf
Total Solids, wt%
0
100
200
300
400
500
600
700
800
900
0
5
10
15
20
25


CaCO3/CaSO4 Synergism in Polyurea Grease:
Four Ball Load Wear Index
LWI
Total Solids, wt%
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
0
5
10
15
20
25
CaCO3 Only
CaSO4 Only
50/50 CaCO3/CaSO4

Other Properties Of This Synergistic Combination

- Provides excellent EP by other commonly used tests
- Provides excellent AW by all the commonly used tests
- Cheaper than ALL base oils
- Naturally inhibits oil separation, even at higher test temperatures, without the need for organo-boron additives
- Dramatically reduces frictional heat under high loads
- U.S. Patent No. 4,986,923 (January 22, 1991)

Conclusions

1. All lubricating grease formulation work falls within one or more of the three formulation categories as described.

2. Some formulation work will have aspects of more than one category. This is especially true for formulation work where aspects of both Category 1 and 2 are present.

3. Most lubricating grease formulation work will mostly, if not entirely, fall into Category 1.

4. Even when only Category 1 formulation is being done, the results can be extremely significant.

5. Category 3 work is the least frequently encountered of the three formulation categories since it requires the discovery of a grease component not previously documented or anticipated by the established literature. However, when such discoveries are made, the results can be noteworthy.