



Innoleo **PGM**

AN MDI-BASED PREFORMED POLYUREA GREASE THICKENER

Innovation and sustainability are key values at Innoleo that drive the strategic direction of the company's development programs. The research team at Innoleo spends most of their time at the interface of these domains, looking for creative ways to solve the world's sustainability challenges.

Innoleo PGM is a preformed polyurea grease thickener in powder form used to prepare different grades of lubricating greases for wide range of applications. There are many advantages of using Innoleo PGM which will be discussed within this white paper. In this white paper, enjoy learning the benefits of using the Innoleo PGM (preformed polyurea thickener), how to use Innoleo PGM, and find success with the solutions we have provided.

Lubricating Grease and Grease Thickeners

Lubricating grease is a tribological material formulated as a uniform dispersion of colloidal thickening agents within a lubricating base oil. These thickening agents, commonly metallic soaps (e.g., lithium, calcium, aluminium) or non-soap thickeners (e.g., polyurea, clay, silica) function to gel the base oil and impart shear stress resistance. This unique characteristic allows grease to adhere to surfaces and provide lubrication under dynamic loading conditions where a typical fluid oil would readily migrate or drain and not provide the proper protection.

Polyurea grease thickeners offer a significant advancement over traditional metallic soap thickeners employed in grease formulations. As depicted in Figure 1, these polyurea thickeners are the product of an addition polymerization reaction between diisocyanates and diamines. Polyurea based greases are heavily used in industrial rolling-element bearing, automotive constant velocity (CV) joints, and sealed for life applications.

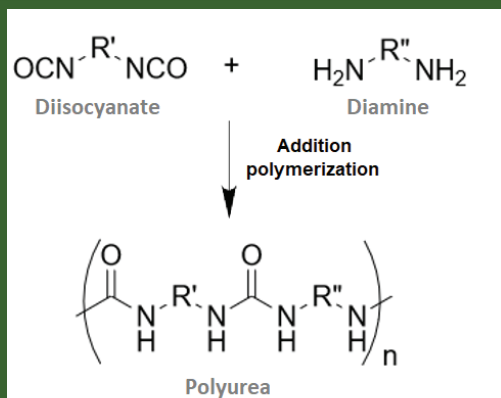


FIGURE 1: SYNTHETIC PATHWAY TO PREPARE LINEAR POLYUREAS.

Characteristics and Benefits of Polyurea Grease Thickener

The reaction to prepare polyurea grease thickeners yields linear, high-molecular weight organic polymers that possess the remarkable ability to self-assemble into a three-dimensional, fibrous network at the microscopic level. This intricate network structure is accomplished primarily by hydrogen bonding forces (Figure 2), and this serves to encapsulate and immobilize the lubricating base oil within the grease matrix and release the oil for lubrication when exposed to stress. It can be clearly visualized in Figure 3 that the hydrogen bonding network with metallic soaps is not as extensive as polyurea.

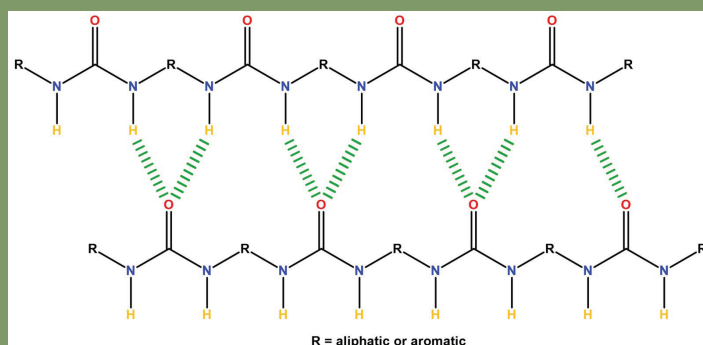


FIGURE 2: GRAPHICAL REPRESENTATION OF A POLYUREA GREASE THICKENER EXEMPLIFYING THE HIGH DEGREE OF HYDROGEN BONDING.

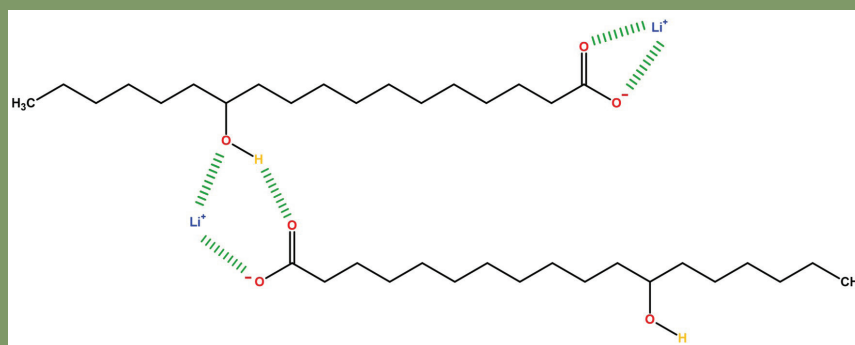


FIGURE 3: VISUAL ILLUSTRATION OF THE HYDROGEN BONDING NETWORK WITH A METALLIC SOAP, LITHIUM 12-HYDROXYSTEARATE.

Advantages of Using Preformed Polyurea Grease Thickener

On average, polyurea greases can have a three to five times better life expectancy than lithium-based greases. Within the realm of polyurea technology itself, there are two main approaches to incorporating the thickener when making a grease:

- 1) *In Situ* method: this method involves the direct reaction of diisocyanates and diamines within the grease formulation itself, typically in a heated kettle. The reaction generates the polyurea thickener network that entraps the base oil.
- 2) Preformed Polyurea Thickener: this procedure involves the addition of pre-synthesized polyurea thickener powder to the base oil and other additives to produce a grease with desired specifications.

Table 1 depicts the advantages of preformed polyurea grease thickener powder over *in situ* generated polyurea. Using preformed polyurea grease thickener allows end-users to develop grease products safely and with consistent quality. Furthermore, the preformed polyurea grease thickener is a significant environmentally friendly solution for grease formulators due to that the polyurea grease thickener:

- is a 100% solid material and does not contain solvents or toxic substances that may harm the ozone layer or contribute to global warming.
- contains no heavy metals or chlorinated compounds.
- does not contain residual diisocyanate substances whereas *in situ* generated PGM greases have the risk of containing these diisocyanates and other byproducts.
- allows customers to be worry-free about tasks of transporting, storing, and disposing of toxic chemicals, solvents, and waste streams.

Features	<i>In Situ</i> Polyurea Grease Thickener	Preformed Polyurea Grease Powder
Safety	Presence of unreacted diisocyanates in fully formulated greases	Eliminates handling of diisocyanates
Consistency	Potentially variable across batches	Consistent performance due to predefined thickener specifications
Environmental Impact	May generate byproducts, involves handling and disposing of toxic waste streams	Cleaner and safer product to use that eliminates byproduct formations, and positively impacts the environment with no waste generation
Storage	Airtight containers with cool and dry atmosphere	Standard containers with moderately cool and dry atmosphere
Shelf Life	Shorter	Longer
PPE Requirements	Gloves, respirators, eye protection	Dust control and PPE recommended

FIGURE 1: ADVANTAGES OF USING PREFORMED POLYUREA THICKENER VS. *IN SITU* GENERATED POLYUREA THICKENER

The impetus for the development of preformed polyurea grease thickener powders is due to the global demand for enhanced lubricant performance by offering a safer and more efficient alternative to *in situ* methods to manufacture Polyurea-based greases. It eliminates the need for hazardous raw materials and complex equipment, thus simplifying polyurea grease production and delivering a finished grease with superior performance, exceptional thermal stability for high-temperature applications, outstanding water resistance for wet environments, extended service life, and reducing maintenance and downtime.

The structural characteristics of polyurea thickeners provide them with several key advantages over metallic soap thickeners as described below and illustrated in Figures 2 and 3:

- **Enhanced Shear Stability:** The robust, fibrous network formed by the polyurea molecules exhibits exceptional resistance to shear forces. This translates to superior shear stability, allowing the grease to maintain its consistency and lubricating properties even under extreme pressure and high operating shear rates.
- **Exceptional Thermal Stability:** The covalent bonds of the polyurea structure demonstrate remarkable resistance to thermal degradation. These are often the preferred choice for sealed-for-life applications as they tend to have high operating temperatures, inherent antioxidative properties, high thermal stability, and low bleed characteristics enabling polyurea greases to function effectively at elevated temperatures where conventional soap-based greases may experience thermal breakdown and subsequent loss of lubricating performance.
- **Absence of Pro-Oxidative Metal Ions:** Metal soap thickeners inherently contain metal cations (e.g., lithium, calcium) as part of their molecular structure that possess the unfortunate ability to act as catalysts, accelerating the oxidation of the lubricating base oil within the grease matrix which leads to a degradation of the base oil's lubricating properties, manifested as thickening, increased friction, and potential wear on lubricated surfaces. Polyurea greases, being entirely synthetic polymers, are devoid of metal ions. This absence eliminates the catalytic effect, thereby significantly enhancing the overall oxidative stability of the grease formulation.
- **Hydrogen Bonding:** The hydrogen bonds between the urea groups ($\text{RNH}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{NHR}$) and carbonyl oxygen (C=O) within urea moiety of adjacent chains can create a secondary physical network. This network, although weaker than the covalent network, does offer two benefits:
 - 1) provides additional structural stability by supplementing the strength and rigidity provided by the covalent bond.
 - 2) improved thickening effect that is generated by the extensive hydrogen bonding that occurs between each polyurea molecule and ultimately contributes to how polyurea molecules can function as encapsulation agents of lubricating base oils.
- **Wet Environments:** Due to their superior water washout resistance, polyurea greases are particularly valuable in applications exposed to water, such as marine equipment and construction machinery operating in wet or humid conditions where a longer grease life is expected. Extreme-pressure (EP) and antioxidant additives may be blended in to help achieve longer life and equipment reliability.
- **Enhanced Dropping Points:** Polyurea greases boast a dropping point around 270°C (518°F) or higher, which is significantly higher compared to many other thickener types. This superior thermal stability allows polyurea greases to maintain their consistency and lubricating properties even in demanding high-temperature and pressure applications. This translates to reliable lubrication performance and extended service life in harsh environments.

General Lab Procedure

To Prepare a Grease Using

Innoleo PGM

- Step 1** Throughout the procedure, a slow steady stream of nitrogen gas is used to provide an inert atmosphere during grease preparation.
- Add the base oil to the grease vessel and agitate at 250 rpm using an overhead mechanical stirrer equipped with a shaft and agitator stir blade. Slowly add Innoleo PGM in portions to the base oil. Once Innoleo PGM has been added, stir the mixture for at least 60 minutes at ambient temperature.
- Step 2** After achieving homogenous dispersion of Innoleo PGM, begin heating the mixture to 140°C at a controlled heating rate of 10°C per 10 minutes.
- Upon reaching the target temperature of 140°C, the grease mixture is continuously stirred and maintained at 140°C for 4 hours.
- Step 3** Heating should now be ceased and continuous stirring should be maintained until the grease gradually cools to ambient temperature over a period of at least 1 hour.
- Step 4** Subsequently, the grease should be subjected to high shear homogenization to ensure optimal dispersion. Typically, the PGM-based greases are processed three times at 600 bar (8700 PSI) using a SRH60-70 homogenizer to achieve a PGM-based grease with an NLGI 2-3 consistency. If your lab has access to a colloidal mill, this is an alternative method to reduce particle size and evenly disperse the grease.

PLEASE NOTE:

The homogenization step serves a critical function in ensuring optimal dispersion of the thickener throughout the base oil, ultimately achieving the desired grease consistency. This consistency can be conveniently evaluated using the P0/P60 penetration ratio.

Following a 24-hour maturation period, the grease is ready for comprehensive performance testing and subsequent application.

Lubricating Grease and Grease Thickeners

During formulation of a polyurea based grease, the amount of Innoleo PGM powder used will dictate which NLGI grade will be generated. As shown below in Table 2, by varying the amount of Innoleo PGM and SN500 used in the grease formulation, a series of NLGI greases were prepared. This clearly shows the versatility of Innoleo PGM and how easy it is to target the performance requirements of various grease applications. Users of Innoleo PGM commonly target NLGI 2-4 depending on the application.

NLGI	0	1	2	3	4
Worked penetration (60 strokes at 25°C)	355-385	310-340	265-295	220-250	175-208
Typical applications	Gear transmissions Bearings Centralized systems Low temperature	Bearings Automotive General machinery Continuous casting Aviation	Bearings Automotive General machinery Continuous casting Aviation Railroad	High-speed bearings Electric motors Heavy industrial	High-speed bearings Electric motors Heavy industrial
Innoleo PGM concentration, %wt	< 7%	7-8%	8-9%	10-12%	13-14%
Base Oil (SN 500), %wt	< 93%	92-93%	91-92%	88-90%	86-87%

TABLE 2: RECOMMENDED DOSES OF INNOLEO PGM FOR THE REQUIRED NLGI GRADES OF PGM-BASED GREASES

Performance Testing of Innoleo PGM in Different Viscosity Base Oils

We evaluated the use of Innoleo PGM in different base oil types and viscosities as the base oil is a very important variable when preparing any grease with a targeted NLGI, overall consistency, and grease stability over time. The grease formulations below in Table 3 shows that the choice of base oil can impact the overall consistency and worked penetration of the grease.

Performance was evaluated using the cone penetration test (ASTM D217), which assesses the consistency of unworked and worked penetration. The unworked penetration provides a baseline consistency after grease preparation and informs the impact of storage conditions on grease consistency. Worked penetration results are necessary to determine the NLGI consistency grade of a grease.

The study's conclusive remarks are as follows:

- Greases 2 and 3, formulated with SN500 base oil (Group 1) and 10-12% Innoleo PGM, exhibited stable and consistent greases (NLGI 2-3 after 60 and 100K strokes). In contrast, Grease 1, containing 8% Innoleo PGM in a Group 1 base oil (SN500), resulted in a lower NLGI grease with poor consistency after 10K and 100K strokes.
- Greases 4 and 5, using a higher viscosity grade Group 1 base oil, produced NLGI 2 (8% Innoleo PGM) and NLGI 3 (10% Innoleo PGM) greases, respectively. These results confirm that viscosity grade affects the NLGI grade of a grease, as observed when comparing Greases 1 and 4. Furthermore, Greases 4 and 5 demonstrated improved consistency after prolonged working compared to Grease 1 when using a higher viscosity Group 1 base oil. Ongoing research aims to increase the amount of Innoleo PGM in higher viscosity paraffinic base oils to evaluate the maintenance of overall consistency after 10-100K strokes.

- The use of naphthenic base oils with Innoleo PGM (8-10%) in Greases 6-10 resulted in finished greases with NLGI grades ranging from 2.5 to 3.5. Grease 6 exhibited stable consistency (NLGI 2) after working (10-100 K strokes). When comparing Grease 7 and 8, using 10% of Innoleo PGM produced an exceptional NLGI 3 grease with high degree of consistency and maintained an NLGI 3 after prolonged work (100K strokes).
- Grease 7, with 8% Innoleo PGM, demonstrated excellent stability (despite reducing to NLGI 2) and consistency, evident in its maintained stability at NLGI 2 after prolonged working. Grease 10 revealed that increasing the viscosity of the naphthenic base oil allows for reduced Innoleo PGM content (8% compared to Grease 7) while producing a finished grease with significant durability and consistency. Grease 9 showed that using 6% Innoleo PGM initially produced an NLGI 2.5 grease, which diminished in quality after working.
- Overall, the testing indicates that:
 - Selecting a Group 1 base oil with a viscosity range of ISO VG 100-480 can produce high-quality greases, requiring 8-12% Innoleo PGM to achieve NLGI 2-3.
 - Durable greases with NLGI 2.5-3.5 and improved consistency necessitate 8-10% Innoleo PGM when using Group 2 naphthenic base oils with various viscosity grades (ISO VG 100-440).
 - All grease formulations exhibited dropping points of 300-310°C.

Grease	Innoleo PGM (wt%)	Base Oil Category	Base Oil ISO VG	Unworked & Worked Penetration (ASTM D217)				NLGI Consistency		
				0 Strokes	60 Strokes	10 K Strokes	100 K Strokes	60 Strokes	10 K Strokes	100 K Strokes
1	8%	SN500 Group 1 - Paraffinic	100	390	307	365	365	1	0	0
2	10%	SN500 Group 1 - Paraffinic	100	236	237	280	286	3	2	2
3	12%	SN500 Group 1 - Paraffinic	100	278	254	266	218	3	2	3
4	8%	Calpar 600 Group 1 - Paraffinic	120	232	234	304	317	2	1.5	1
5	10%	Calpar 2500 Group 1 - Paraffinic	480	266	264.5	307	310	3	1.5	1
6	10%	Hydrocal 500 Group 2 - Naphthenic	100	203	208	280	288	3.5	2	2
7	8%	Hydrocal 1200 Group 2 - Naphthenic	220	242	240	293	302	3	2	2
8	10%	Hydrocal 1200 Group 2 - Naphthenic	220	220	221	253	245	3	3	3
9	6%	Hydrocal 2400 Group 2 - Naphthenic	440	277	252	305	361	2.5	1.5	0
10	8%	Hydrocal 2400 Group 2 - Naphthenic	440	222	215	230	230	2.5	3	3

TABLE 3: EVALUATION OF THE WORKED PENETRATION OF INNOLEO PGM IN VARIOUS BASE OILS

Performance Testing of Innoleo PGM versus a Commercial Polyurea Thickener Source

As depicted in Table 4, the Innoleo PGM was comparatively evaluated against a commercial source of polyurea grease thickener. The comparison revealed that Innoleo PGM produced a finished grease with improved worked penetration and overall consistency compared to the other commercial polyurea grease thickener that resulted in a lower NLGI 1 after 100K strokes. This data clearly demonstrates that Innoleo PGM provides a high-performance grease for long term and consistent use.

PGM Source (PGM Amount)	Base Oil Category	Base Oil ISO VG	Unworked & Worked Penetration (ASTM D217)				NLGI Consistency		
			0 Strokes	60 Strokes	10 K Strokes	100 K Strokes	60 Strokes	10 K Strokes	100 K Strokes
Innoleo PGM (10 wt%)	SN500 Group 1	100	236	237	280	286	3	2	2
Commercial Source Polyurea Grease Thickener (10 wt%)	SN500 Group 1	100	229	234	284	325	3	2	1

TABLE 4: COMPARATIVE ASSESSMENT OF INNOLEO PGM VS. COMMERCIAL GRADE POLYUREA GREASE THICKENER

Discussion of Results

The performance of Innoleo PGM was assessed in various base oils to understand how the quality and consistency of the prepared greases change over time when worked according to ASTM D217. Additionally, the dropping points were evaluated to track the attributable performance of each of the prepared greases.

The penetration values are measured following ASTM D217. This method determines the hardness and consistency of a grease and how a grease will react over time while in service and prolong wear. The higher the penetration value, the softer the grease, and vice versa. To better understand unworked penetration and various levels of worked penetration, here is a clear explanation shown in Table 5.

Penetration Type (ASTM D217)	Description
Unworked (0 strokes)	Generally used for storage stability studies.
Worked penetration (60 strokes)	Typical method to compare various greases and assign NLGI grades to greases.
Worked penetration (10K strokes)	Used to predict the stability of the grease during use.
Prolonged worked penetration (100K strokes)	Used to assess the stability of the grease during extended use.

TABLE 5: DESCRIPTION OF PENETRATION TESTING VIA ASTM D217

The data generated for Greases 2 and 3 using SN500 exhibited marginally better performance compared to Grease 4 and 5, likely due to differences in sulfur content between the two paraffinic base oils. Typically, SN500 base oils contain 0.03% sulfur, whereas other refined paraffinic base oils contain 0.002-0.01% sulfur. The presence of sulfur additives in polyurea greases can impact grease structure, leading to hardening, softening, or oil bleed, and sometimes can improve the grease's overall performance and durability as a perceived improvement with consistency. Despite relatively low sulfur levels, this difference can affect grease structure, consistency, and durability due to sulfur's affinity for metal surfaces and anti-wear and EP properties. The use of paraffinic oils produced suitable NLGI 2-3 greases with Innoleo PGM, suggesting an optimal Innoleo PGM concentration of 10-12%. Further evaluation of higher Innoleo PGM loadings with Calpar 600 and Calpar 2500 base oils is underway to determine long-term stability and consistency. Generally, greases with higher thickener content exhibit harder consistency, improved stability against water-wash-out and high temperatures, and better oil retention, potentially extending grease lifespan.

The grease formulations (Greases 6-8 and 10, refer to Table 2) incorporating 8-12% of Innoleo PGM in various naphthenic base oils with different viscosities yielded excellent penetration results, meeting NLGI 2-3 grade requirements and demonstrating a high degree of consistency. This consistency was maintained through prolonged usage, as evident from both the 10,000 stroke and 100,000 stroke penetration data.

A comparison of the performance results using Innoleo PGM in paraffinic versus naphthenic base oils revealed that high-performing greases can be produced depending on the amount of Innoleo PGM utilized and the viscosity of the base oil. It was observed that the higher viscosity naphthenic base oils (Greases 7 and 10) required less Innoleo PGM to achieve the same performance as Greases 2 and 3 that used SN500 at 10-12% Innoleo PGM. Furthermore, Greases, 2, 6, and 7 provided nearly identical consistency results with Greases 2 and 6 using ISO VG 100 base oil and 10% Innoleo PGM, whereas Grease 7 used an ISO VG 220 base oil with reduced loading of Innoleo PGM (8%). This clearly shows the Innoleo PGM can be used with different base oil types of varying viscosity and achieve either the same performance or improved performance based on how much Innoleo PGM is used or if a heavier viscosity base oil is employed in the formulation. Naphthenic base oils are emerging as a preferred option for polyurea greases, offering enhanced solvency that promotes a stronger, more efficient bond with the thickener, resulting in a more stable and reliable grease with reduced oil bleed and lower thickener requirements, presenting a promising alternative to paraffinic oils.

The quality of a grease can be differentiated by its change in worked penetration after exposure to prolonged shear conditions. As shown in Table 3, the commercial grade PGM exhibited a lower consistency (at 100,000 strokes), indicating poor grease quality and longevity, whereas Innoleo PGM resulted in a higher quality grease with higher consistency (NLGI 2) and endurance. This finding demonstrates that Innoleo PGM will provide a high-quality grease that performs with stamina and stability.

The dropping point, a measure of a grease's heat resistance, represents the temperature at which the grease transforms from a semi-solid to a liquid state under specific test conditions (ASTM D2265). In essence, the dropping point of a lubricating grease serves to provide additional information regarding the quality of the prepared grease. A higher dropping point indicates an improved ability to maintain structure at higher temperatures. Conventionally, a dropping point above 220°C is deemed satisfactory, as metallic soaps typically have dropping points ranging from 175-205°C. The NLGI 2 and NLGI 3 greases prepared using Innoleo's PGM exhibited exceptionally high dropping point values of 300-310°C, further supporting the stability of the polyurea grease in high-temperature applications.

Conclusion

Innoleo has successfully demonstrated the use of our Innoleo PGM and that the performance properties of the prototype greases are particularly suitable for a wide array of greases applications (automotive, agricultural, marine, military, construction, off-highway, mining, textiles). Based on Innoleo PGM's molecular structure, it has proven that it creates a strong matrix network that provides superior structural stability and improves the thickening effect that is generated by the extensive hydrogen bonding that occurs between each polyurea molecule and ultimately contributes to how polyurea molecules can function as encapsulation agents of lubricating base oils. The added benefit of using Innoleo PGM provides formulators the ability to easily and consistently manufacture high quality polyurea greases that function with superior performance.

If you are interested in commercial opportunities related to acquiring Innoleo PGM, or any other projects, feel free to contact us at ccrawford@biosynthetic.com.