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Quantum Leap in the manufacturing of polyurea grease (PUG)

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Abstract - The concept and use of pre-form polyurea grease thickener (PUGT) is not new and has been sought for in the industry for decades. However, it has met with failures and commercial difficulties while trying to make a reliable and high quality polyurea grease. This paper discloses a new and well-defined type of PUGT thickener with markedly improved consistency and thickening efficiency that allows grade two polyurea grease to be made at dosage as low as 6%. The grease conversion process is carried out via simple heating/mixing of the PUGT powder with a variety of base oils. This simplicity and the ease in handling and processing is indeed a quantum leap in the manufacturing of polyurea grease that is traditionally made via in-situ method involving the handling of toxic substances such as Methylene Diphenyl Diisocyanate (MDI) or Toluene Diisocyanate (TDI) and hazardous amines, that is particularly troublesome for grease plants that are not equipped to manage such a difficult chemistry. We expect the consistency and well-defined nature of PUGT as described shall offer the opportunity and flexibility in the creation of new and robust polyurea grease compositions.

Introduction

The recent surge in the demand for electrical vehicles (EV) and thus the concerns over the availability of Lithium has alarmed the grease industry. Today EV sales have reached 2 million units (Reference 1). In order to reach 2°C temperature reduction by 2040, International Energy Agency (IEA) projects 600 million EVs would be required. That equates to 7 million tons of Lithium requirement which is almost half of the known world Lithium reserve – 16 million tons according to the United States Geological Survey (USGS).

Much is unknown. Will technology advances such as recyclable batteries, easier/cheaper mining, or alternative battery technologies help us to reach this EV target? The escalated prices (Figure 1) and rapid change in Lithium market demand (Figure 2, 11% to 8% for grease) have the grease industry on the lookout for alternatives.

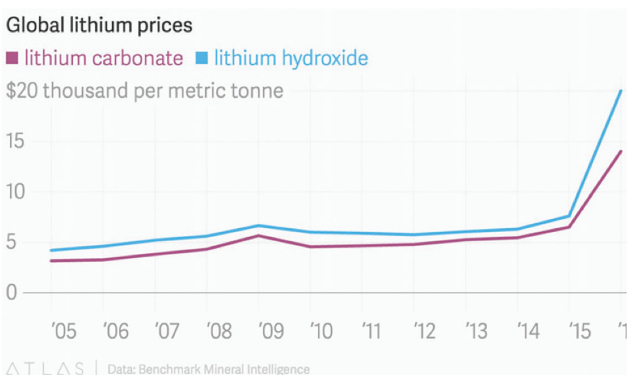

Figure 1: *Global Lithium prices.*

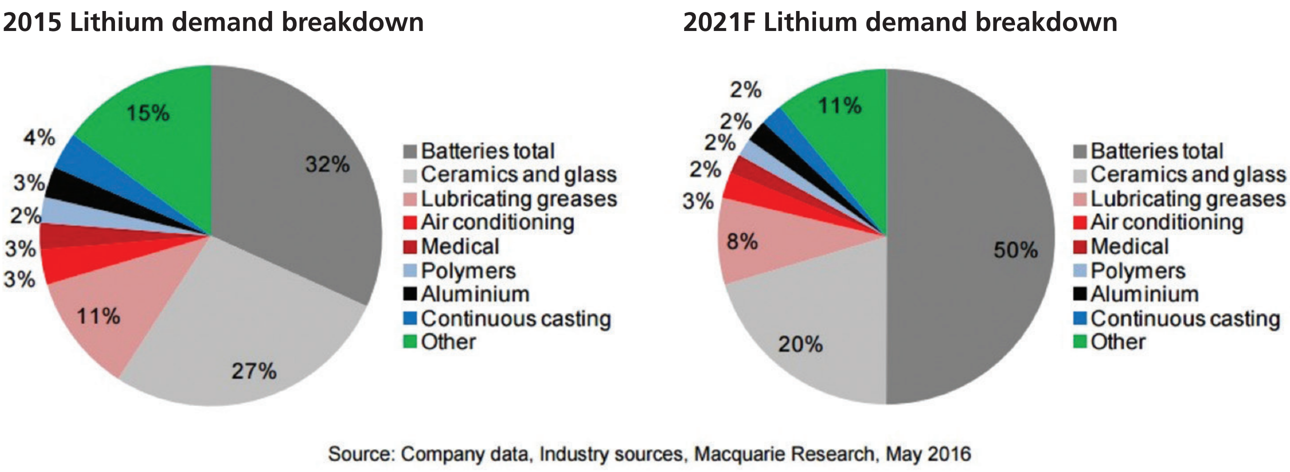

Figure 2: *Projected market share erosion from 11% to 8% (2015 to 2017).*

According to the National Lubricating Grease Institute (NLGI) 2017 Global Production Survey, Lithium based grease (soap and complex grease) comprises 74% of the total grease market share. Among the remaining four grease types, summarised in Table 1, Calcium based grease, Aluminium grease and Overbased Calcium Sulphonate Grease (OBCSG) three that are considered specialty greases that have specific uses and benefits. For instance, OBCSG has gained popularity attributed to its inherent Extreme Pressure (EP) performance. Neither is expected to become the mainstream option to replace Lithium grease. PU grease, currently at 6% globally, on the other hand, is recognised as a non-metallic grease with similar soap (hydrogen bound capable) thickener structures and is known for its high temperature stability, low noise characteristic (since it is non-metallic thickener), and good mechanical, oxidation and high-shear stability (since it is organic thickener). These unique characteristics make it the original equipment manufacturers' (OEMs) and users' first choice for sealed-for-life bearings, ball bearings, constant velocity joints (CVJ), electric motor applications, and for high temperature applications such as continuous casting in steel mills. The widespread use of PU grease (abbreviated as PUG) is evident in Japan (29%, see Table 1 under JP).

However, the limitation in the use of PU grease elsewhere is in part due to the difficulties in its manufacturing. Once that is overcome, we believe polyurea grease, with OEM's acceptance and the growing recognition of its unique performance, will be the future/next generation grease to replace Lithium.' Most of the PUG and traditional manufacturing today requires the use of MDI and TDI that are highly toxic and sensitive to temperature and moisture, and the amines that are hazardous and reactive (see Figure 3

Type of Grease	Total(2017)	US	EU	JP	CN	India
Calcium Sulfonate	3%	6%	5%	0%	2%	1%
Aluminum Soap and Complex	4%	8%	5%	2%	1%	2%
Polyurea Grease	6%	7%	6%	29%	4%	0%
Calcium Soap & Complex	8%	4%	9%	5%	11%	3%
Total Lithium Soap & Complex	74%	67%	71%	58%	78%	84%

Table 1: *2017 NLGI global grease production survey.*

for PU chemistry) via the so-called in-situ method. The need of specialised equipment such as a refrigeration unit and personnel safeguard measures have made it difficult for the small to medium grease manufacturers to get in and to do it safely and easily.

Even for the grease manufacturers that are fully equipped to manufacturer PUG, the in-situ method poses a challenge to modify and to introduce new PUG compositions. For decades, the concept of pre-form PUGT exists whereby the thickener is first made with or without the solvent or the diluent/others and is then converted to grease via grease making process. The concept is attractive as it takes away the difficulties presented by the in-situ method. However, there are numerous failures and too few successes in attempting to control the morphology of the pre-form PUGT thickeners, and during the grease making process, to achieve the desired PUG grease products with consistency.

In this paper we wish to present our solutions to the pre-form thickeners that not only provide the chemistry required to make the desirable thickener composition but also address/control the challenges posed by the thickener to thickener interactions during the so-called gelling process in the making of PU grease day in and day out with reliability and consistency.

The design and the construction of PUGT is a critical part of the powder making. By varying the types of amines, from primary to secondary, aliphatic to aryl, mono amine to poly amine, and from amines to alcohols (see Table 2), a variety of powder can be produced, tuned to specific needs with the consistency required for the subsequent grease making. The process is a multi-step proprietary process. The PUGT products thus formed are in fine powder forms and can be shaped into pellets or extrudates, mixed with diluents and base oils, or even made into masterbatch forms with pre-determined oil contents prior to grease making process.

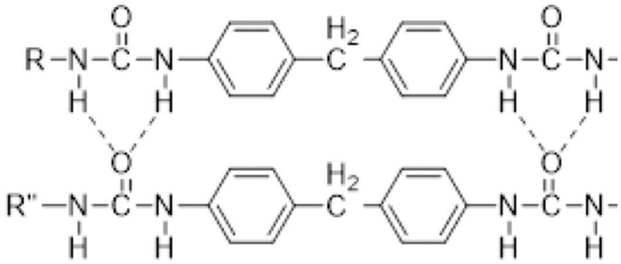

Figure 3: *PUGT chemistry.*

Isocyanate	R (mono and poly amine)
MDI	Aliphatic & Alicyclic
MDI	Aromatic
TDI	Aliphatic & Alicyclic

Table 2: *PUGT component composition.*

Prior to our discussion in the making of polyurea grease, it is important to recognise the unique thickening characteristics for the urea molecules to gel and form extensive intermolecular interactions via hydrogen bonding (see Figure 3) that is vastly different than traditional soap based grease. For instance, the soap grease making process is a gelling forming process after the formation/melting of the soap thickener. For polyurea grease made via the in-situ method, such gelling begins almost instantly as soon as the urea molecule is formed in the process. For PUGT however, the gelling (or the formation of hydrogen bonds) has already taken place in the powder. Any attempt to breakup or to enhance the extent of the gelling is a delicate process.

An interesting observation is made in an atomic force microscopy (AFM) study (Figure 4, Reference 2) where the entrapped thickener in the rolling EHL lubricated contact under fully flooded conditions at medium speeds, is shown to exist in fibre forms (Lithium soap and complex grease), platelets (PUG), and spheres (OBCSG). The formation of platelets, which may be viewed as the bundle of fibres, is an indication of higher film strength under rolling conditions. This observation makes sense for an enhanced thickener-thickener interaction for polyurea grease under stress.

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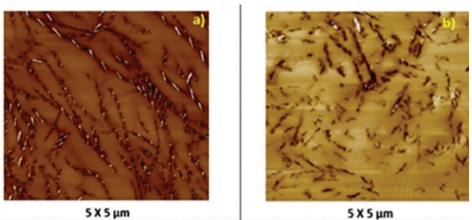
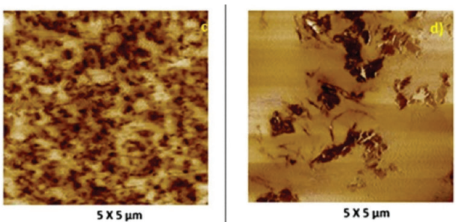


Grease	Lithium (Li/SS)	Lithium Complex
Shape	Twisted entangled fibres	Fibres
Average length (L)	≈ 2± 0.40 µm	≈ 0.4± 0.15 µm
Average diameter (D)	≈ 0.1 ± 0.02 µm	≈ 0.1± 0.02 µm
Average Volume (V)	≈ 0.0157 μm^3	≈ 0.003 μm^3



Grease	Calcium sulfonate complex (CaS/M)	Polyurea
Shape	Spherical	Platelets
Average Length (L)	-	≈ 0.65 ± 0.15 µm
Average Diameter, width (D,W)	≈0.26 ± 0.05 µm	≈0.5 ± 0.1 µm
Average Volume (V)	≈ 0.009 μm^3	≈ 0.016 µm3* *Assuming height = 0.05 µm.

Figure 4: *AFM study of EHL contact on entrapped thickeners.*

Recognising the extensive thickener interactions is the key in the design of the patent pending powder making process.

In the case of PUGT in the fine powder form, its morphology resembles that of flour (see Figure 5 for an analogue of the powder: flour). In many ways the grease conversion process is similar to the making of dough from the flour and is ideally carried out in a two-stage process (Scheme 1). In stage one the PUGT powder is mixed well under agitation with the base oil under conditions and proper dosages enough to provide the maximum thickening efficiency. The thickening is such that milling is recommended to smooth out the lumps and bumps and that gives noodle-like hardened grease in grades 4-6, which we called "noodle" or masterbatch (PUGM).

The choice of the base oil or other components (like the baking soda or yeast) dictates the extent of the maximum thickening efficiency (Table 3) and hence the grease yield of the subsequent oil back to the desired grease grades.

The thickener dosage is typically ranged from 15% to 30%. Higher thickener dosage reduces the process time but would make the agitation difficult. Milling is always required in the making of PUG via the in-situ method. In the PUGT process milling is also important for both stages.

Figure 5: *Flour ready for the dough making.*

Scheme 1: *Two-stage conversion from PUGT to PUG: 1) Gelling, and 2) Oil back*

Base Oil Type	% PUT	# of Milling	Yield to #2 Grade Grease
AB	20%	2 X	8%
AN	20%	2 X	6%
ADPO	20%	2 X	9%
SHC*	20%	2X	6%
PAG	20%	2 X	8%
Ester	20%	2 X	15%
Naphthenic Oil	20%	2 X	10%
Paraffinic oil	20%	4 X	12%

*SHC: Synthetic hydrocarbon oils

Table 3: *Base oil effects on PUGT grease conversion.*

Within the proper dosage range the choice of base oil is essential to give higher thickening efficiencies and thus higher yield. For instance, at 20% PUGT dosage (see Table 3), AN and AB fluids and PAG give excellent thickening effect with good milling characteristics (usually 2 x milling is enough). Insufficient process conditions and improper PUGT dosage in the first stage would require many times more milling and/or lead to low grease yield. The alternative 1-stage conversion is not recommended due to extended process time and lower grease yield.

Table 4 compares the structural (mechanical) and high temperature stability of the commercial PUG made via the in-situ method with the PUG made via the two-stage method via PUGT. PUG made via the two-stage method (PUG-1) clearly outperforms one of the commercial greases (PUG-A) and is on par with the other two commercial candidates (PUG-B and C). The ease in the use of PUGT allows PUG to be easily made in the lab, pilot plant, and well as any commercial plant.

Grease ID	Process	Penetration	# Change 50K Strokes	D1831 (160C/12h)
PUG-1	PUGT 2-Stage	253	8	11
PUG-A	In-Situ	276	23	28
PUG-B	In-Situ	269	6	10
PUG-C	In-Situ	258	23	140

Table 4: *Mechanical/HT stability comparison of PUG via PUGT powder or via in-situ method.*

When compared to OBCSG grease, via rheological testing under thermal stress (a temperature sweep from 25 to 150 C, Figure 6), OBCSG grease shows substantial softening (G', the storage modulus, dropped nearly 70%) for OBCSG Grease whereas polyurea Grease PUG-1 had a minimum reduction in G', a clear sign of far superior temperature stability.

Grease	Stress Sweep	25° C	150° C	Difference
OBCSG	G' (pa)	29,140	9,278	(19,862)
	G'/G"	687	71	(616)
PUG-1	G' (pa)	6,509	6,116	(393)
	G'/G"	596	238	(359)

Figure 6: *Rheological grease data under thermal stress.*

	Polyurea Grease made with PUGT	Lithium Grease Made with LCSA
Dropping Point	>300C	>260C
Mechanical stability	Excellent	Good
Noise	Low	High
ASTM D2596	Load Wear Index Performance	
Solid S/P Additive	3%	3%
DMTD Additive	3%	3%
Mo DTC Additive	1%	1%
LNS Load	126 Kgf	126 Kgf
Weld Load	>800 kgf	>800 kgf
LW Index	147 Kgf	145 Kgf

Table 5: *Boosted Load Carrying Performance.*

Performance additives such as extreme pressure, anti-wear, friction modifier, and rust preventive can be added in the second step during the PUGT conversion. In Table 5, via the addition of commonly used EP additives, polyurea grease made with PUGT easily matches up and exceeds lithium complex grease made with preform thickener.

Work is in progress within Novitas to develop alternative PUGT options in addition to PUGT powder to further simplify and streamline the conversion process. For instance, the noodle formed after the first step would be difficult to go beyond more than 30% PUGT content with the typical batch processing equipment. It is now easily manageable via continuous mixer such as Twin-Screw Extruder that produces the PUGM masterbatch in noodle or extrudate forms.

Summary

Recent and continued surges on Lithium pricing and the escalation on the needs of electric vehicles in the foreseeable future have prompted many in the grease industry to look for the alternatives to Lithium base grease. Polyurea grease is one of the best options but is difficult to explore for grease manufacturers that are not equipped to handle toxic TDI and MDI and hazardous amines. This paper offers a quantum leap approach in the manufacturing of polyurea grease whereby pre-formed polyurea grease thickener can be easily converted to polyurea grease.

Acknowledgements

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Reference

[1] June 7, 2017: https://www.iea.org/newsroom/news/2017/june/electric-vehicles-have-another-record-year-reaching-2-million-cars-in-2016.html

[2] Tribology Letters, February 2016, 61:18: Effect of thickener particle geometry and concentration on the grease EHL film thickness at medium speeds, F. Cyriac and et al.