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Grease Polymers and Their Benefits to Grease

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Abstract

Polymers have long been used to modify the performance of greases and lubricants. “Grease polymers” are a special class of polymer additives that form an interpenetrating network (“IPN”) between the polymer and the grease thickener. A strong polymer-grease network provides several benefits to grease: 1) greater adhesion, 2) reduced oil bleed, 3) elevated tackiness, 4) added yield, 5) superior shear resistance, and 6) enhanced water resistance.

This study details how and why grease polymers provide the six benefits to grease based on findings from the last decade of grease polymer R&D and recent work.

1. Introduction - What are grease polymers?

”Grease polymers” is a term of art for polymers which provide notably high improvement in one or more areas of grease performance. In comparison, highly soluble and amorphous lubricating oil polymers (viscosity modifiers, thickeners, VI improvers) appear to provide lesser effects comparable to increasing the base oil viscosity.

Grease polymers modify a grease’s structure. Normally, grease is held together by several types of short range interactions as shown in **Figure 1** for lithium 12-HSA. These non-covalent bonds have varying strength and effects on grease stability: consider the melting points of stearyl alcohol (60°C) vs. C18 alkane (30°C) vs. lithium stearate (220°C).

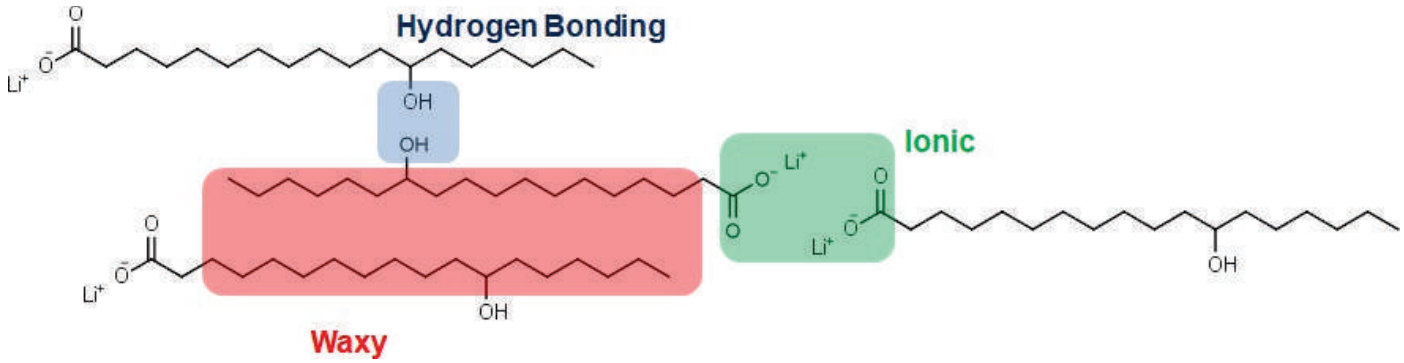


Figure 1: Three short range interactions of various strength hold a thickener network together in grease

Grease polymers are chosen based on their ability to form a second network of polymer which is complementary to the grease thickener network. A good metaphor is rebar and concrete – grease polymers form flexible networks over long ranges (many carbon-carbon bonds in the polymers) inside of a tough but brittle inorganic structure (short range, non- covalent bonds). An effective grease polymer will most often be a very poor viscosity modifier for lubricating oils due to the formation of haze, precipitation, or gel. These results are considered defects in fluids but critical for greasemaking.

Figure 2 demonstrates the merging of the polymer network into the grease network: an “interpenetrating network” or “IPN”. Applied heat overcomes the weaker attractions (waxy and hydrogen bonding types in **Figure 1**) to allow the grease thickener network to become more open, thin the base oil, and allow the polymer to diffuse efficiently through the grease. Temperatures of 80-140°C, far below dropping point, are typically used in this stage. The polymer is then added in liquid or solid form and then mixed for a period of time until homogeneous. The thickener and polymer networks reform as the grease cools and rests.

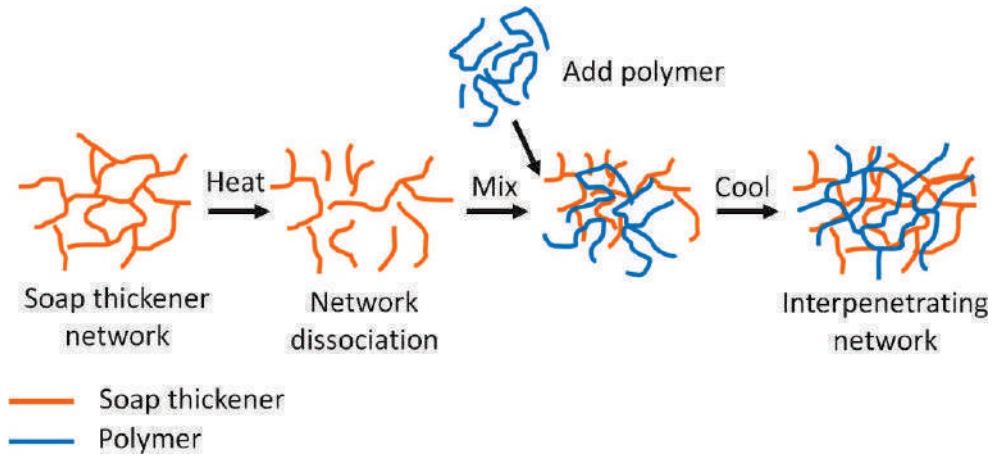


Figure 2: Interpenetrating network formation between grease and grease polymer. Oil fills the surrounding voids.

Three main mechanisms are used to ensure that polymer network forms and remains locked around the grease network. These mechanisms are related to the three short range interactions that hold grease together in **Figure 1**. **Figure 3** depicts the three mechanisms with a chemical structure and metaphor to remember the explanation.

- **Temperature Sensitive** – Long uninterrupted runs of one monomer (ethylene, styrene, etc.) along the backbone of the polymer form waxy crystallites between chains. May be called semi-crystalline.
- **Hydrogen Bonding** – Polar nitrogen and oxygen sites on the polymer separate from the non-polar oil and associate together in an acid-base attraction
- **Reactive** – Acid anhydride sites on the polymer react with metal ions to form insoluble coordination complexes (like diacids) or react with –OH sites to form covalent bonds in the thickener (like boron esters)

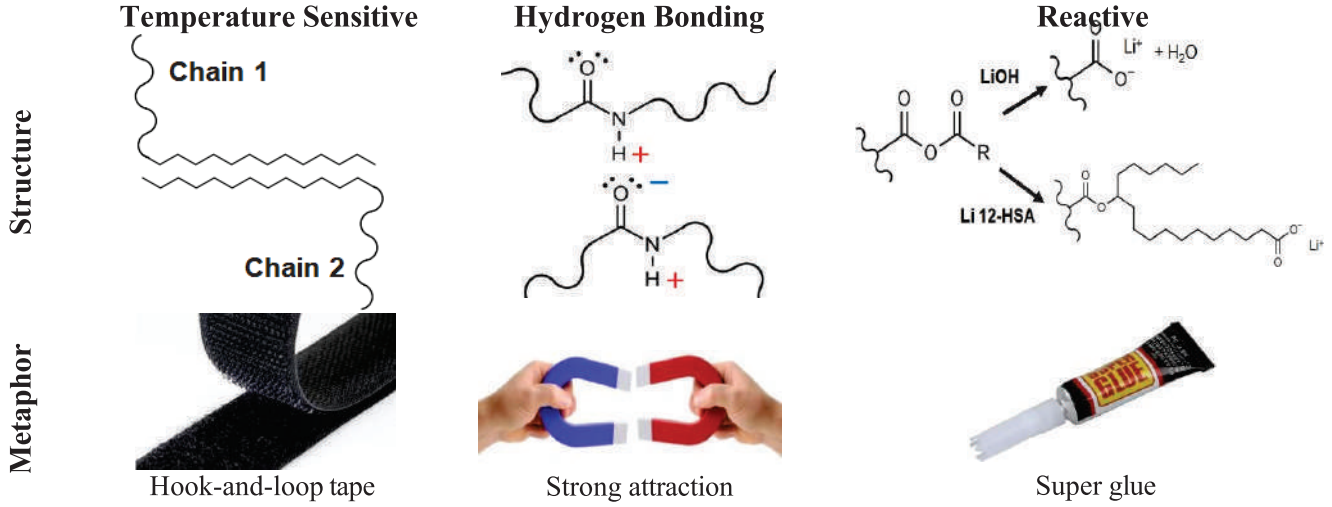
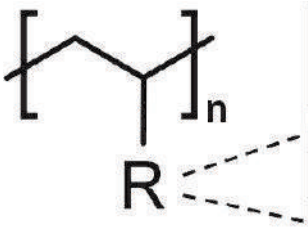


Figure 3: Comparison of the three main mechanisms for IPN formation by grease polymers and a metaphor to help remember how each one works.

2. Materials – Grease polymer options

Figure 4 shows the common structures found in each of the three grease polymer types.[1] The monomer ratio, polarity, crystallinity, and MW are key parameters that will determine the polymer's effectiveness. Many are based on an olefin copolymer (OCP) structure as shown on left in **Figure 4**.



R =	Hydrogen H	Alkyl C_xH_y	Styrene	None *C=C in backbone*	Amide HN O	Alcohol OH	Ester	Anhydride
Temp. Sens.	X	X	X					
H-Bonding	X			X	X	X	X	
Reactive	X	X	X				X	X

Figure 4: Typical functionality of the three grease polymer mechanisms

In addition to the three mechanism, or types, of grease polymers these products can be prepared in many forms. The preferred option for a given formulator will depend on their people, equipment, and scheduling.
Consider the case of two formulators:

Formulator A may find that a grease polymer in solid flake form is easy to rapidly add to the kettle and offers the best treat rate. Formulator A will need to handle more pieces of packaging but will not need to heat drums or wait for viscous liquids to pour. Extra care must be taken to ensure the polymer is dissolved completely.

Formulator B may instead prefer to use the polymer diluted in oil so it may be easily pumped and will blend faster. The treat rate for Formulator B is higher due to the diluent oil but production does not need to spend time dissolving polymer, is able to use higher viscosity or low solvency base oils, and is no longer concerned about undissolved polymer in filters.

Formulators A and B may find solid or liquid grease polymers to be better to use for opposite reasons. Formulator A may be a smaller company with "more time than money" and equipment while Formulator B may be a major blender who needs the fastest cycle time possible and can invest in more equipment to meet demand. **Figure 5** compares this solid vs. liquid trade-off.

Form	Options	Advantages	Disadvantages
Solid	Flake Pellet Bale Powder	• Lowest treat rate (0.25 to 1.0wt%) • Most efficient shipping • Bags can be sized for batch size • No diluent oil added to grease	• Longer blend times • Possibility of undissolved polymer • More packaging to handle • Pellet/flake can cold flow during storage • Flake can agglomerate in kettle if added too fast
Liquid	Dilute Concentrated Emulsion	• Shorter blend times vs. solid • No undissolved polymer to filter • Able to pump to kettle or store in tanks • Easy to adjust wt% during production	• High treat rate (1.5 to 6.0wt%) • Need to account for addition of diluent oil • Requires high viscosity pumps and hoses • Drums may require heating • Cleaning high viscosity polymer out of hoses

Figure 5: Advantages and disadvantages to using different forms of grease polymer products

3. Methods – How to blend grease polymers into grease

Figure 6 provides a guideline for new formulators based on the mechanism the grease polymer uses to form the IPN and the form. A formulator should attempt these recommended times and temperatures in lab and pilot-scale tests first.
Ultimately the optimal parameters depend on the formulator, the formula, and the kettle.

Mechanism	Form	When/How
Temperature Sensitive	Solid, Liquid	Add at end, with cooling oil Mix 1 – 3 hours @ 80-100°C / 176-212°F
Reactive	Liquid	
Lube Oil Viscosity Modifiers	Solid, Liquid	
Hydrogen Bonding	Solid, Liquid	Add at end, with cooling oil Mix 1 – 3 hours @ 100-120°C / 212-248°F
Temperature Sensitive (Styrene or High Melt Point)	Solid	
Reactive	Solid	Add after soap reaction when heat of reaction peaks
Lube Oil Tackifiers	Liquid	Add after milling to prevent shearing

Figure 6: Best practices for when and how to add polymers to grease. Lube oil polymers may be used in conjunction with grease polymers in some greases.

If a solid grease polymer does not dissolve adequately according to **Figure 6** then it is recommended to increase the temperature in 5°C increments (up to +20°C over recommended temperature) and mix for another hour. Once the times and temperatures are confirmed in lab or pilot trials then the process is ready to scale.

Excessive heating and oxidation of the base oil and polymer can prevent the polymer from dissolving or cause agglomerates to form. 0.1wt% of antioxidant (e.g. butylated diphenylamine or high molecular weight phenolic AO) is recommended to be added before the polymer.

4. Results & Discussion – G.R.E.A.S.E.

To meet a customer's technical requirements, a formulator will likely start from either the most appropriate thickener closest to the job's needs or utilize their experience in adapting a versatile thickener to many applications. Each grease thickener alone will have a variety strengths and weaknesses across many performance categories. Some thickeners will exceed in more categories than other thickeners but typically at higher cost. Finally, additives are included to improve the initial properties of the grease to fit the specifications.

Grease polymers in particular offer six major benefits to grease:

1) Greater adhesion
2) Reduced oil bleed
3) Elevated tackiness
4) Added yield
5) Superior shear resistance
6) Enhanced water resistance

The key advantage to formulators is that they may use a more economical grease thickener yet achieve similar performance to more costly or difficult to use thickener systems. Grease polymers also improve a formulator's flexibility since the low treat (0.1-1.0wt% active) allows the additive to be included as an option to a favored formula.
The following sections will introduce the technical problems, the polymer-based benefits, key test methods, and data showing how polymer choice affects performance.

Greater Adhesion

Metal surfaces are coated in a polar oxide layer which is a poor substrate for hydrocarbon fluids. Unmodified grease can easily be wiped away or fail to transfer between parts in a gear train. Polymers act as both anchor and scaffold on which to secure a lubricant or grease to a metal surface. **Figure 7** shows the dispersion of polymers to the metal surface.

Polymers are also hydrocarbons like oil but due to its length a polymer can contact the surface at many points which must all be desorbed simultaneously to remove the polymer. Adsorption can also occur deep in the asperities of the surface to provide not only a chemical but physical attraction as well. The remainder of the polymer remains suspended throughout the bulk of the grease as loops and coils which couples the dissimilar grease and metal together.[2]

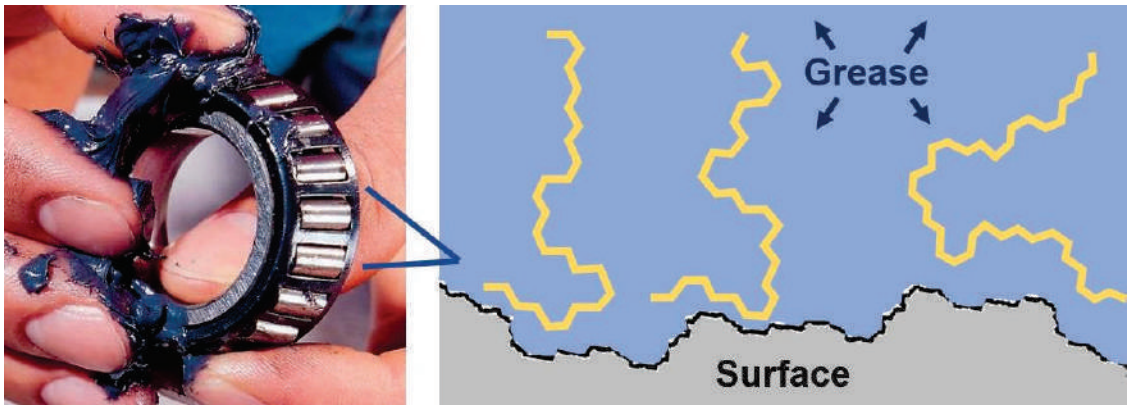


Figure 7: Schematic of polymers (yellow) adsorbed onto a surface (gray) within an applied grease (blue)

Grease polymers are ideal for adhesion in grease. Hydrogen bonding and reactive grease polymers are aided by strong polar attractions to the metal. Temperature sensitive polymers have low surface energy and wets into the crevices of the surface more easily.

Test methods for adhesion are varied and the grease industry lacks a standard method for directly assessing the adhesiveness of grease. Instead, adhesion is known to be a factor in various dynamic test methods that require grease to remain adhered on a moving surface or while impinged upon by water or a mechanical impact.

More direct methods for measuring the phenomenon of adhesion can be taken from the adhesives and coatingsindustries. Pull-off force with a simple spring force gauge and solid plate pushed into the grease is an easy test to implement.[3]

Reduced Oil Bleed

Oil bleed (shown in **Figure 8**) is a complex requirement. Oil must bleed from the grease system to lubricate but too much oil bleed causes changes in the grease consistency and can alarm customers when observed after long storage. Oil bleed occurs due to the mismatch in polarity between an ionic thickener and a non-polar base oil. Each component seeks to separate from the different component. Lower NLGI grade and synthetic greases are prone to oil bleed.

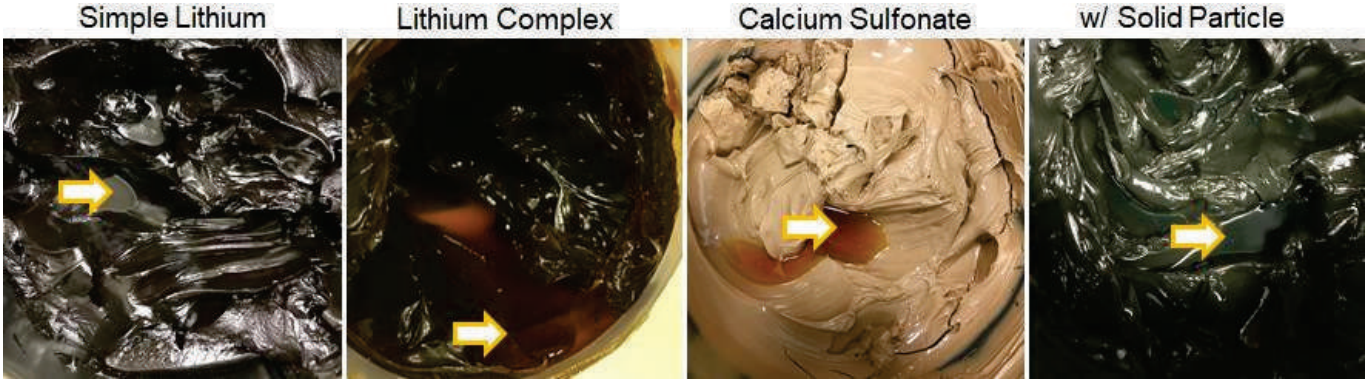


Figure 8: Observed oil bleed on the surface of various base greases

Polymers provide an inherent and unique benefit in the area of oil bleed adjustment. Polymer coils in grease absorb base oil and swell to an equilibrium size (**Figure 9**). If oil would be expelled from the grease over a period of time then the polymer coils will also lose oil and shrink. However, much like a spring the polymer seeks to maintain its equilibrium size

and will oppose the oil bleed by spontaneously absorbing oil back into the grease. The effect is called “osmotic pressure” and is similar in concept to seal swelling. Low temperature testing by Lincoln ventmeter has shown that while polymers help grease retain oil it does not impede the fluidity of the oil within the grease.[4]

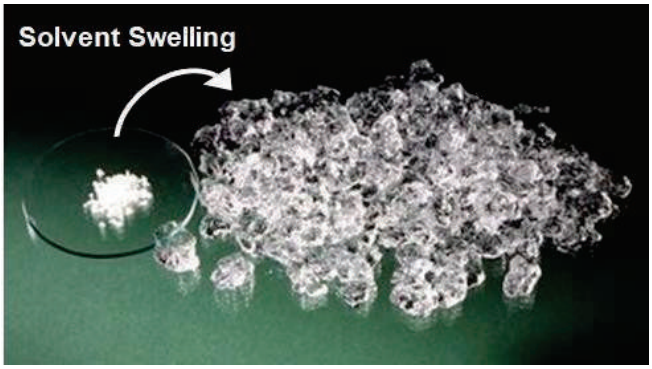


Figure 9: Polymers are thermodynamically driven to absorb solvents even with minimal heating or stirring

Oil bleed can be measured as a static (stationary) or dynamic (in motion) test under a variety of conditions. ASTM D6184, Oil Separation from Grease (Conical Method), is common and easy to implement.

Figure 10 shows compares the results of ATSM D6184 oil bleed for a series of polymers in a #2 calcium sulfonate grease. The base grease exhibits a 3.30% oil bleed over 30hrs at 100°C. The use of polymer reduces the 3.30% bleed by 24.6- 86.0% (meaning 2.49-0.46% total loss).

The trend in polymer selection versus performance favors higher molecular weight polymers. The solid polymers performed in order of molecular weight. This is rational since osmotic pressure, the force drawing the oil back into the grease, increases with molecular weight.

Sample	D6184 Oil Bleed
NLGI #2 Calcium Sulfonate base grease	**3.30**
1% liquid OCP tackifier	-24.6%
2% liquid OCP tackifier	-32.0%
1% solid styrene OCP	-35.3%
1% solid semi-crystalline OCP flake	-49.3%
3% liquid reactive polymer	-52.2%
1% solid 50 SSI OCP	-74.9%
1% solid crystalline OCP	-80.3%
1% liquid rubber emulsion	-86.0%

Figure 10: Percent change in ASTM D6184 oil bleed with added polymer (-100% = zero oil bleed)

Liquid products showed no clear trend but there is an explanation. The tackifiers performed marginally, likely due to their high dilution relative to solid polymer or highly concentrated emulsion. The liquid emulsion performed the best due to it having the highest molecular weight of the polymers and its very high concentration (~60% active). Surprisingly the liquid reactive polymer, which is roughly the same concentration as a tackifier but much lower MW, gave better than average performance. In this case, the oil-soluble reactive polymer becomes grafted to the insoluble thickener network which makes the thickener less dissimilar from the oil.

Elevated Tackiness

Tackiness, or stringiness, is one of the first qualities of a grease that an end user will experience. This tack is a sign of greater cohesion which is the resistance of the tackified product to breaking apart into multiple pieces. Centrifugal fling- off on high speed gears or loss of sealing performance in a grease is a sign of weak cohesion.

Enhanced Water Resistance

Water resistance is a challenge for grease due to the soap- or detergent-like nature of many grease thickeners.[10] **Figure 15** demonstrates three ways water can cause grease to fail to stay in place or protect a surface:

- **Cohesive Failure** – A fluid or moving element channels through the grease to expose the surface.
- **Adhesive Failure** – A stiff grease may have poor adhesion and become peeled away from the surface.
- **Permeation** – Water diffuses through the grease to the metal surface and causes corrosion

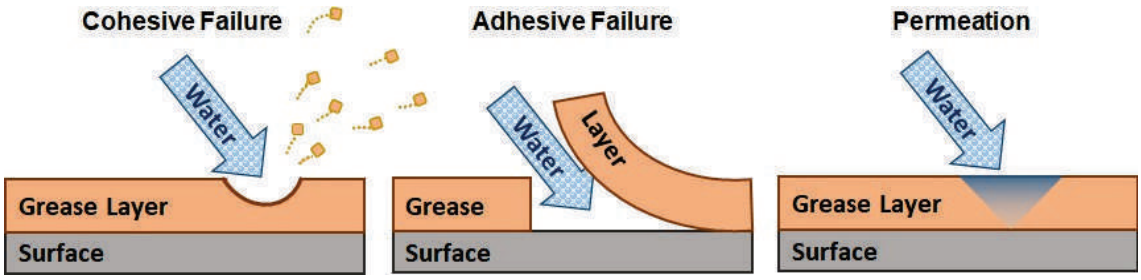


Figure 15: Three ways in which water can compromise a grease

Adhesive and cohesive effects of grease polymers have been previously described. Polymers can reduce the permeability of water since polymers seek out and diffuse to interfaces (air-grease, grease-metal) where the polymer acts as a barrier between the water and a hydrophilic thickener.

Water resistance is commonly measured by a combination of D4049 water spray-off (40 psi spray of water at 37.8°C for 5 min) and D1264 water washout (a bearing filled with grease is spun with circulating water at 600 rpm at 79°C for 60 min). Additionally, test methods for mechanical stability may be adapted to run with up to 10wt% water blended into the grease.

Figure 16 compares various polymers in three greases. Soap-based greases like lithium complex have a wide range of options for improving water resistance. Detergent or particulate greases like calcium sulfonate and silica tend to be more difficult to improve, and require higher treat of more specifically chosen grease polymers.[11]

	WSO (D4049)	WWO (D1264)
NLGI #2 Lithium Complex	**52%**	**26%**
+1% solid semi-crystalline OCP	24%	11%
+1% solid styrene OCP	9%	12%
+1% liquid reactive polymer	23%	14%
+0.25% solid reactive polymer	26%	25%
+4% blend of OCP and reactive	7%	2%
NLGI #2 Calcium Sulfonate	**72%**	**-**
+0.5% solid semi-crystalline OCP	16%	-
+1% solid semi-crystalline OCP	7%	-
+0.25% solid reactive polymer	47%	-
+0.5% solid reactive polymer	4%	-
NLGI #2 Clay Grease	**49%**	0.0%
+5% liquid OCP	48%	1.3%
+4% liquid reactive polymer	12%	-2.2%
+1% liquid rubber emulsion	10%	29%

Figure 16: Water spray-off (D4049) and washout (D1264) for a variety of greases and polymers

5. Conclusions

Grease polymers can be a versatile tool for grease formulators seeking to differentiate their product in performance and cost. Polymers impart unique benefits that many other additives or thickeners do not provide. The work shown demonstrates how performance can vary significantly with different grease polymer types and thickeners.

There are some basic rules-of-thumb to begin testing but ultimately each grease is unique in its composition and production which requires testing several grease polymers to find the best fit. It is most effective to first try one example from each of the three grease polymer types to see which creates the largest response in the desired properties. Then the formulator should test several options from that best type of grease polymer to refine their selection.

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Grease Production, CO_2 emission.... a New Relationship!

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Abstract

Manufacturing conventional lithium grease is a very energy intensive operation and, surprisingly, to the knowledge of the authors, no one prior to a recent technical paper [1] has studied the energy consumption and possible environment impact of the grease manufacturing process associated with the base oil used. It is well known that carbon dioxide has been shown to be the major contributor to greenhouse emissions and global warming and energy consumption can be directly related to the manmade contribution of this gas.

The aim of this paper is to measure the energy consumption on an industrial scale production of conventional lithium grease when a pressurized reactor is used and is further compared to traditional open kettle reactor. All the process parameters have been kept constant as well as the viscosity of the base oils used. The selected based oils are naphthenic and paraffinic Group I that are typically used in the preparation of lubricating greases.

The total energy (electrical for mechanical operations such as pumping, mixing and homogenizing, as well as fuel for heating) consumed for production purposes is recorded for all production stages: vessel charging, cooking, cooling/diluting and homogenizing. The measured energy consumption used for each batch is then converted to normalized CO_2 emission and savings in utilities for each of the batches evaluated. In order to make this comparative study more accurate, the finished greases have also been characterized according to the specification required by the end-users.

In total, eight full-scale lithium-based greases were manufactured using two different base oil viscosities. Considering the batches with the same base oil viscosity, it can be concluded that, for the grease with an ISO VG 220 oil, an overall reduction in CO_2 emissions of 21.5 % per metric ton of

produced product can be achieved by switching from a paraffinic base oil in an open kettle to a paraffinic/naphthenic base oil mixture in the Contactor™ reactor.
The authors believe that the outcome of this study could be a milestone in assessing grease production in terms of significant reduction of CO_2 emissions and increase awareness of the impact of our industry in the global environment.

Keywords
Lubricating grease, Manufacture, Energy, CO_2 emissions, Carbon footprint, Paraffinic oil, Naphthenic oil, Pressurized reactor, Open kettle

1. Introduction

The basic technology for production of soap type greases has been essentially unchanged for the last fifty or more years. This is certainly true for the type of lubricating grease that is most commonly used in the global market, namely lithium-based greases, which typically represent 75 % of global grease production [2]. In a way, the production methods utilized by our industry have remained stagnant, while the products that are the outcome of this process are becoming ever more sophisticated and suitable for high end and extreme applications, often thanks to the use of more efficient additives.
Recently, the grease manufacturers are witnessing several challenges, such as a rapid increase in the price of lithium hydroxide due to the extreme growth of the lithium-based battery industry. Some of the recent publications (e.g. Fathi-Najafi et.al. [3]) are suggesting that, by using high viscous naphthenic oils, the thickener content could be reduced to about 4.6 (wt.%) in the case of conventional lithium grease when targeting NLGI grade 2 consistency.
Another challenge that grease makers sooner or later should cope with is how manufacturing of lubricating greases can be optimised from an energy consumption point of view. The reduction of the energy required for grease production using base oils of different solvencies has been demonstrated in the past [1] on a laboratory scale, in which It was demonstrated that, by using naphthenic versus paraffinic base oils, a reduction of approximately 12 % in energy consumption could be obtained. The findings from that pilot plant project was then transferred to this full-scale production study. Hence, the aim of this paper is to demonstrate how the total energy consumption and, subsequently, CO_2 emission per mass of fully formulated conventional grease could be obtained.

2. Background to the manufacturing process of lithium-based greases

Conventional lithium grease is manufactured in a two-stage process. The first consists of the reaction stage (cooking) and the latter one being the finishing stage. Typically, two separate vessels are used for the two steps, with the cooking stage being carried out in either an open kettle under atmospheric pressure or a closed kettle, as shown in Figure 1. In the closed process, either an autoclave or a Contactor™ reactor (as shown in Figure 2), where the reaction occurs under pressure, is typically used. In the Contactor, the design also involves increased heat and mass transfer rates, thus enhancing dispersion and further reducing production times. This has been demonstrated in numerous studies [4], with the process time being significantly lower when the STRATCO® Contactor™ technology is utilised.
Typically, for the finishing stage, scraped-wall vessels with cooling (and sometimes heating) capabilities are used in conjunction with various mixing geometries that will depend on a number of factors, such as the vessel overall size, width to height ratio and type of product it has been

designed to handle. The finishing vessel is connected to the auxiliary equipment required to produce a commercial grease, such as mills, homogenisers, filters, deaerators, etc. In some cases, "hot milling" is done during the cooking stage.

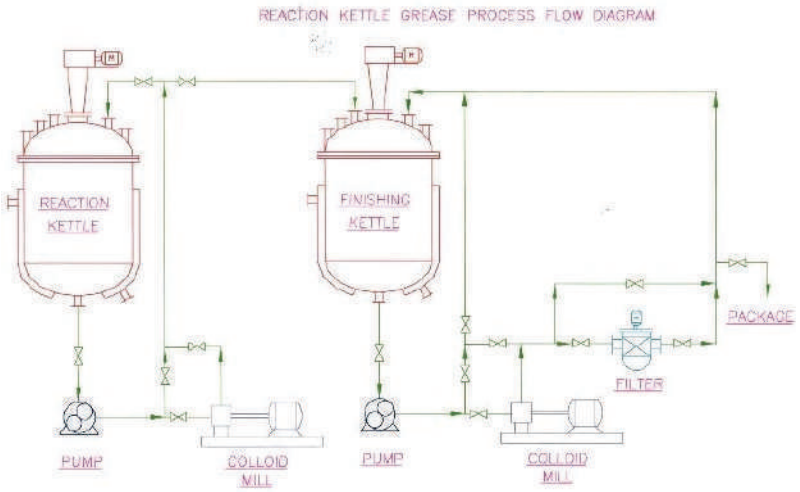

Figure 1. Typical grease production process, Kettle process.

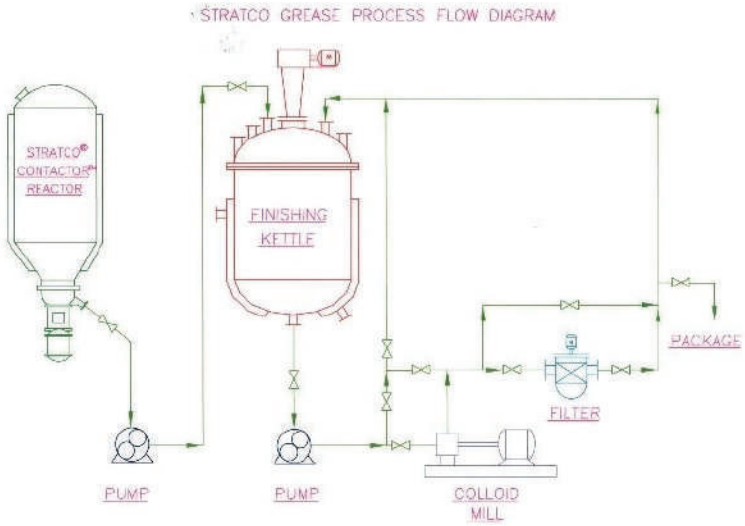

Figure 2. Typical grease production process, STRATCO® Contactor™ process.

Despite advances in the equipment used to finish the product, such as high-pressure homogenisers, self-cleaning filters and in line measuring/monitoring, very little has changed in the way the fatty acid and alkali are reacted or in the way that the grease is handled inside the finishing kettle in the past 60 years. Some attempts have been made to produce grease in a continuous process, but application in the field is very limited with only a few facilities worldwide having the required facilities and capacities to produce using such a mode of operation.

3. Energy requirements for lubricating grease manufacturing

With the development of electrically powered commercial and passenger vehicles, the role of lubricating grease will become increasingly important with numerous studies being carried out to show the energy efficiency of modern soap type lubricating greases for electrical motor applications. According to studies the energy dissipated in large electric motors can be reduced by 60 percent at lower speeds; $6x10^4$ Hz (1000 rpm) and up to 90 % at higher speeds, $1.5x10^5$ Hz (2500 rpm) when the correct grease is being used. Comparing this to modern energy conserving engine oils, such as API SN RC, we can see that the aim is a reduction of 0.9 percent in energy consumption of the internal combustion engine [6].

As one might imagine, the energy saving potential in the forthcoming years can be significant with the use of the more optimized grease. But, then how much energy can be conserved in the production stage of lubricating grease? It is well known that, in comparison to other lubrication products used for commercial and industrial applications, lubricating greases are significantly more energy intensive in the production stage.

To produce lubricating oil products, typically 2.5 - 4 kWh per metric ton of product are required to mix and pump the product, as well as low intensity heating to, usually, below 70 °C, which is a much simpler process of blending, as shown in Figure 3. Comparing this to lithium grease where, in the reaction stage, the temperature needs to approach 200 °C and the mixing and pumping energy is significantly higher due to the highly viscous nature of the product, it is understandable that the overall energy requirements are also more significant. As a matter of fact, the energy requirements for heating during grease production – including the heat of reaction – are considerably greater due to the additional heating, mixing and pumping energy associated with the much more viscous product than the same base oil in formulating a lubricating oil.

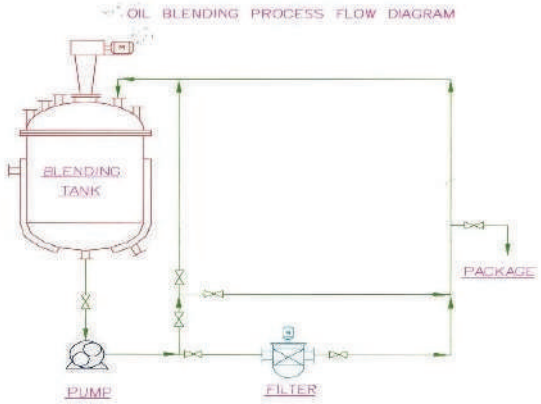

Figure 3. Typical oil blending production process.

In principal, for any lubricant's manufacturer, making process improvements, such as improving an oil/gas heater efficiency, higher heating medium circulation speed, improved insulation, more efficient electric motors on pumps, etc. would, generally, provide a seven-fold energy benefit on grease production as compared to oil blending. This is based on the theoretical energy requirements of each process, without taking into the account any system losses, overdesign or other factors that will limit efficiency. Considering this, the biggest portion of potential savings can be seen on the heating energy

that accounts for almost 80 percent in a typical grease production process. The above implies that, when looking at optimizing the energy usage of a lubricants manufacturing facility, starting with the grease production willhave greater impact both on economic and environmental terms.

The largest proportion of energy used today is linked to fossil fuel. The heating oil or gas consumed for the production process can be directly correlated to CO_2 emissions. The electricity consumed for mixing, pumping and auxiliary uses is indirectly related to fossil fuel as the source of power generation is most often linked to fuels ranging from coal to oil, natural gas and renewable sources. The fuel mix is often variable and will need to be verified by the utility supplier. As a result of any process optimization, the reduction of energy will also lead to a reduction in CO_2 emissions and, thus, the carbon footprint linked with the product being put on the market, even before this is used. The reduction of the energy requirements for grease production using base oils of different solvencies has been demonstrated in the past [1], in which It was shown by using naphthenic versus paraffinic base oils a reduction of approximately 12 % in energy consumption could be obtained, as shown in Table 1. The comparative results from that pilot plant project formed the basis of this full-scale production study. If the correlation is demonstrated on an industrial scale, then a reduction of the total energy consumption, and subsequently CO_2 emission per mass of fully formulated conventional grease, could be obtained.

Properties	**Method**	**Grease A**	**Grease B**	**Grease C**
Base oil	-	T110	SN525	T110:SN525 (1:1)
Base oil Type	-	Naphthenic	Paraffinic	Naph + Paraf
Thickener content, wt.%	-	7.92	9.02	7.82
Pen (60), mm^{-1}	ASTM D217	239	258	272
Dropping Point, °C	ASTM D2265	206	207	209
Dropping Point, °F		402.8	404.6	408.2
Energy Consumption, kWh	-	15	17	15

Table 1. Energy consumption and thickener content for conventional lithium-based greases, [1].

4. Grease Production

A series of batches were produced on an industrial-scale under closely monitored conditions. A total of eight batches were evaluated. The selected viscosity grades (VG ISO 100 and VG ISO 220) were chosen since these are the typical grades for multipurpose lithium greases in the industry. The production stage, time, temperature, electricity and LPG consumption were recorded throughout each batch. Temperature inside the vessel was recorded continually during the cooking stage and measured

by contact and infraredthermometers during the finishing stages.

Remarks	Type of Cooking Vessel	Type of Base Oil	Viscosity of the Oil @40°C, [mm²/s]
TB 01	Pressurised (Contactor)	Naphthenic	100
TB 02	Pressurised (Contactor)	Naphthenic	220
TB 03	Pressurised (Contactor)	Paraffinic	220
TB 04	Pressurised (Contactor)	Naphthenic + Paraffinic	220
TB 05	Atmospheric (Open)	Paraffinic	100
TB 06	Pressurised (Contactor)	Paraffinic	100
TB 07	Atmospheric (Open)	Naphthenic + Paraffinic	220
TB 08	Pressurised (Contactor)	Naphthenic + Paraffinic	100

Table 2. Batch base oil profile data.

The base oil profiles of the eight batches are presented in Table 4 and selected characteristics of the baseoils used in this study are shown in Table 3.

Remarks	Visc. @40 °C, [mm²/s]	Visc. @100 °C, [mm²/s]	Viscosity Index	Aniline Point, [°C]	Pour Point, [°C]	S-content, [wt.%]
Paraffinic 1	103	11.1	92	108	- 9	0.44
Paraffinic 2	218	18.7	95	105	- 8	0.52
Naphthenic 1	22.3	3.7	-3	75	- 45	0.06
Naphthenic 2	150	10.2	8	89	- 27	0.13
Naphthenic 3	600	21.5	-12	89	- 12	0.30

Table 3. Typical characteristics of the base oils.

In order for an unbiased comparison of produced batches to be made, a target of grease consistency with worked penetration of 270 (mm^{-1}) was set. Also, based on prior knowledge of the art, the thickener base was adjusted accordingly between batches in order to produce similar quantities of finished grease. This approach was chosen as similar batch sizes in the finishing stage mean that variations in energy required for the finishing stage (mixing, cooling, homogenizing, etc.) will only be affected by the thickener contentand the viscosity of the base oil.

The final grease was enriched with a commercial antioxidant and anti-wear additive package at a typical treat rate recommended by the supplier. The nature of these additives does not affect the rheology of the product and were required to convert the base grease into a formulated commercial product, as wasrequired in the scope of this study.

During the production phase of the test batches, several biases were observed, namely, the ambient temperature and the time between production batches. Ambient temperature affects the energy requirement of the production process in the following two ways: a) energy required to pump the oil fromthe storage tank to the cooking and finishing vessels and b) the energy required to heat the base oil fromambient to the reaction temperature. During the test period the ambient temperature varied with a ΔT=17 °C, which affected the viscosity up to + 220 percent, depending on the base oil type. Also, with an average specific heat capacity of 1.67 (kJ/kg K) [8], approximately 15 kWh of heating energy variation canbe attributed to ambient temperature differences.

Time between production batches will affect the residual heat in the production system, particularly in the Contactor, where an energy consumption variation of up to 12.2 % was observed between starting a batch in a cold vessel after prolonged dormancy and back-to-back batch production. In order to compensate for the variability described above, a starting point of 70 °C was selected for the energy measurements.

5. Performance characteristics of the produced greases

Throughout this study, it was critical to demonstrate that the produced greases not only met the production parameters specified in the above paragraph but also met the required performance characteristic of a commercial grease, as required when full-scale production is done.

The test parameters evaluated provide the required evidence that each of the full-scale batches produced are representative of a fully formulated commercial grease. As previously mentioned, several parameters, such as oxidation stability, were enhanced using commercial additives. The intent is to further demonstrate that these properties can also be affected and, as a matter of fact, be enhanced by manipulating the appropriate manufacturing parameters and/or starting components of the grease. Notably, that all the process parameters were kept the same when these batches were produced.

One parameter that was kept outside typical commercial specification is the worked penetration of the test batches. Typically, greases will be marketed with a worked penetration 280 - 285 (mm^{-1}). However, the test batches were further treated with performance enhancing additives that brought the penetration to the required value. Table 4 and 5 show some of the measured characteristics of the greases.

Characteristics	Test Method	TB 01	TB 05	TB 06	TB 08
Thickener content (wet), [wt.%]	-	7.2	8.9	8.2	7.1
Base Oil -type	-	Naphthenic	Paraffinic	Paraffinic	Napht+Paraf
Cooking vessel - type	-	Pressurised Contactor	Atmospheric Kettle	Pressurised Contactor	Pressurised Contactor
Pen (60), [mm^{-1}]	ASTMD 217	264	274	270	266
Dropping point, [°C]	IP 396-02	200	203	201	202
Oil separation, [wt. %]	ASTMD 1742	< 0.5	3.61	2.84	2.12
Water wash out, [wt. %]	ASTMD1264-18	6.3	4.3	2.7	5.9
Diff in Pen. after 10^5 str, [mm^{-1}]	ASTM D 217	+ 31	+ 27	+ 35	+ 46
4-Ball wear scar, [mm]	ASTM D2266	0.95	0.82	0.64	0.88
Copper corrosion, [rating]	ASTM D4048	1b	1a	1a	1a
Oxidation stability@140 °C, [min]	ASTM D7575	510	769	1042	762

Table 4. Characteristics of the greases (VG ISO 100).

As stated in Table 4, lower thickener content can be obtained by using naphthenic (TB 01) in lieu of paraffinic (TB 05). In fact, TB 08, which is a blend of naphthenic and paraffinic oil, confirms that the lower soap content can be obtained, even if partly naphthenic oil is used. This batch (TB 08) was cooked in naphthenic oil and then cooled by paraffinic oil.

Some of the performance characteristics of these four batches are not in line with each other. For

example, the oil separation increases when paraffinic oil is used, but then, on the other hand, the oxidation stability is improved. Water washout follows the soap content.

If we study the impact of manufacturing grease in an open kettle compared with a pressurised reactor for the two paraffinic based batches (TB 05 with TB 06), it seems that the use of the pressurised Contactor reactor contributes to: a) a reduction of the soap content and b) a reduction of the risk for the grease being oxidised during the cooking stage. This can be attributed to the fact that, since the reaction time is reduced, the base oil is subjected to higher temperatures for a shorter period. Furthermore, thepressurisation of the process using the steam generated by the chemical reaction limits the ingress of atmospheric oxygen to the system, also contributing to the improved results.

Surprisingly, when the average viscosity of the base oil at 40 °C was increased from 100 (mm^2/s) to 220 (mm^2/s), several the characteristics were improved. Table 5 illustrates some of the measured propertiesof these greases.

Characteristics	**Test Method**	**TB 02**	**TB 03**	**TB 04**	**TB 07**
Thickener content (wet), [wt.%]	-	4.8	7.5	5.4	7.6
Base Oil - type	-	Naphtheni c	Paraffini c	Napht+Para f	Napht+Para f
Cooking vessel - type	-	Pressurised Contactor	Pressurised Contactor	Pressurised Contactor	Atmospheri c Kettle
Pen. (60), [mm^{-1}]	ASTMD 217	269	273	278	273
Dropping point, [°C]	IP 396-02	205	207	208	204
Oil separation, [wt. %]	ASTM D 1742	< 0.5	1.96	2.85	3.74
Water wash out, [wt. %]	ASTM D 1264-18	4.7	4.7	3.6	4.5
Diff in Pen. after 10^5 str., [mm^{-1}]	ASTMD 217	+ 46	+ 33	+ 44	+ 31
4-Ball Wear scar, [mm]	ASTM D 2266	0.68	0.61	0.65	0.61
Copper corrosion, [rating]	ASTM D 4048	1a	1a	1a	1a
Oxidation stability@ 140 °C, [min]	ASTM D 7575	750	1082	1099	861
Flow pressure @ -25 °C, [hPa]	DIN 51805	620	1320	695	N/A
Flow pressure @ -30 °C, [hPa]	DIN 51805	1020	1595	1145	N/A

Table 5. Characteristics of the greases (VG ISO 220).

If we compare the greases that are cooked in the pressurized reactor (TB 02, TB 03 and TB 04), the significantly lower thickener content in the case of TB 02 and TB 04 can only be related to the use of the naphthenic oils with higher degree of solvency and viscosity.

The measured characteristics of the greases also indicate the following:

a) the oil separation increases with the use of paraffinic oil, regardless the type of cooking vessel.
b) the oxidation stability for greases that are cooked in the pressurised reactor and contain paraffinic oil (TB 03 and TB 04) is better than the other batches. However, a result of 750 minutes or higher can still be regarded as good to excellent.
c) the flow pressure, which is a good indication of the degree of the pumpability of a grease is, as expected, in favor of the greases that contain naphthenic oils.
d) all other characteristics are in line with each other and within the frame of the specification for thistype of grease.

6. Test batch energy requirements

Two separate parameters have been investigated with regards to the energy requirements of the grease production process. Firstly, the effect of the process equipment used, i.e. atmospheric versus pressurised production vessels. Secondly, the effect of the base oil used. With regards to the latter, the effect of paraffinic versus naphthenic base oil has been investigated. Furthermore, the viscosity of the final product has also been considered by looking at a series of ISO VG 100 and ISO VG 220 base oil blends for the final product.

6.1 The impact of the manufacturing processes on the energy consumption

For each of the stages given below, detailed measurements of time, system temperature and energy requirements (electricity and LPG consumption) were made. As discussed in section 4, in order to minimise any bias attributed to environmental or process conditions, the energy requirements used for test batch comparison are limited to the electricity and LPG values recorded when the base oil for the cooking stage was charged and the temperature in the cooking vessel reached 70 °C. This means that the energy measurements made are biased only by any inefficiencies of the facility installation.

The fuel used for heating purposes was Liquified Petroleum Gas (LPG) which, based on supplier information, is an 80/20 mixture of Butane/Propane providing an equivalent energy output of 31.13 (kWh/m^3). It is noted that LPG measurements were made in m^3 supplied to the burner, but for reporting consistency this has been converted to the equivalent kWh. Based on the information provided by the utility provider, during the period of the production of these batches, approx. 84 % of the energy was generated from fossil fuel, and 16 % came from renewable sources.

In order to ensure the validity of the fuel measurements for this study, no other heating operations took place in the production facility during the execution of the test batches. It must be noted that, due to extent of piping, there are expected to be fewer losses in the test batches made in the pressurised vessel compared to the “open” kettle, based on the distances the heating oil has to travel.

Since we are looking at the energy consumed at the source (actual amount of fuel used), the efficiency of the installation will significantly affect the net result. So, if the theoretical heating energy requirements are used, 134 (kWh /MT) of heating energy are required to heat and react the raw material and heat the base oil and water of the process. Looking at the production schedule summarised in Table 6 for atmospheric versus pressurised production, there is a significant difference in the amount of time required for the cooking stage.

According to the information in Table 6, there is a difference of 225 minutes – almost 4 hours in total production time – when TB 04 and TB 07 are compared. Looking at the average values, the net gain in terms of time is 232 minutes and the maximum difference is 280 (minutes). This difference is noted between TB 07 and TB 03.

Production Stage / Test Batch	Pressurized, TB 04 (N/P+ISO 220) [min]	Atmospheric, TB 07 (N/P+ISO 220) [min]	Difference (TB 07 – TB 04) [min]
Cooking	245	450	+ 220
Finishing	150	170	+ 20
Homogenising - Drumming	150	145	- 5
Total Process Time	**540**	**765**	**225**

Table 6. Batch production schedule; **P** stands for Paraffinic oil and **N** for Naphthenic oil.

The major gain is obtained in the cooking stage of the process, with 220 additional minutes being required when production is carried out in the "open" kettle. In the finishing stage, there is an additional 15 minutes gained on average, but this is not considered significant, hence it is believed that this step has great potential to be optimized further, based on the manufacturer's experience and the repeatability ofproduced batches.

These results are not surprising – or new to the industry - as one of the main benefits of using a pressurised vessel is the time required to complete the cooking stage. Focusing on the cooking stage, Figure 4 presents the product temperature as a function of time for all evaluated batches. There is good repeatability of the processes – for both processes. For the pressurised vessel, this can also be seen fromthe actual temperature recordings shown in Figure 4.

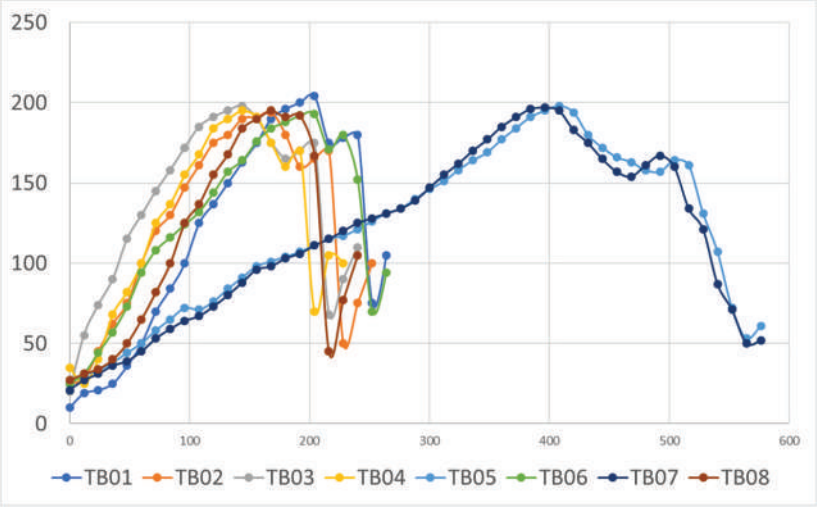

Figure 4. Time vs temperature Charts TB01 to TB08 from reactor charging to reactor discharge.

One of the reasons the temperature ramp is flatter for the atmospheric process is the fact that a larger amount of water is required to assist in the saponification reaction, which absorbs more energy. The greater dispersion of reactants in the more turbulent Contactor vessel significantly improves the reaction kinetics, ensuring a more complete and quicker reaction. Looking at the values in Table 7, heating and evaporation of process water accounts for up to 11 % of the heating energy needs in the atmospheric process. Also, since we have an open system, significantly more energy is lost to the environment compared to using a pressurised kettle. Another reason for the ramp profile is that the heat transfer in the kettle is limited by surface area and lower heat transfer rates due to lower product flow rates within the vessel as compared to a Contactor type reactor. These conditions explain the results obtained and listed in Table 7. Comparing the heating energy recorded versus the theoretical energy for lithium greaseproduction in a pressurised vessel (134 kWh per MT) the efficiency of the process, from fuel tank to finished product, varies with an average of 53 % for the pressurised vessel and 41 % for the atmospheric process.

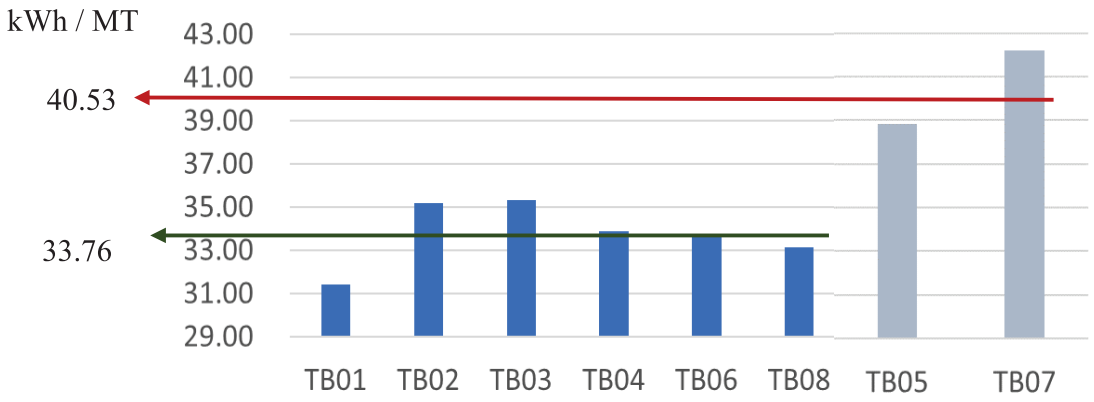

Figure 5. Electricity consumption per MT of grease: atmospheric vs pressurised.

Production Batch	**TB 01**	**TB 02**	**TB 03**	**TB 04**	**TB 06**	**TB 08**	**TB 05**	**TB 07**
Cooking [kWh/MT]	15.79	16.71	17.09	15.57	17.94	16.89	22.13	21.28
Finishing [kWh/MT]	15.62	18.45	18.23	18.28	19.68	16.25	16.72	20.92
Overall Electricity [kWh /MT]	31.42	35.16	35.32	33.85	37.62	33.14	38.85	42.20
Overall Heating [kWh/MT]	213.11	187.76	198.66	170.21	191.4	181.76	272.8	234.5
Total Energy, [kWh/MT]	**244.53**	**222.94**	**233.99**	**204.06**	**229.02**	**214.9**	**311.65**	**276.7**

Table 7. Energy requirements for batches in pressurised and atmospheric process.

Looking at the electrical energy for production, it can be seen that there are no significant variations in terms of the amount of electricity per MT of product, particularly in the finishing stages of the grease. This is expected, as energy required is proportional to the amount of product that needs to be processed in this stage. In the cooking stage there are notable variations, as with the heating energy.

In order to accurately evaluate the above stated results, several factors need to be considered, namely, the variations in the heating energy between the batches and the variations in the electricity energy in different stages of production, which is summarized in Table 8. All values for energy are normalized per Metric ton (MT) of grease produced. This means that batches that produce a higher yield, or lower thickener content, will benefit from lower results in the cooking stage and, in particular, the heating energy that accounts for approximately 85 % of all energy required.

Remarks	**TB01**	**TB02**	**TB03**	**TB04**	**TB05**	**TB06**	**TB07**	**TB08**
Heating Energy, [%]	87.2	84.2	84.9	83.4	87.5	85.1	84.7	85.3
Electrical Energy, [%]	12.8	15.8	15.1	16.6	12.5	14.9	15.3	14.7

Table 8. Heating vs electrical energy requirement of batches per MT of produced grease.

Considering the average values as shown in Figure 5, it is noted that there is a reduction of approximately 16.7 percent in the electrical energy requirement for pressurized reaction versus atmospheric. Looking at the most (TB 01) and the least (TB 07) electrical energy efficient batches, more than 25 % difference can be observed. This is something that is overlooked as, typically, the power requirement for the pressurized vessel is much higher than for an open kettle in order to provide the improved mixing rate that is desired.

Remarks	**Base Oil**	**Energy kWh per MT**	**Normalised Energy**	**Ranking ***
TB 04	**N/P** (ISO 220)	204.06	1.00	**1**
TB 02	**N** (ISO 220)	222.94	1.09	**2**
TB 08	**N/P** (ISO 100)	224.90	1.10	**3**
TB 06	**P** (ISO 100)	225.02	1.10	**4**
TB 03	**P** (ISO 220)	233.99	1.15	**5**

Table 9. Energy ranking of 5 batches in pressure process. **ranking: **1** lowest to **5** highest.*

With regards to the heating energy, it must be noted that all measurements are taken with a hot oil pan as a starting point, but after the first production batch the gas supply was turned off before the cooking stage was completed to take advantage of the residual heat in the furnace and minimise the energy requirements. This explains the reduced LPG consumption in batches following TB 01. This methodology was applied both to all the atmospheric and pressurized batches.

With regards to the electricity consumed, variations between the recorded production stages can be observed and in the finishing stage. This can be attributed to the attempts needed to adjust the test batch finished product to the desired consistency. Care was taken to make sure the test batch target properties were prioritized, which meant that, for some batches, many minor adjustments had to be made in either the first or the second stage. Nevertheless, for each test batch these two stages included the electrical energy required to mix, pump, homogenise and package the grease.

By comparing the two different processes, the following observations can be utilised; when looking at the open kettle, significantly more heating energy is required to cook the grease. This is in line with previous findings using pilot scale data [1] and what is expected when considering the reduced efficiency of a traditional open kettle in terms of both heat and mass transfer compared to a Contactor reactor.

An additional point that needs to be made is that, of the total energy, approximately 85 percent for both processes is comprised of the heating energy that goes into the system. This can be directly converted to CO_2 emissions, as the amount of fuel is measurable. Any improvement in this production parameter will have significantly greater impact on the reduction of the required energy for the production process, irrespective if an open or a closed production system is used.

6.2 The impact of the base oils on the energy consumption

The essential part of the reduction in energy requirement, when it comes to the paraffinic/naphthenic based grease, comes from the reduction of the thickener content. A higher yield clearly means reduced energy requirement per unit product. Nonetheless, it can be observed that, also, the overall energy requirement in purely naphthenic batches (such as TB02) compared purely paraffinic batches (such as TB03), is lower by about 5 % when looking at the absolute values.

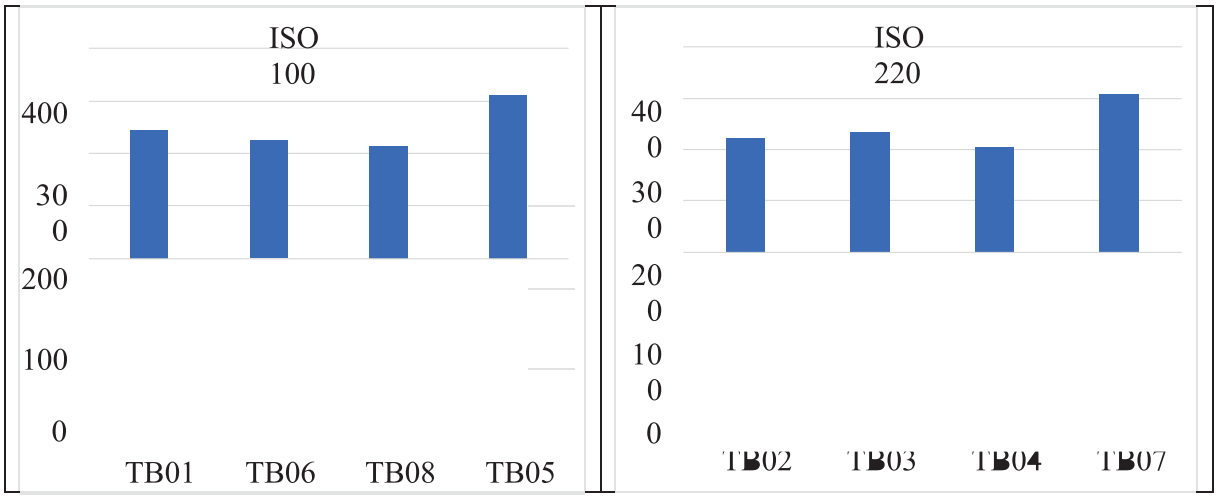

Figure 6. Total Energy requirement in kWh per MT of produced grease for TB01 – TB08.

Looking at the results, there is significantly more energy required for the test batches produced in the open kettle process. The difference is as high as 33.5 percent for the ISO VG greases 220 and 31.0 percent for the ISO VG 100 greases produced in the open kettle compared to the pressurized vessel.

Also, there is a small advantage when formulating in a higher viscosity base oil, as for three out of four cases the energy required is lower. This is mainly due to the yield benefit. This can be seen in Table 10 where the energy savings is in the region of 5 %. It is noteworthy that for TB07, a naphthenic/paraffinic blend was used instead of a paraffinic as for TB05. If a fully naphthenic base oil blend was chosen, a bigger difference would probably have been observed based on the other generated data.

Remarks	TB 01 Naphthenic ISO 100	TB 06 Paraffinic ISO 100	TB 08 N/P ISO 100	TB 05 Paraffinic ISO 100
Energy [kWh/MT]	244.53	225.02	214.9	311.65
Batch No.	TB 02 Naphthenic ISO 220	TB 03 Paraffinic ISO 220	TB 04 N/P ISO 220	TB 07 N/P ISO 220
Energy [kWh/MT]	222.94	233.99	204.06	306.7
Energy Saving, [%] ISO 220 vs. ISO 100	9.7	- 3.8	5.3	1.6

Table 10. Energy requirement versus base oil type.

One additional factor to consider is that heating energy losses for the "Open" kettle process are significantly higher than those of the pressurized vessel and, also, the time required is much longer (on average 107 versus 288 minutes). Consequently, the energy required for mixing is also increased (approximately 16.3 (kWh) in the pressurised vessel versus 21.71 kWh on the open kettle).

Looking at the obtained results, it should be noted that all grease batches produced in an ISO VG 220 base oil blend starting with a high viscosity naphthenic base oil in the cooking stage and then finishing the grease with a lighter naphthenic or paraffinic base oil showed an improved yield. This in turn means that the energy requirement on a kilowatt to kilogram basis will be lower. This is irrespective of the manufacturing procedure and was found both on the atmospheric and pressurised batches. When formulating the grease on a paraffinic base this was not observed and as a matter of fact there was a small energy penalty for the ISO VG 220 where in terms of the electricity required there was an additional requirement of approximately 4 % in the cooking stage and 7 % in the finishing stage.

7. Carbon Footprint

Throughout industrial and commercial applications, the reduction of greenhouse gasses (GHG) is seen as part of corporate responsibility, with many large and small corporations setting targets of becoming carbon neutral in the future. The first step towards this is usually taken by applying a standardized reporting system such as the GHG Protocol [9] which allows the organization to uniformly account for and manage CO_2 and other emissions. This forms part of a greater requirement of sustainability by managing all resources including material, financial and people. The most commonly considered gases are HFC gases, methane, NOx, and carbon dioxide with the latter accounting for approximately 80 % of the beforementioned emissions on a global scale. Figures provided from the US EPA [15], show that over the past two decades, they have been relatively constant despite the numerous attempts through UN initiatives such as the Paris Agreement in 2015 and the more recent COP24 climate summit in Poland as well as the work done by NGOs.

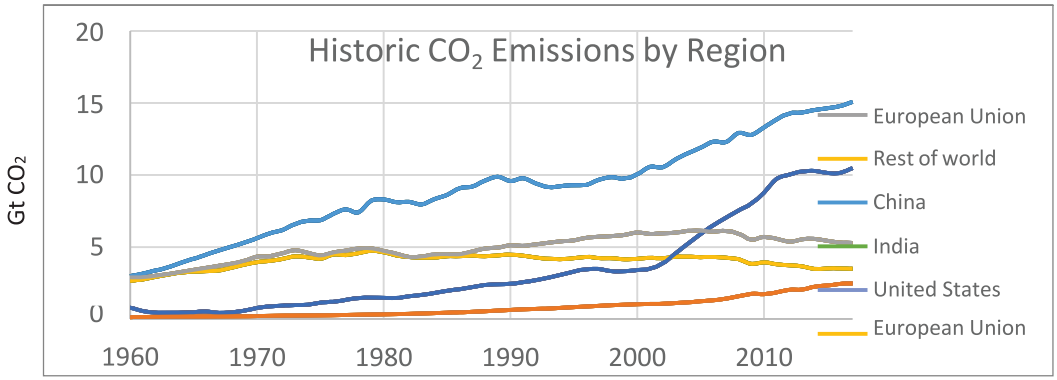

Figure 7. Major contributors to CO_2 global emissions.

In the study conducted, there are two elements that have to be accounted for in the case of grease production: the energy usage in the form of electricity and the energy usage in the form of heating.
There are various tools available to evaluate the carbon footprint of the electricity provided by local utility companies. Today there are utility companies that can provide energy that is produced using exclusively renewable sources. Nonetheless in various global regions, the energy source will vary from coal to nuclear and renewables, such as water, wind and solar. Where renewable sources are used, the overall resulting CO_2 emissions from a given operation can theoretically be zero.
As seen from the results of this study, the electricity consumed during grease production only represents a small amount of the total system energy, ranging from 12 – 16 %. Most of the energy comes from the heating requirements. Currently, apart from small scale operations where the circulating medium can be electrically heated (pilot scale), there are only a few novel processes that use electricity as a means of heating, with the most discussed method being microwave heating for grease production [10]. The supply of high-pressure steam as a utility, where available, presents a unique energy calculation, but, in this case, the source of steam generation also needs to be evaluated.
For fuel fired systems, the CO_2 emissions can easily be accounted for by applying a GHG model [9] applicable for the energy source used by the local utility supplier. For most of the grease plants, fuel for the heating source is some sort of fossil fuel. This could be Natural gas, LPG, Diesel, a heavier distillate or an alternative fossil fuel derived source. Depending on the region and supplier, these sources can incorporate a sustainability factor, such as, for example, biofuel for diesel.

Fuel	Emissions in [kgCO_2/ kWh]	Emissions in [kgCO_2/ GJ]
Lignite	0.36	101.2
Hard coal	0.34	94.6
Fuel oil	0.28	77.4
Diesel	0.27	74.1
Crude oil	0.26	73.3
Kerosene	0.26	71.5
Gasoline	0.25	69.3
Refinery gas	0.24	66.7
Liquid petroleum gas	0.23	63.1
Natural gas	0.20	56.1

Table 11. CO_2 emissions per kWh, Source: Fachbuch Regenerative Energiesysteme and UBA.

In order to evaluate the overall carbon footprint of the production stage of the operation considered, the different test batches were compared. The production in the pressurized kettle using a blended naphthenic/paraffinic base stock of ISO 220 (TB 04) was used as a bench mark as this gives the overall lowest results in terms of energy demands.

For LPG, the fuel used, the CO_2 emissions per kWh is given in Table 11. Also considering the electricity production fuel mix during the batch production period (43% Lignite, 37% Diesel, 12% LNG & 8%Renewable) the average CO_2 emission values can be calculated to give the values in Table 14.

Energy source	CO_2 emissions
Heating	0.23
Electricity	0.28

Table 12. CO_2 Emissions for production batches in kg eCO_2 per kWh.

Batch	Base oil-Type	Viscosity @ 40°C, [mm^2/s]	Thickener content,[wt.%]	Cooking Vessel - Type	Kg eCO_2 per MT	Normalised CO_2 emissions per MT
TB 04	Naph/Paraf	220	5.4	Pressurised Contactor	48.62	1
TB 02	Naph	220	4.8	Pressurised Contactor	53.04	1.091
TB 08	Naph/Paraf	100	7.1	Pressurised Contactor	53.38	1.098
TB 06	Paraf	100	8.2	Pressurised Contactor	53.44	1.099
TB 03	Paraf	220	7.5	Pressurised Contactor	55.58	1.143
TB 01	Naph	100	7.2	Pressurised Contactor	57.81	1.189
TB 07	Naph/Paraf	220	7.6	Atmospheric Kettle	65.75	1.352
TB 05	Paraf	100	8.9	Atmospheric Kettle	73.62	1.514

Table 13. Normalised CO_2 emissions from production batches.

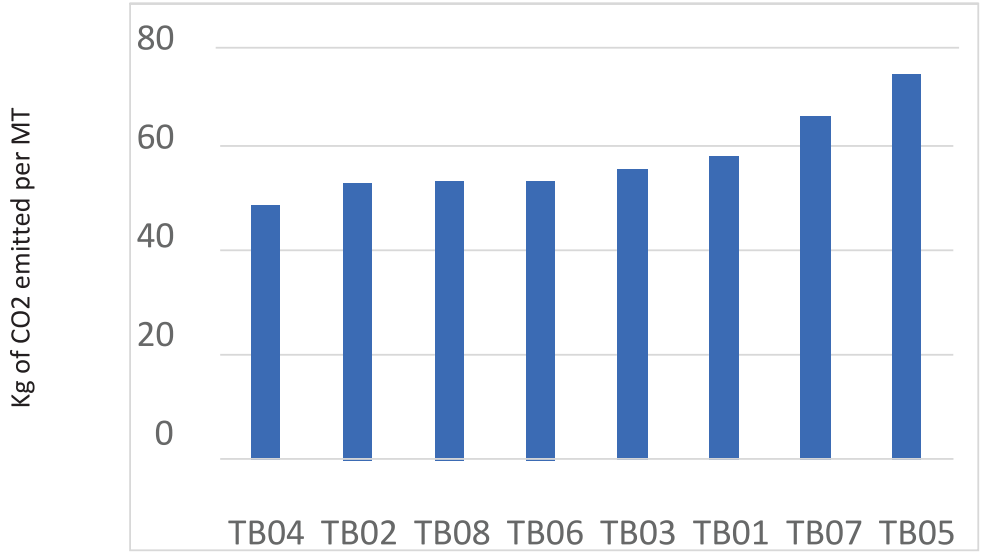

Figure 8. kg CO_2 emitted per MT of grease produced.

Considering the test batches with the same base oil viscosity, it can be seen that, for the grease with an ISO VG 220 oil, an overall reduction in CO_2 emissions of 35.2 % can be achieved by switching from a paraffinic base oil in an open kettle to a paraffinic/naphthenic base oil mixture in a pressurized process. Similarly, considering a grease with an ISO VG 100 oil, an overall reduction in CO_2 emissions of 41.6 % can be achieved by switching from an open kettle production process using a paraffinic/naphthenic base oil blend.

Batch	MT CO_2 emissions per 1000 MT Heating	MT CO_2 emissions per 1000 MT Electrical	Combined CO_2 emission reduction potential per 1000 MT grease
TB 04	39.15	9.48	-
TB 02	43.18	9.85	4.41
TB 08	44.10	9.28	4.76
TB 06	44.02	9.41	4.81
TB 03	45.69	9.89	6.96
TB 01	49.02	8.80	9.19
TB 07	53.94	11.82	17.12
TB 05	62.74	10.88	25.00

Table 14. Emission reduction potential of using each batch process by energy stream.

Looking at the absolute per metric ton values for every 1000 MT per year production, the annual reduction of CO_2 emissions between open and closed kettle process is estimated at 18 – 20 MT for paraffinic base oil and up to an additional 5 MT saving if the base oil used is naphthenic. Some CO_2 emission equivalents can be seen in Table 15 below.

CO_2 emission saving between TB 04 and TB 05…	**Emission offset**
…per 8 MT batch	**200 kg CO_2** *or* 1,800km *in a modern EURO 6passenger car (111 gr. CO_2/km)*
…per 80 x 180 kg drums shipped in container	**360 kg CO_2** *or* Sea freight of container fromRotterdam to **Singapore** (36 gr. *CO_2/Nautical mile)*
…per 1000 MT produced	**25,000 kg CO_2** *or* 250,000 km travelled by roadtrucks with company goods (100 gr *CO_2/km)*

Table 15. Examples of CO_2 saving offset.

Looking at published industry data by a lubricants manufacturer that is a producer of both lubricating oils and greases [11], it can be noted that an average energy consumption of approximately 232 (kWh per metric ton) of produced product is reported. This value includes all activities on a given production location. Noting that the average energy consumption of the grease batches measured is 245.5 (kWh perMT) only considering the production process parameters it can be deducted that any optimization in this type of products (greases) can have a significant impact on a company's sustainability rating. The measured results show that a significant improvement of over 40 % in some cases can be obtained in what is indisputably the most energy intensive production activity within the lubricants industry.

8. Summary

This study is based on the production of lithium grease on an industrial scale, in which the impact of several key parameters, such as the nature and the viscosity of base oils and the production technologies, on the energy consumption and CO_2 emission mass basis of finished grease were evaluated.

In total, eight batches (8000 kg each) of lithium-based grease was manufactured. The selected base oils were two paraffinic group I oils, three hydrotreated naphthenic oils and the blend of paraffinic and naphthenic oils. The viscosities at 40 °C were 100 (mm^2/s) and 220 (mm^2/s), since these are the typical grades for multipurpose lithium greases in the industry.

Based on the obtained results in this study, the following conclusions can be made:

1. Considering the test batches with the same base oil viscosity, it can be concluded that, for the grease with an ISO VG 220 oil, an overall reduction in CO_2 emissions of 21.5 % per metric ton of produced product can be achieved by switching from a paraffinic base oil in an open kettle to a paraffinic/naphthenic base oil mixture in the Contactor reactor.

2. The essential part of the reduction in energy requirement, when it comes to the paraffinic/naphthenic blend-based grease, comes from the reduction of the thickener content. A higher yield clearly means reduced energy requirement per unit product. Nonetheless, it can be observed that, also, the overall energy requirement in purely naphthenic batches (such as TB 02) and purely paraffinic batches (such as TB 03), is lower by about 5 percent when looking at the absolute values. Looking at the results, it can be clearly seen that there is significantly more energy required for the test batches produced in the open kettle process. The difference is as high as 33.5 % for the ISO VG 220 greases and 31.0 % for the ISO VG 100 greases produced in the open kettle compared to the pressurised vessel.

3. Production of lithium-based grease could be optimised by cooking the grease in a pressurised condition (e.g., STRATCO® Contactor™ reactor) in lieu of at atmospheric pressure. This benefit regarding the yield can then be maximised when the viscosity of base oil is increased from 100 (mm^2/s) to 220 (mm^2/s) at 40 °C and naphthenic oils are used.

4. One additional factor to consider is that heating energy losses for the open kettle process are significantly higher than those of the pressurised vessel and, also, the time required is much longer (on average 107 versus 288 minutes). Consequently, the energy required for mixing is also increased, by approximately 15.57 kWh in the pressurised vessel and by 21.28 kWh in the Atmospheric (Open) kettle.

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APPENDIX A

Calculation of theoretical Energy requirements:

i. Heating Energy

Heating Energy required to heat the mixture/reaction components is calculated using equation (1)

$$\sum Q = \sum_1^n \left(\frac{M_n}{M_T} Cp_n \Delta T\right) + H_S + E_A \quad [J]$$

where

n are the components of the mixture M_n is the mass of each component M_T is the total mass of the system

Cp_n is the average specific heat capacity of each component over the mixing/reaction temperature range

ΔT is the temperature difference between T_0 at the beginning of the mixing and T_{max} , peak temperature

E is the enthalpy of steam which includes the: H_S, the latent heat of vaporisation at T_S (the temperature of saturation) and H, the enthalpy of superheated steam at the operating temperature.

E_A is the reaction activation energy.

For simple oil mixing, assuming the specific heat capacities of the oil and the additives are the same, equation (1) is reduced to

$$Q = \frac{M_1}{M_T} Cp\Delta T \text{ [kJ]}$$

where

$M_1 = M_T$ and

$\Delta T = (T_{max} - T_o) = 70 - 20 = 50$

So,

Q = 1 x 1.67 x 50 = 83.5 kJ/kg *or* 0.023 kWh/kg

Similarly, for grease production making the following production assumptions.

a) A thickener base with 15.5 (wt.%) thickener content
b) Production in a pressurized vessel with an operating pressure of 400 (kN m^{-2}) = (4 bar)

The mixture will consist of the components listed in the table below

Component	Base oil (SN 500)	Fatty acid (12-HSA) [13]	Alkali LiOH·H 2O	Water
Cpaverage [kJ kg^{-1} K^{-1}]	1.67	2.74	2.07	4.18
Mn/MT	0.821	0.136	0.012	0.031

The water mass fraction is derived from the following parameters

- the water contained in the alkali, typically 40 (wt.%) of the added alkali,
- the water released during the saponification reaction, approximately 6 (wt.%) of the Fattyacid added for 12-HSA, and
- the water added to the system to promote the reaction.

Considering an operating pressure of 4 (bar), the saturation temperature of steam is 143.63 (^{o}C) [8]

assuming equilibrium conditions, water is heated to the above temperature, steam is generated and then it is superheated to the maximum operating temperature of T_{max}=200^{o}C, when it is vented.

Hence, the heating energy can now be calculated as shown below:

for the thickener components:

Component	Base oil (SN 500)	Fatty acid (12-HSA) [13]	Alkali LiOH·H 2O
Cpaverage [J kg^{-1} K^{-1}]	1670	2740	2070
Mn/MT	0.821	0.136	0.012
ΔT K	180	180	180
Qn J kg^{-1} K^{-1}	246,991.45	67,018.11	4,521.62
Qn kWh kg^{-1}	0.0686	0.0186	0.0013

for the water:

Component	Energy to heat the water to evaporation	Latent heat of Evaporation Hs	Enthalpy of superheated steam H
Cpaverage [J kg^{-1} K^{-1}]	4180		
Mn/MT	0.029		
ΔT [K]	123.63		
Qn [J kg^{-1} K^{-1}]	15,151.68		
QH [J kg^{-1}]		62,536.14	83,737.27
Qn [kWh kg^{-1}]	0.0042	0.0173	0.0233

From published data [7] the E_A for lithium thickened grease in a non-polar (paraffinic) oil is approximately 2.2 10^4 (J mol^{-1}). This can be converted to (kWh/kg) by using the mass fraction of thickener in the base since the saponification reaction is a 1:1 mole ratio.

E_A = 2.2 10^4 [J mol^{-1}] *or 2.2* 10^4 [kJ kmol^{-1}] x $\frac{1}{306.42}\frac{kmol}{kg}$ x$\frac{1}{3600}\frac{1}{s}$ = 0.02 [kWh kg^{-1}] [14]

So, adding all the above we see that:

$\sum_i^n Q$ = 0.1328 [kWh kg^{-1}]

Solid lubricant and organic additives interactions: Performancebooster or performance killer?

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Abstract

Lubricating greases have to fulfil many different tasks including lubrication and surface protection in order to increase the lifetime of working parts. Base oil and thickener have to be chosen carefully to give to the lubricant its basic properties. The fine-tuning of the composition can be achieved by adding different types of additives: tackifiers, corrosion- and rust inhibitors, anti-oxidants, metal deactivators, extreme-pressure and anti-wear additives as well as solid lubricants. High performance additives can be in competition with each other as they generally interact with the metallic surface.

This study aims to observe the interaction between common organic additives and solid lubricants based on synthetic metal sulfides.

Key Words: solid lubricant, metal sulfide, organic additive, greases, high performance

I. Introduction

There are numerous grease compositions, which can be formulated to meet the requirements of industrial applications. One of the advantages of using grease over oils is the possibility to use solid additives with wide specification in terms of particle size (nano- up to micrometric). Several thousands of compositions are currently in use worldwide and each ingredient contributes to the properties of the grease. Typical grease compositions contain 65 to 95% w/w base oils, 5 to 35 % w/w thickeners and 0 to 10% additives. According to the latest market study lithium and lithium complex thickened greases still represent three quarters of the base soap used worldwide and 90 % contain mineral oil. Usually greases contain the following additives in different concentrations to fulfil different tasks: antioxidants, corrosion inhibitors, extreme pressure (EP) and antiwear (AW) additives, metal deactivators, solid lubricants and tackifiers. The mechanism of lubrication of some additives is partially explained by a reaction with the metal surface. This is the case for some corrosion inhibitors, metal passivators and sulfur carriers used as EP additives. Solid lubricants and particularly metal sulfides also act on the metallic surfaces. The lubricating mechanism of molybdenum disulfide is for example partly explained by the lamellar structure and the adhesion to the metal surface. Therefore when additives are combined, competitive mechanisms can occur. In this study, interactions between common organic additives and solid lubricants based on the metal sulfides molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), tin disulfide (SnS_2) and bismuth sulfide (Bi_2S_3) are investigated.

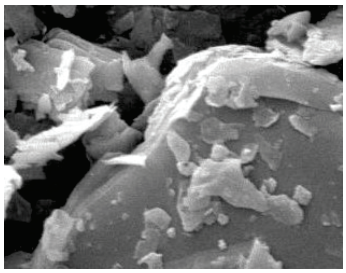
II. Additive Review

a) Solid lubricants

Solid lubricants are necessary for improved emergency running properties. They are also used for extreme pressure and high temperature applications, due to their high load carrying capacity and thermal stability. They effectively reduce friction and wear between contacting surfaces in relative motion. The most important property for metal sulfides remains the high load-carrying capacity.

The most common and still the most widely used metal sulfide in greases is molybdenum disulfide. In this study, the MoS_2 comes from a natural ore while tungsten, tin and bismuth sulfides are manufactured synthetically. The purity of the synthetic products is over 99%.

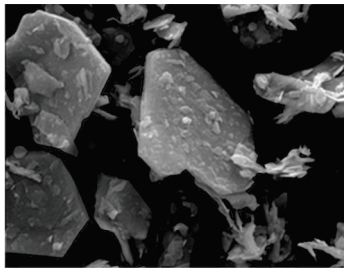
Molybdenum disulfide is a structural lubricant. It adheres readily to most substrates. The hexagonal and lamellae structure (picture 1) provides good friction properties.



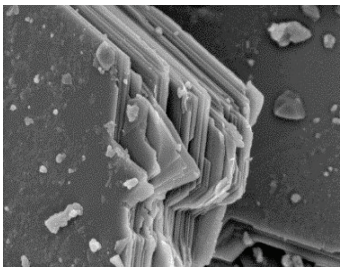
Picture 1: MoS2

While adhesive forces between molybdenum disulfide and solid substrates are usually high, the cohesive forces between the lamellae of molybdenum disulfide are low. It follows that the coefficient of friction between lamellae will be much lower thanthat between a lamella and a ductile substrate and slip will take place preferentially between the lamellae.

Tungsten disulfide and tin disulfide also have a lamellar structure (picture 2 and 3) and therefore show similar mechanism of lubrication. Tungsten disulfide has been generally reported as having better oxidation resistance than molybdenum disulfide [1].

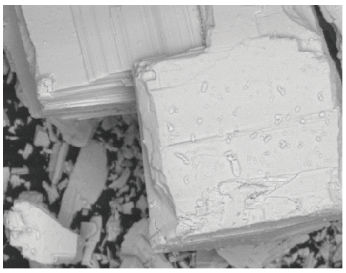


Picture 2: WS2



Picture 3: SnS2

The substrate adhesion of tin disulfide is not as good as that of molybdenum disulfide. This is the reason why it needs a supporting medium like oil, grease or a coating. In SnS_2, the tin is present in its more stable tetravalent form and not readily able to change its valence. The formation of bonds as well as the decomposition generally needs higher activation energy [2].



Picture 4: Bi_2S_3

Bismuth sulfide is in use in heavy duty and mining applications where high load carrying capacities are needed.The face-centered orthorhombic crystal structure of the bismuth sulfide allows direct contact of the bismuth atoms with the metal surfaces making the formation of the "intermetallic compound" bismuth-iron easier. This intermetallic layerprotects the surfaces from wear [3].

In a previous review, it has been demonstrated that effective improvement can be achieved bycombining different solid lubricants [4].

b) Organic additives

Organic additives build reaction layers on the metallic surface. The organic additives used thesupposed mechanisms are listed in the table below [5, 6].

Table 1: Additives and mechanisms

Additive Type	**Chemical Name**	**Mechanism and properties**
Mixed additives (sulfur phosphorous)	Metallic dithiophosphates (Mo, Zn)	Polyphosphates and metal sulfide (FeS_X, ZnS) formation [5].
	Zinc ditiophosphate (ZnDTP)	AW, antioxidant and corrosion inhibitor
	Molybdenum dithiophosphate(MoDTP)	Friction modifier, AW
Sulfurous additives	Molybdenum dithiocarbamate(MoDTC)	Extreme pressure (EP) additives, formation of metal sulfide.
	Dialkyl-2,5-dimercapto-1,3,4- thiadiazole (DMTD)	
	Calcium sulfonate (R-SO_3)(rust inhibitor)	Molecules with long alkyl chains and polar groups, can be adsorbed on the metal surface forming densely packed, hydrophobic layers.
Phosphorous additive	Triisobutylphosphate (TBP)	Anti-Wear additive (AW). Iron phosphate glass formation, or ironphosphide formation.

Because of high surface activity, anticorrosion additives compete with other polar additives like antiwear and extreme pressure additives for the metal surface and can therefore reduce efficiency.

Several investigations about the synergy between organic additives are available. For example, **MoDTC** contributes to the tribochemical formation of MoS_2. In the presence of ZnDTP, the formation of MoS_2 at the contact area is enhanced. In the figure 1 the mechanism of formation of MoS_2 from MoDTC proposed by M.I. de Barros Bouchet and his team is shown figure 1 [7]. The precursor for MoS_2 formation might be oxysulfide species coming from the degradation of the MoDTC molecule. The role of ZnDTP is principally to provide the sulfur atom to complete the sulfurization of the oxysulfide and another is to form an effective antioxidant layer.

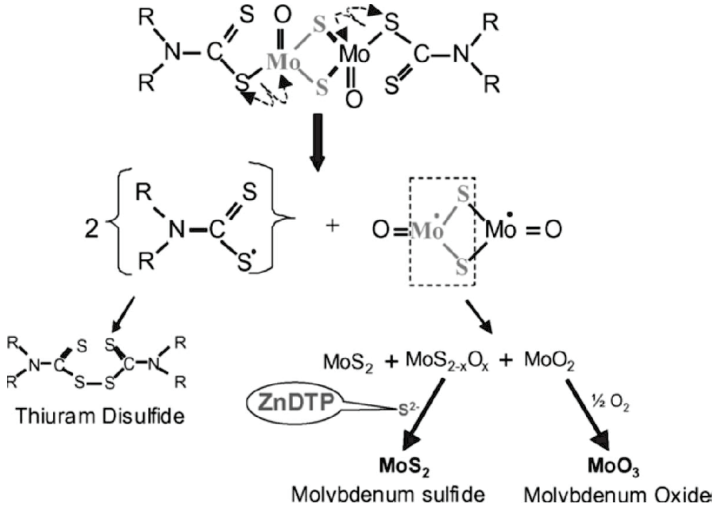


Figure 1: Formation of MoS2 from MoDTC [7].

DMTD (Dialkyl-2,5-dimercapto-1,3,4-thiadiazole) derivatives are usually known as metal passivators and sulfur scavengers, but they also exhibit excellent EP properties. They function as sulfur scavenger as described in figure 2.

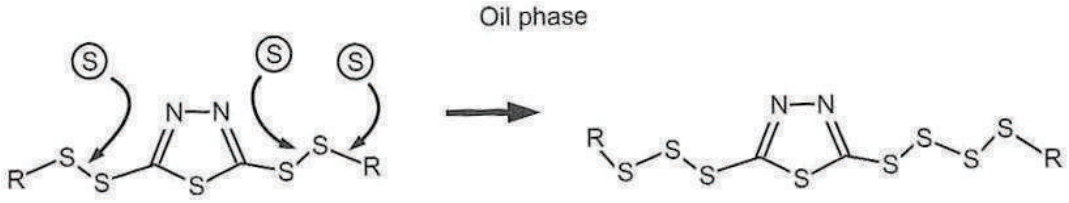


Figure 2: Function of DMTD as sulfur scavenger [8].

Aili Ma's team showed a synergy between 2% (w/w) DMTD and 2% (w/w) MoDTP on the four- ball test wear and weld point [9].

The mechanism of sulfur containing organic additives is linked with the formation of metal sulfide at the surface. This study aims to observe if the performance can be further enhancedwith the presence of metal sulfides.

III. Grease preparation and test methods

Greases are prepared and homogenized with a triple roll mill. The base grease consists of lithium 12-Hydroxystearate soap with a paraffinic oil. The concentration (w/w) of organic additive is between 0.5% and 1% depending on the recommendation of the raw material supplier. Solid lubricants are added at a 3% treat rate.

Greases are tested with two different oscillating friction tribometers: SRV and OFT 2000. Different testing methods cover procedures for determining coefficient of friction, wear protection ability and extreme-pressure properties in linear oscillating motion. The testing methods are shown in table 2.

Table 2: Parameters of oscillating test methods applied on SRV and OFT 2000.

Method	Result	Temp. [°C]	Freq. [Hz]	Stroke [mm]	Duration [min]	Load
ASTM D 5707	Coefficient of friction and wear	50	50	1	120	200 N
OFT 2000	Coefficient of friction and wear	80	14	3	65	500 N
ASTM D 5706	Pass load	50	50	1	40	+100 N/2 min

The **four-ball apparatus** is one of the oldest and well-known simple bench tests for liquid andsolid lubricants. The test consists of a steel ball rotating at constant speed and constant load on three fixed steel balls. The three-point contact is lubricated with the lubricant of interest. It allows the determination of the wear preventive properties by measuring the average wear scar of the fixed balls (DIN 51350-05) [10]. The testing procedure DIN 51350-4A describes how to determine the welding load of lubricants [11]. The load level is increased stepwise until welding occurs. The welding load is the

lowest applied load at which sliding surfaces seize and then weld. The parameters of the standardized Four-Ball testing methods used in this studyare summarized in table 3.

Table 3: Parameters of the Four-ball test methods used in this study.

Method	Result	Temperature [°C]	Rotating speed [rpm]	Duration [seconds]	Load [kg]
DIN 51350-05-E	Wear	18-40	1420	60	100
DIN 51350 -4A	Weld point	27 ± 8	1420	60	Load steps

In order to increase the precision of the results, at least two repeating measurements are carried out for each standard test method and the average results are described in the following sections.

IV. Results

a) Analysis of the coefficient of friction

i. SRV ASTM D 5707

The effect of organic additives used as single components is shown figure 3. MoDTP strongly influences the behavior of the grease and significantly reduces the coefficient of friction. ZnDTP, MoDTC and TBP show a lower and more stable coefficient of friction than the base grease. Calcium sulfonate and DMTD show unstable behaviors with transient peaks under the condition of this test.

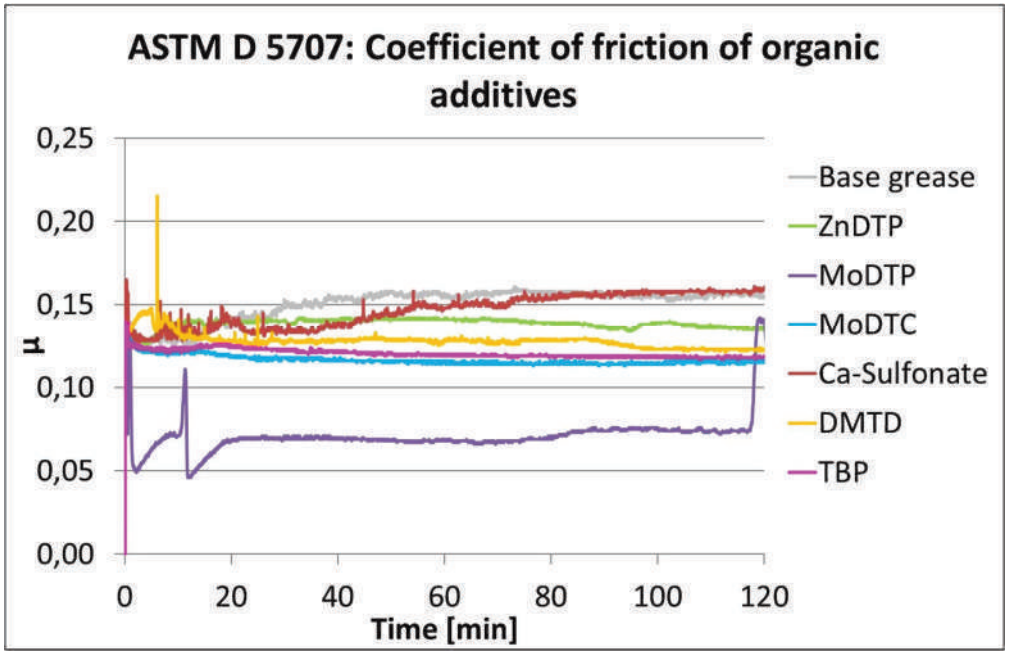


Figure 3: ASTM D5707 - coefficient of friction of organic additives

The effects of pure sulfides as single components are shown in figure 4. MoS_2, WS_2 and SnS_2 contribute to a significant reduction of the coefficient of friction while Bi_2S_3 shows unstable behavior with transient peaks.

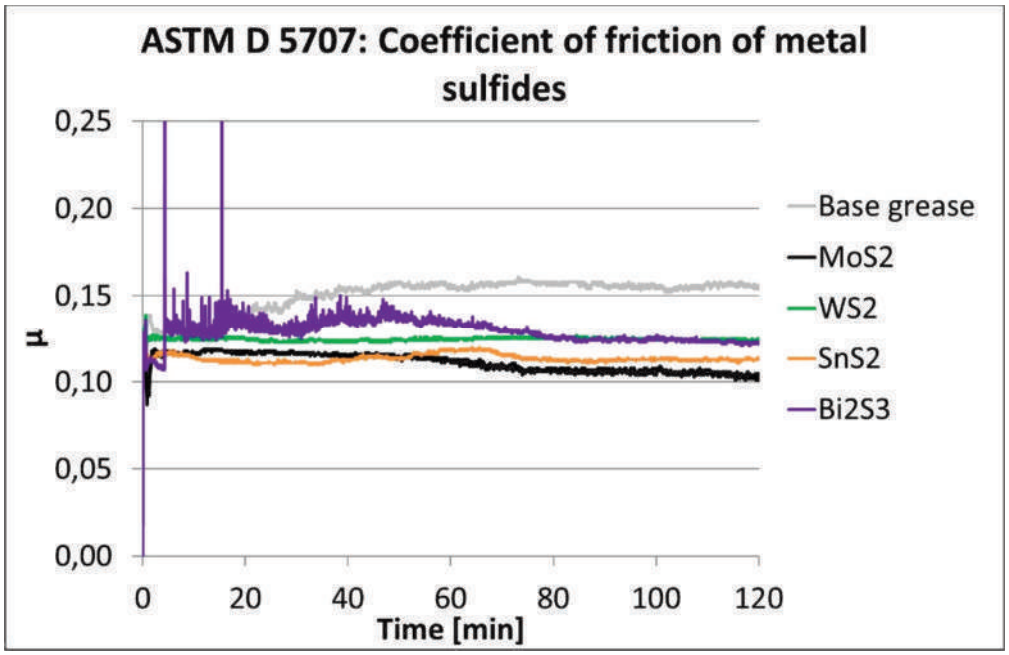


Figure 4: ASTM D5707 - coefficient of friction of metal sulfides

The results of the combination of organic additives and metal sulfides are presented in figures5 to 8.

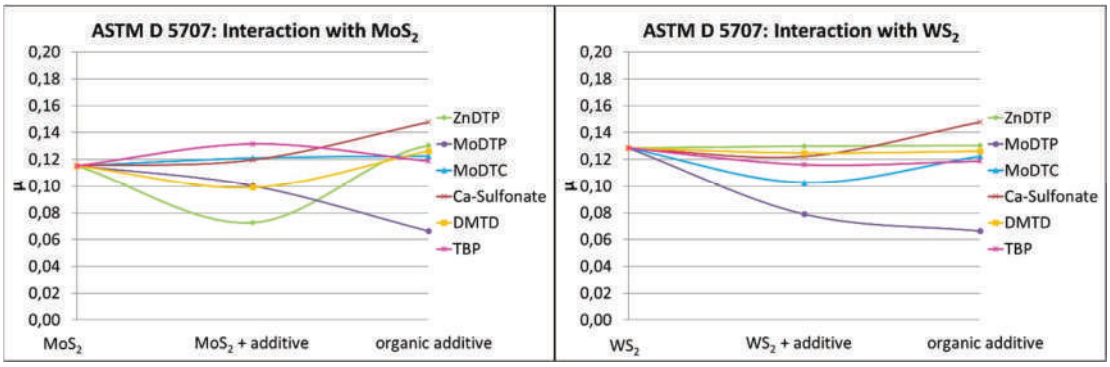


Figure 5 & 6: ASTM D 5707 - Interaction between organic additives and MoS_2 (left) and WS_2 (right)

For MoS_2, a strong synergy concerning the coefficient of friction is observed in combination with ZnDTP. In the presence of MoS_2 and MoDTP, the coefficient of friction is only slightly improved but does not reach the level of MoDTP used as a single component. MoS_2 combined with DMTD shows positive interactions while the MoS_2 combined with TBP rather shows poorperformances.

There is a synergy between WS2 and MoDTC under this testing condition. MoDTP in combination with WS2 shows a very low coefficient of friction, but does not reach the level ofMoDTP as a single substance. The coefficients of friction of WS2 combined with the other tested organic additives are within the same range.

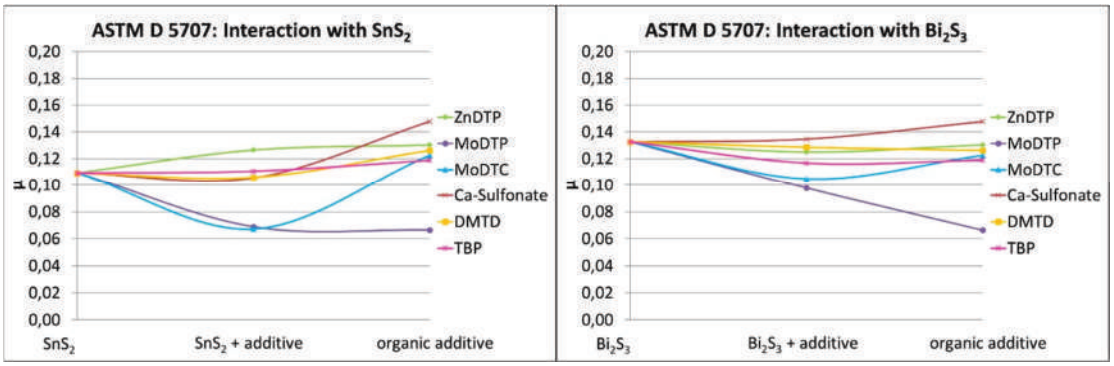


Figure 7 & 8: Interaction between organic additives and SnS2 (left) and Bi2S3 (right)

Under the conditions of this test, SnS2 and MoDTC are acting synergistically reaching very low values of coefficient of friction. The combination of SnS2 with MoDTP also leads to very low coefficient of friction. The performance of MoDTP seems to be dominant in this case.

Under oscillating condition, Bi2S3 shows a high coefficient of friction and a lot of transient peaks. The addition of MoDTP, MoDTC and TBP leads to the stabilization of the coefficient of friction. According to figure 8 (left) Bi2S3 shows a slight synergy with MoDTC.

ii. OFT 2000

Some additives need higher energy to build a tribolayer. This is why further tests are being carried out with higher stroke (3 mm), higher load (500N), higher temperature and lower speed, in order to remain in the mixed and boundary friction area and to simulate extreme conditions. The effect of organic additives as single components are shown below.

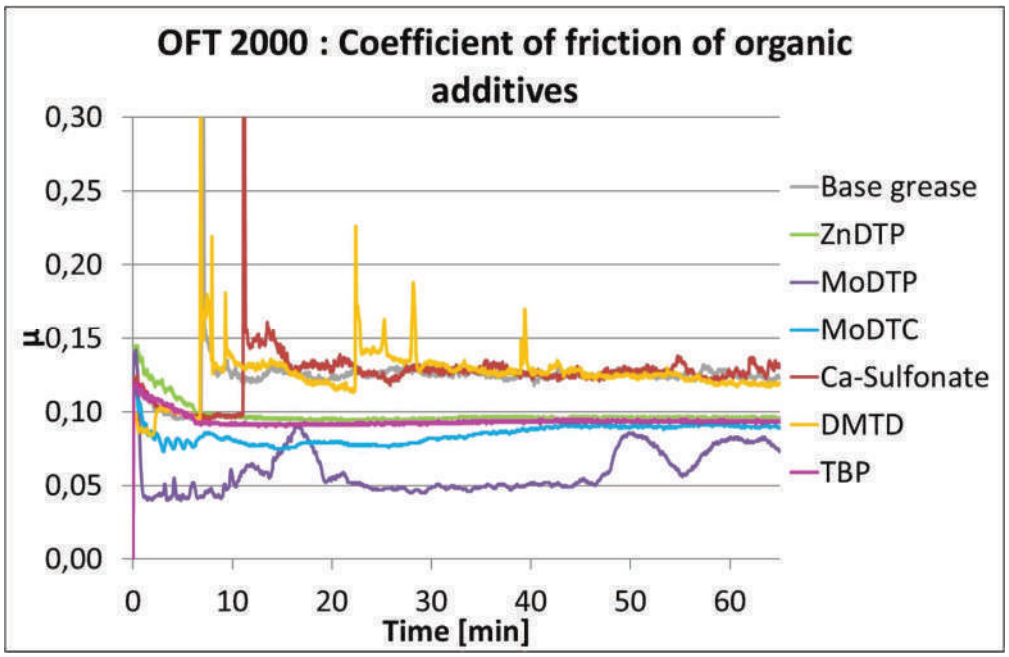


Figure 9: OFT 2000 – Coefficient of friction of organic additives

Under higher load and lower speed, both DMTD and Calcium Sulfonate show transient peakswhile other additives reduce friction in comparison to the base grease. The very low coefficient of friction of MoDTP is confirmed, and the results obtained are similar to those obtained on SRV test rig.

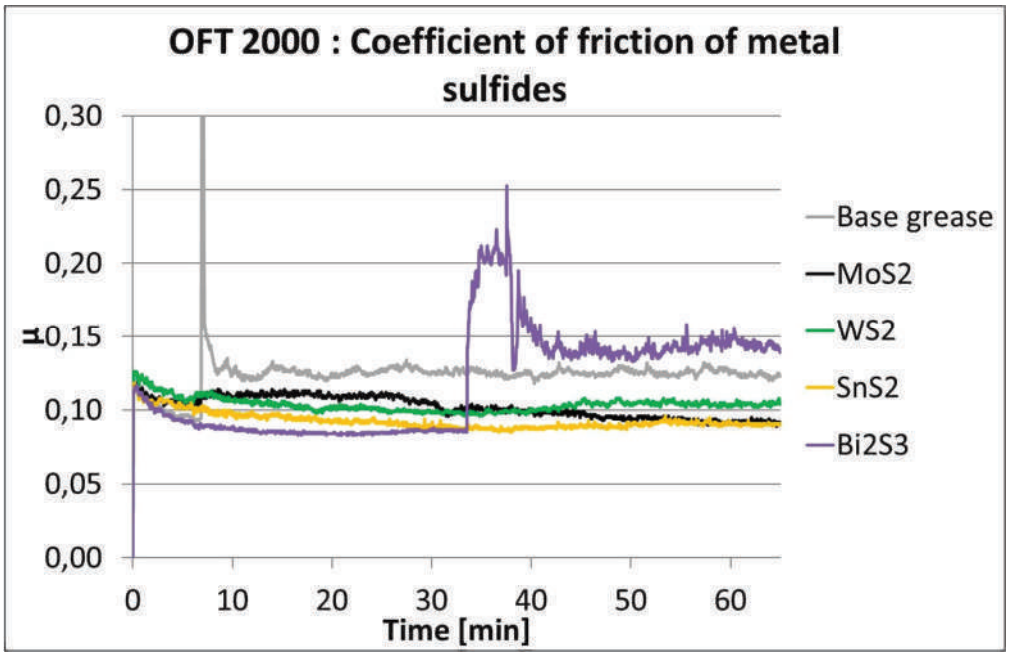


Figure 10: OFT 2000 – Coefficient of friction of binary sulfides

Under the condition of this test Bi_2S_3 shows partial welding at the middle of the test, while other metal sulfides have a more stable coefficient of friction.

The interactions between metal sulfides and organic additives are presented figure 11 to 14.

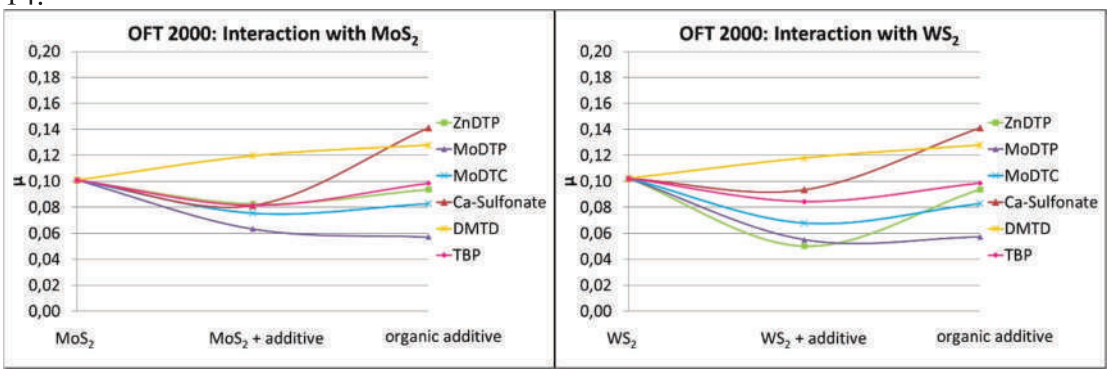


Figure 11 & 12: OFT 2000 - Interaction between organic additives and MoS2 (left) and WS2 (right)

MoS2 and WS2 react similarly at higher load, in the presence of organic additives. They showa synergy in the presence of ZnDTP and MoDTC.

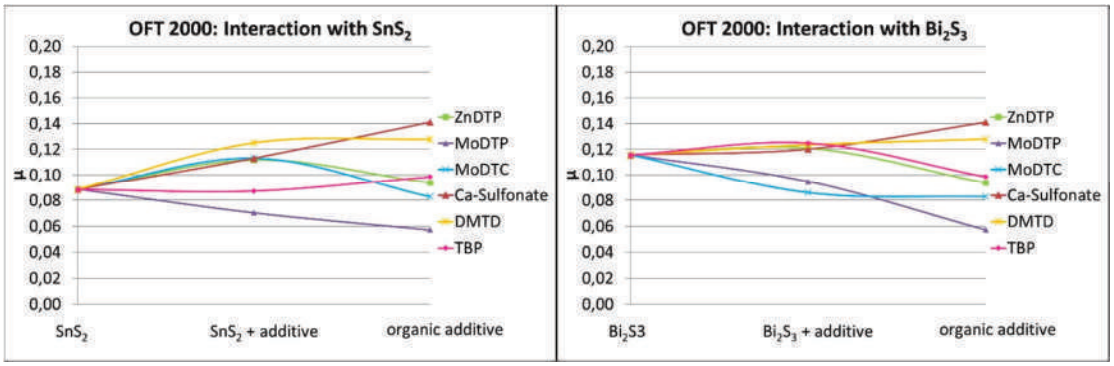


Figure 13 & 14: OFT 2000 - Interaction between organic additives and SnS2(left) and Bi2S3 (right)

While there is a synergy between ZnDTP and MoS2 and between ZnDTP and WS2, there is no synergy of ZnDTP with either SnS2 or Bi2S3 in terms of coefficient of friction.

A competitive mechanism seems to occur at higher loads between SnS2 and MoDTC as the performance of the combination is worse than the performance of single components. This result was fully unexpected, because under lower load and higher speed conditions as for theASTM D 5707, SnS2 and MoDTC worked synergistically.

The use of MoDTP significantly reduces the coefficient of friction for all sulfides although forBi2S3 the effect is not as high as for other binary sulfides. The addition of MoDTP and MoDTCto Bi2S3 leads to the stabilization of the coefficient of friction.

b) Wear analysis after oscillating tests

The wear scar areas of the balls used for the tests under oscillating motion are measured witha light microscope and the results are reported in table 4.

MoS2 is acting synergistically with MoDTP and ZnDTP. There is a synergy with DMTD but only for SRV – wear.

The combination of MoS2 with TBP leads to competitive mechanism and decrease the wearperformance in both tests. It was totally unexpected as TBP positively influences the wearbehavior of SnS2 and WS2, which are very close to MoS2 in terms of chemistry

and structure. **WS_2** in combination with organic additives leads to wear scar values situated between the values of the single components. WS_2 is compatible with most organic additives.

SnS_2 shows a particular wear behavior. The combination of SnS_2 with ZnDTP shows a synergy in terms of wear for the SRV test. On the contrary, according the OFT 2000 wear values the combination of ZnDTP with SnS_2 shows higher wear than the single components. Similar observations are made with MoDTC and SnS_2. Different lubricating mechanisms are probably involved in the presence of SnS_2 under the different testing conditions. The combination of SnS_2 with MoDTP leads to a synergy in terms of wear.

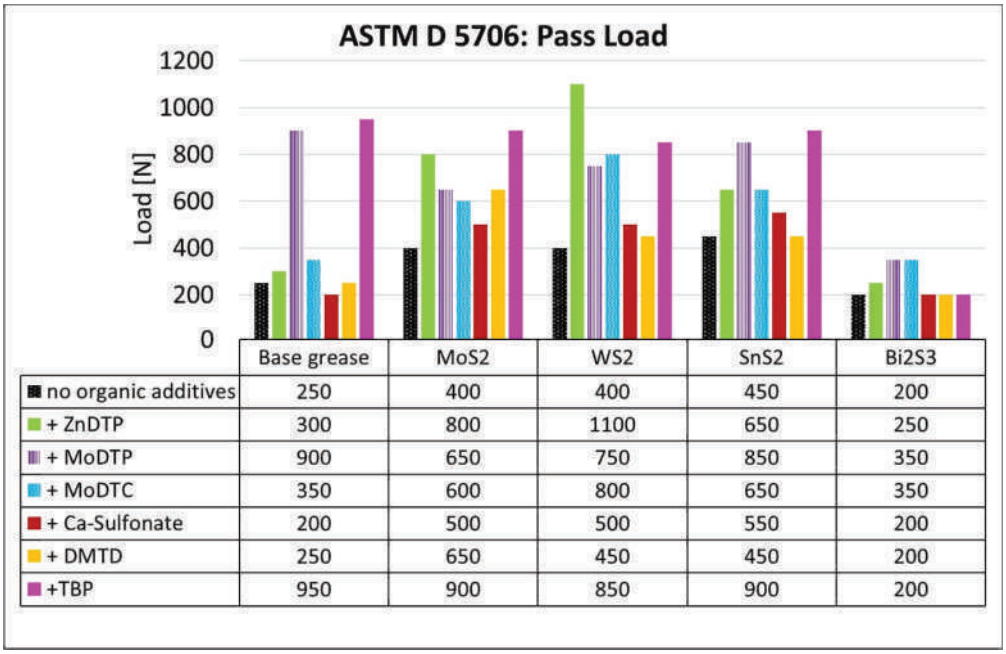
Due to the behavior of **Bi_2S_3** during oscillating motion the standard deviation of wear results is extremely high for this product as transient peaks and microwelding occured. Only MoDTP and MoDTC can lead to a stabilization of the coefficient of friction and reduce the wear in this case.

Table 4: Wear analysis on SRV Test and OFT 2000 tests.

	ASTM D 5707 Wear scar area [mm²]					**OFT 2000 Wear scar area [mm²]**				
	Base grease	MoS_2	WS_2	SnS_2	Bi_2S_3	Base grease	MoS_2	WS_2	SnS_2	Bi_2S_3
Without Additives	0,52	0,19	0,22	0,23	0,70	0,93	0,31	0,37	0,39	0,69
ZnDTP	0,25	0,15	0,23	0,16	0,30	0,30	0,31	0,34	0,44	1,09
MoDTP	0,22	0,18	0,25	0,18	0,24	0,35	0,29	0,34	0,34	0,52
MoDTC	0,29	0,22	0,20	0,17	0,24	0,27	0,30	0,30	0,47	0,50
Ca-Sulfonate	0,55	0,21	0,22	0,24	0,66	0,91	0,28	0,30	0,40	0,96
DMTD	0,41	0,16	0,35	0,23	0,46	1,39	0,87	0,44	1,13	0,71
TBP	0,15	0,37	0,19	0,18	0,26	0,30	0,38	0,33	0,35	1,56

The wear analysis shows that different testing conditions lead to different results and synergies.

c) ASTM D5706: Pass load



	Base grease	MoS2	WS2	SnS2	Bi2S3
no organic additives	250	400	400	450	200
+ ZnDTP	300	800	1100	650	250
+ MoDTP	900	650	750	850	350
+ MoDTC	350	600	800	650	350
+ Ca-Sulfonate	200	500	500	550	200
+ DMTD	250	650	450	450	200
+TBP	950	900	850	900	200

The pass loads of the greases are shown in figure 15.

Figure 15: ASTM D5706 – Pass load

MoDTP and TBP used as single components significantly improve the pass load of the basegrease.

The pass load of MoS_2 is improved when organic additives are added to the greases and synergies with ZnDTP and MoDTC are observed.

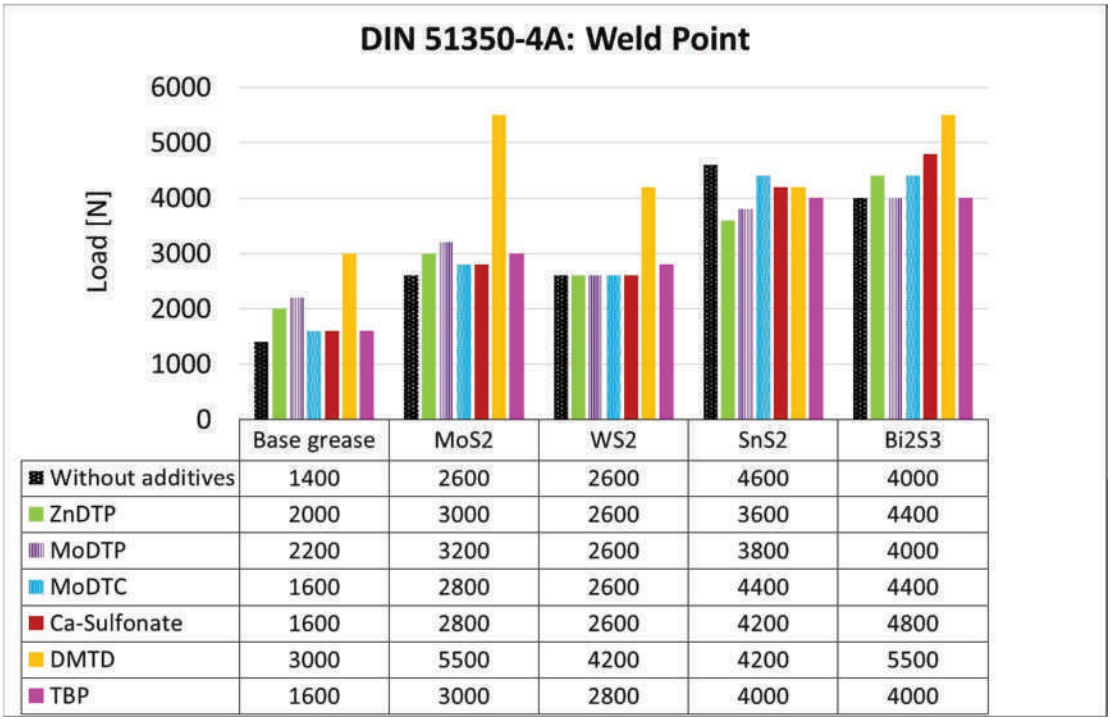
WS_2 and SnS_2 show similar behaviors in the presence of organic additives. The synergy between WS_2 and ZnDTP leads to the highest pass load of this series.

Bi_2S_3 shows poor performance in terms of pass load. The combination with organic compounds slightly improves this behavior, but does not lead to superior performances.

This test shows that organomolybdenum compounds (MoDTC, MoDTP), and phosphorous compounds (ZnDTP and TBP) generally improve the pass load of metal sulfides.

d) Four ball tests: DIN 51350-4A and 5E

The greases are tested with the four-ball bench test according to DIN 51350-4A and 5E. Figure 16 shows the results for weld point.

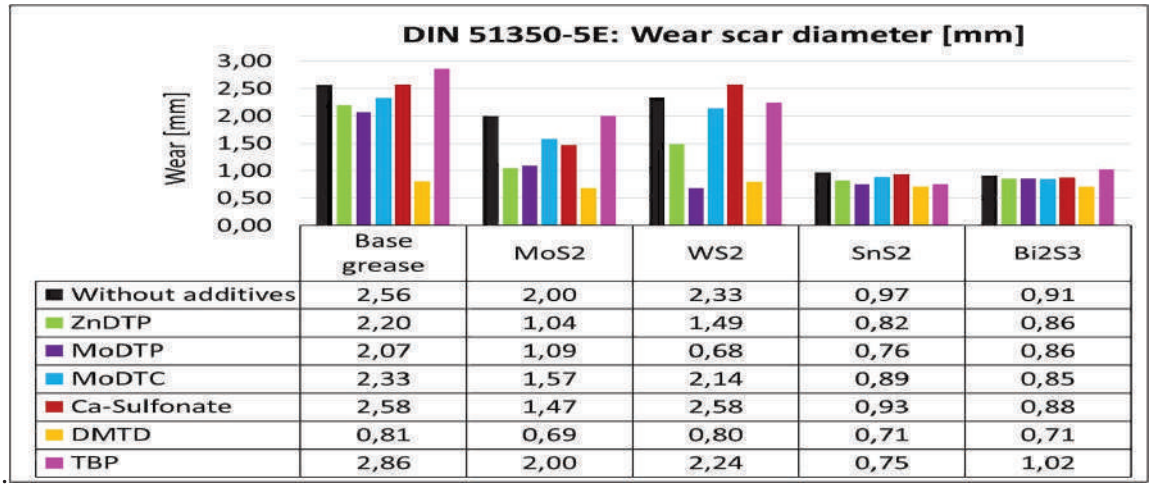


	Base grease	MoS2	WS2	SnS2	Bi2S3
Without additives	1400	2600	2600	4600	4000
ZnDTP	2000	3000	2600	3600	4400
MoDTP	2200	3200	2600	3800	4000
MoDTC	1600	2800	2600	4400	4400
Ca-Sulfonate	1600	2800	2600	4200	4800
DMTD	3000	5500	4200	4200	5500
TBP	1600	3000	2800	4000	4000

Figure 16: DIN 51350-4A - Weld point

Generally, the weld point remains very close to the value of the metal sulfides alone. DMTD is the exception. It shows very interesting properties and contributes to a synergistic improvement of the performances in combination with MoS2, WS2 and Bi2S3SnS2 has a particular behavior. While the use of organic additives either improves or does not have any influence on other sulfides, it seems that the use of organic additives adversely affects the performance of SnS2, particularly the use of MoDTP and ZnDTP.

The DIN 51350-5E is performed on the greases and the wear results are presented in figure17



	Base grease	MoS2	WS2	SnS2	Bi2S3
Without additives	2,56	2,00	2,33	0,97	0,91
ZnDTP	2,20	1,04	1,49	0,82	0,86
MoDTP	2,07	1,09	0,68	0,76	0,86
MoDTC	2,33	1,57	2,14	0,89	0,85
Ca-Sulfonate	2,58	1,47	2,58	0,93	0,88
DMTD	0,81	0,69	0,80	0,71	0,71
TBP	2,86	2,00	2,24	0,75	1,02

Figure 17: DIN 51350-5E – Wear on four-ball test.

DMTD improves the wear behavior of the greases independently from the combination, underthe conditions of this test. The addition of MoDTP and ZnDTP to sulfides leads to an improvement of the performances, particularly the combination of WS2 with MoDTP. SnS2 and Bi2S3 lead to lower wear, independently from the organic additives.

V. Discussion

A ranking system from 0 up to 10 points has been created to better observe synergies between the components, 10 points meaning good performance. Performance overviews of combination of metal sulfides with additives are shown in figures 18 to 21.

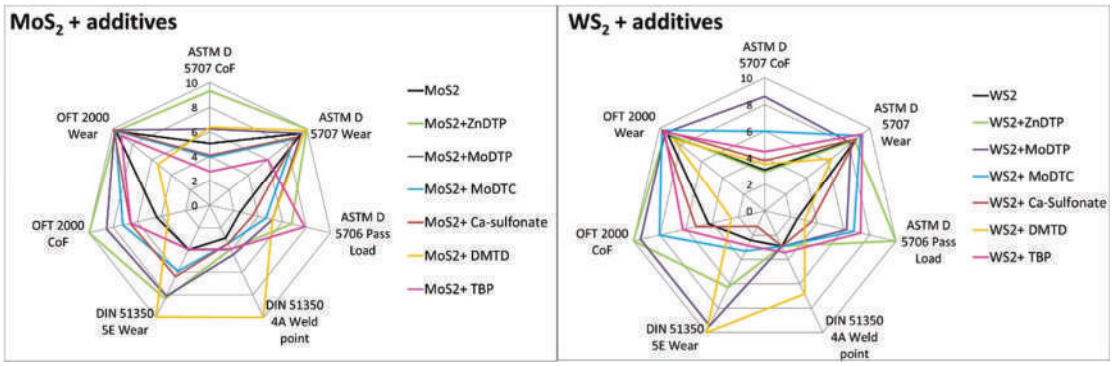


Figure 18 & 19: Performance overviews of combination of metal sulfide and organic additives MoS2 (left)and WS2 (right)

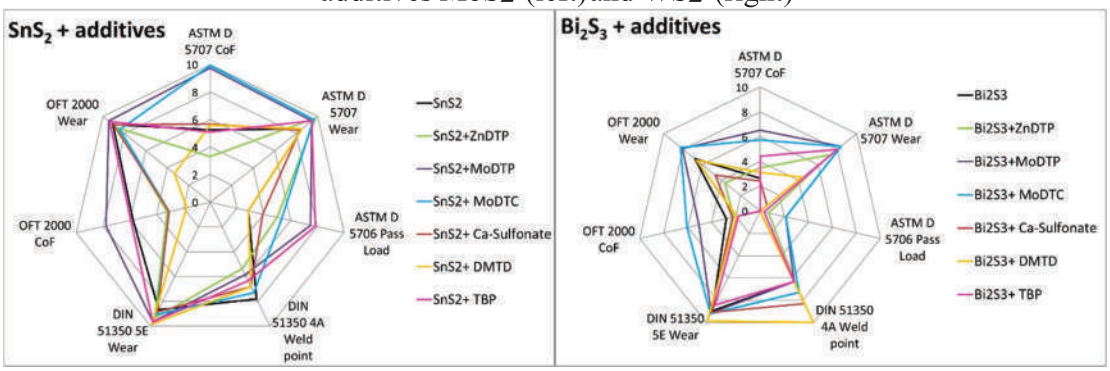
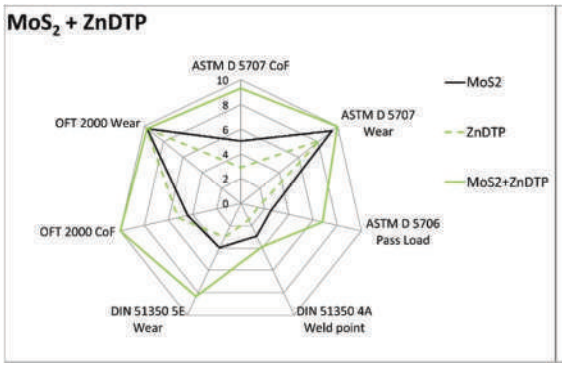


Figure 20 & 21: Performance overviews of combination of metal sulfide and organic additives SnS2 (left)and Bi2S3 (right)

Combination of binary sulfides and organic additives can lead to strong performance improvements either for specific tests or in general.

Synergies were identified between the following components:

- MoS2 and ZnDTP (figure 22)
- WS2 and ZnDTP, WS2 and MoDTC (figure 23)
- Bi2S3 and MoDTC (figure 24)



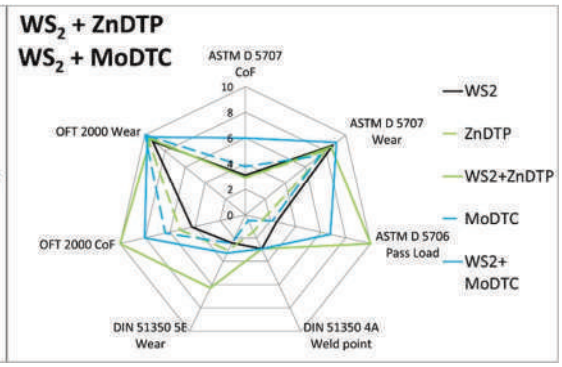


Figure 22: Synergy MoS2 and ZnDTP Figure 23:Synergy WS2 and ZnDTP / MoDTC

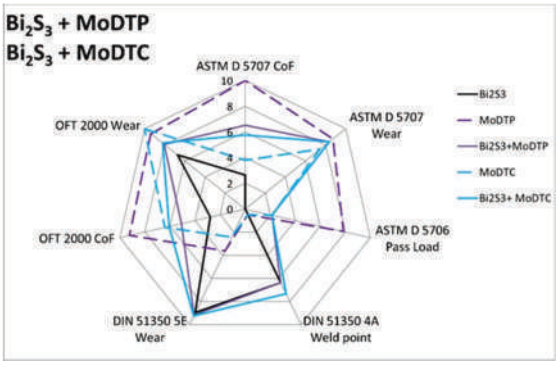
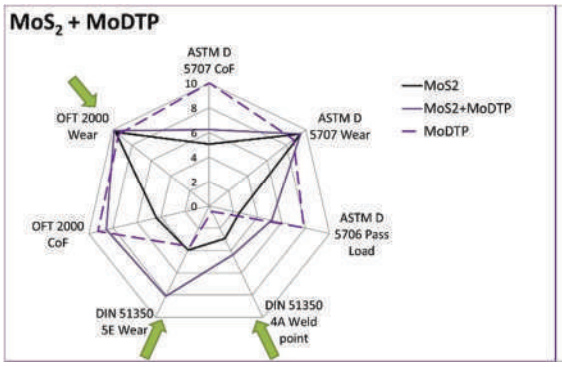


Figure 24: Synergy Bi2S3 and MoDTC

Positive interactions and synergies in specific tests are observed for the followingcombinations:

- MoS2 and MoDTP (figure 25)
- WS2 and TBP ,WS2 and MoDTP (figure 26)
- SnS2 and MoDTP, SnS2 and TBP (figure 27)



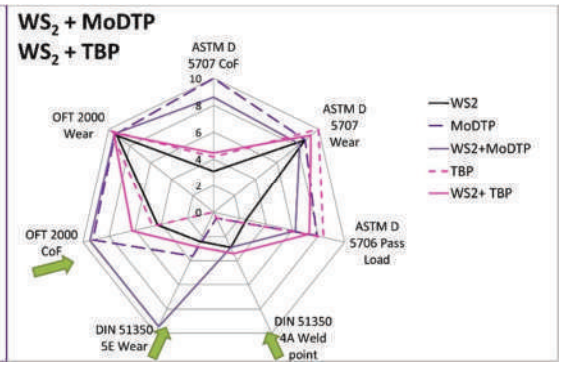


Figure 25: Positive interaction MoS2 and MoDTP Figure 26: Positive interaction WS2 and MoDTP / TBP

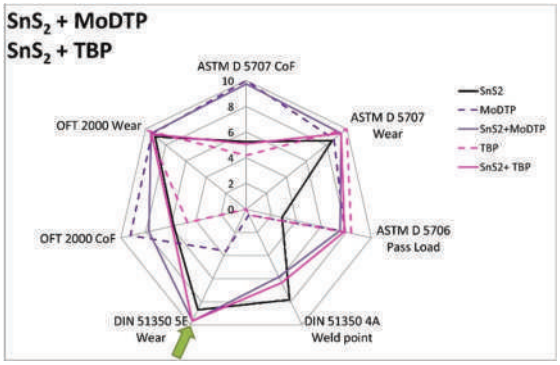
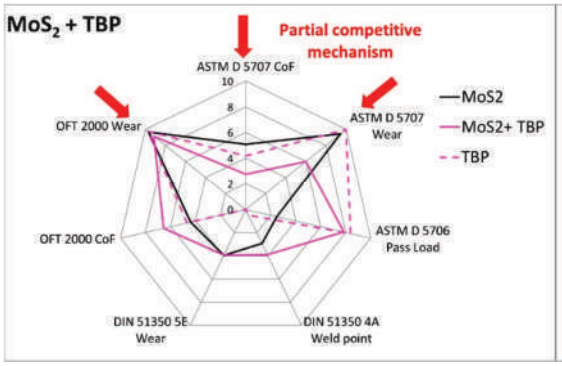


Figure 27: Positive interaction SnS2 and MoDTP / TBP

Negative interactions are observed between:

- MoS2 and TBP increase of wear (figure 28)
- SnS2 and ZnDTP increase of coefficient of friction (figure 29)
- Bi2S3 and ZnDTP, Bi2S3 and TBP (figure 30)



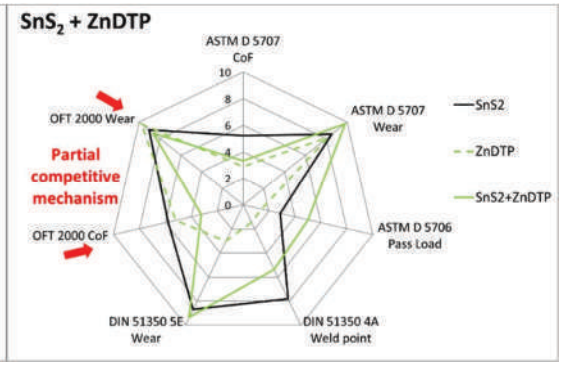


Figure 28: Competitive mechanism MoS2 and TBP Figure 29: Competitive mechanism SnS2 and ZnDTP

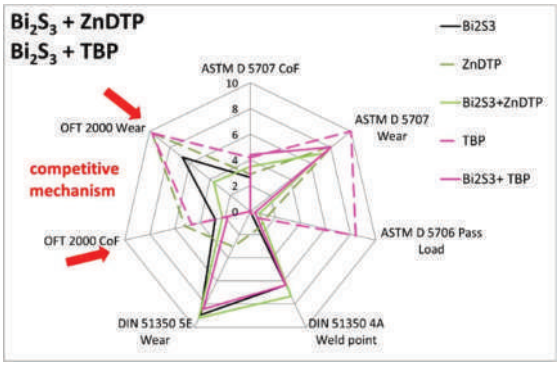


Figure 30: competitive mechanism Bi2S3 and ZnDTP / TBP

VI. Conclusion

It is shown that the identification of synergies strongly depends on the testing conditions. The same combination of organic additive and metal sulfide reacts differently when the testing conditions change.

Although the metal sulfides used in this study have related chemistry, the interactions with thesame organic additives lead to different results.

Strategies to improve grease performances with metal sulfides as solid lubricants, should include optimization of additive concentration to generate the best performance-boost.

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Synthesis and Application of Magnetorheological (MR) Grease: A Review

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KEY WORDS: Magnetorhelogical Fluids, Magnetorhelogical, MR Fluids, MR Grease, Grease, NLGI, Stability, Consistency, Thickening agent, MR brake, MR damper.

ABSTRACT
Magnetorhelogical (MR) materials are a kind of smart materials whose mechanical properties such as apparent viscosity and shear stress can be altered dramatically and reversibly when stimulated by a magnetic field. They have ability to change from a low viscous liquid state to high viscous semi solid or solid state instantaneously upon application of magnetic field. This response of MR fluids to the magnetic field makes them suitable for engineering applications which necessitate variable dynamic performance such as brakes, dampers, clutches and isolators, etc. However MR fluids suffer from the problems like gravitational settling and agglomeration of magnetic particles. They also require sealing/replenishing mechanism to keep themselves within the devices. This emphasize the need of grease like composition which has variable flow behavior like MR fluids and can remain within the device without any aid of sealing mechanism and also has very good resistance against settling of the magnetic particles. This necessity leads to Magnetorhelogical (MR) grease formulation. MR grease shows variation in its consistency on application of magnetic field without suffering from problems of sedimentation & leakage and therefore can be used as more effective substitute of MR Fluids in engineering applications.
This review paper discusses the important issues like MR Effect produced by MR grease; synthesis and scope of application of Magnetorhelogical (MR) grease and presents a comprehensive review on the current scenario, recent updates and developing trends in the field of Magnetorhelogical Grease.

1. INTRODUCTION:

Magnetorhelogical (MR) fluids were discovered by Jacob Rabinow in 1948 at national bureau of science, USA [1,2].These fluids are known for change in their flow behavior i.e. viscosity on application of magnetic field. MR fluids have the ability to change from a fluid state to a semi solid or solid state instantaneously upon application of magnetic field and thus exhibit variable yield stress. This unique ability makes these fluids suitable for application in devices demanding controllable behavior i.e. dampers, brakes, shock absorbers, clutches and engine mounts [3]. But there are some problems associated with these fluids. Magnetorhelogical fluids require sealing / replenishing mechanism to keep themselves within the devices .They also suffer from the problems like gravitational settling and agglomeration of magnetic particles. This emphasize the need of grease like Magnetorhelogical composition which has variable flow behavior like MR fluids and can remain within the device without any aid of sealing mechanism and also has very good resistance against settling of the magnetic particles. Magnetorhelogical (MR) Grease is one such type of composition.
This review paper describes the important issues related to MR Grease with current level of technical capabilities and limitations. It also provides an updated review of recent MR Grease researches with different references. In addition, a case study related to synthesis and performance evaluation of Magnetorhelogical Grease has been presented.

2. MR TECHNOLOGY:

Magnetorhelogical (MR) fluids can be considered as smart lubricant that find its application in bringing dynamic change in performance measures like damping resistance as in MR-dampers and braking torque in MR-brakes. MR fluids are suspensions of non-colloidal, multi domain; micron sized soft-magnetic particles in non magnetic carrier medium [4]. Magnetic material is usually Iron and carrier fluids may be mineral oil, synthetic oil, water etc. Under the influence of magnetic field, these particles polarize and form columnar structure parallel to the applied field, thus increasing the apparent viscosity of the fluid. The viscosity change is very rapid and completely reversible.

Therefore During the past few years a number of commercially available products (or near commercialization) have been developed [5]:

- Linear MR dampers for real-time active vibration control systems ,
- Linear / rotary brakes for low-cost, accurate, positional & velocity control of pneumatic actuator systems,
- Rotary brakes to provide tactile force-feedback in steer-by wire systems,
- Linear dampers for real-time gait control in advanced prosthetic devices,
- Adjustable real-time controlled shock absorbers for automobiles,
- Large MR fluid dampers to control wind-induced vibrations in cable-stayed bridge
- Very large MR fluid dampers for seismic damage mitigation in civil engineering structures,
- MR dampers for washing machines,
- Magnetorhelogical fluid polishing tools,

3. CONCEPT OF MAGNETORHELOGICAL (MR) GREASE & ITS APPLICATIONS:

As mentioned earlier MR fluids suffers from some problems. Magnetorhelogical fluids are unable to show enough resistance against gravitational settling of magnetic particles due to the large density difference between densities of magnetic particles (generally Iron with ρ =7.86 g/cm^3) and carrier fluid (i.e. ρ =1 g/cm^3). Moreover they also require seals to prevent their leakage due to their low off-state viscosity.Single and optimum solution of both of these problems may be the addition of a thickening agent like grease in synthesis of Magnetorhelogical fluids.

Actually the ability of a medium to suspend isolated particle or prevent a particle from settling is given by following equation [6],

$$Y_G = \tau_0^G / [gR(\rho^P - \rho) \quad (1)$$

Where r_o^G is the yield stress of the suspending medium (e.g., oil, grease), g is the acceleration due to gravity, R is the particle radius, ρ_P is the particle density, and ρ_0 is the density of the medium. Higher value of Y_G means higher the sedimentation stability. Generally grease has higher value τ_o^G compared to any liquid (i.e. oil), and for that reason grease is a better option compared to any other liquid lubricant and Iron particles remain suspended in grease while settling in silicon oil .

Therefore there is an advantage of a Magnetorhelogical grease composition which controls liquid flow and resists settling of soft-magnetic particles. Such grease will have unique quality to change its flow behavior e.g. consistency on application of magnetic field without suffering from problems of sedimentation & leakage and therefore can be used as more effective substitute of Magnetorhelogical fluids in engineering applications. MR grease is a family of smart materials with reversible rheological properties controlled by an external magnetic field, which is generally prepared by dispersing soft magnetic particles in grease matrix. In a way, MR grease is more like MR elastomer but with softer matrix, which is expected to demonstrate a higher MR effect than its elastomeric brother and lower MR effect than the fluidic member. MR grease carries the family heritage of the MR materials on large MR effect while possesses little sedimentation issue, which provides a reliable and simple solution to design MR devices. Some potential applications for Magnetorhelogical grease have been tabulated in table-1.

Table 1: Potential Applications of MR Grease

1	Automotive Clutches (MRG Clutches)
2	Automotive Brakes(MRG Brakes)
3	Automotive Dampers (MRG Dampers)
4	Earthquake Dampers
5	Prosthetic Knee Dampers
6	Shock Absorbers
7	Engine Mounts
8	Actuator Systems
9	Seals
10	Polishing Devices

4. REVIEW OF AVAILABLE RESEARCH WORK RELATED TO MR GREASE:

As MR grease is relatively new development in the field of MR technology, the studies conducted on MR grease are very few in comparison to studies carried out with MR fluids but recently some important research work has been undertaken on MR Grease. Different researchers have worked on different aspects like effect of type of magnetic material, particle volume, particle shape and size, effect of temperature on performance of MR grease. Some important conclusions drawn from some studies are reported here:

(A) COMPOISION OF MAGNETORHELOGICAL GREASE:

Similar to the synthesis of MR fluids, synthesis of MR grease requires soft magnetic material, a carrier fluid, anti wear, anti oxidant, anti friction and anti corrosion additives. One additional requirement is the thickening agents based grease as the higher value of τ_o^G of the grease helps to prevent sedimentation of particles. Magnetic material and carrier fluids used for synthesis of MR fluids are generally used for the MR grease synthesis. Magnetic material should have properties like high saturation magnetization and low coercivity. Coercivity is the resistance to reversal of magnetization. Though many magnetic materials have these qualities, the most widely used magnetic material for synthesis of MR fluids is Iron specifically Carbonyl Iron derived from thermal decomposition of Iron penta carbonyl as reported in the literature [1, 2, 7, and 8]. Iron has very high saturation magnetization (2.1 T) and very low coercivity (1 Oe =1 Oersted) [9]. Other magnetic materials for MR fluids reported in the literature are Nickel Zinc ferrite [10], Iron oxide coated polymer composite particles [11] and Iron Cobalt alloy [12,13] etc. Though Iron Cobalt alloy has highest saturation magnetization (2.43 T) but its density (8.1 g/cc) is greater than Iron which aggravates the sedimentation problem. Moreover it is costly also therefore has limited applications.

Similar additives are also used in synthesis of MR grease to prevent sedimentation, agglomeration, wear, and oxidation. However different researchers have used different thickening agents for preparation of MR Grease**.** Mostly Lithium-based grease has been used [14, 15]. However other greases have also been used. M.Hari Prasad and K V Gangadharan [16] in their study used clay-thickened grease NLGI 2 Nyco Grease GN 22 for synthesizing various compositions of MR Grease.

(B) RHEOLOGICAL BEHAVIOR OF MR GREASE:

As known, the properties of the matrix have considerable impact on the rheological performance of MR materials. As grease matrix itself is a kind of viscoelastic material, its impact on the rheology of MR grease should be carefully examined and properly understood. The performance of lubricating greases depends on the nature of its components and the microstructure under different operating conditions. In general, lubricating greases are highly structured colloidal dispersions consisting of a thickener dispersed in mineral or synthetic oil.

Huseyin Sahin et al [17] studied the rheological properties of MR grease. In this study MR grease was prepared by mixing magnetic particles with commercial grease. A MR grease with 31.7 % volume fraction of iron particles was characterized using both shear rheometer and flow mode MR rheometer. The results showed that MRG has higher yield stress then conventional MR fluids and MRG has high shear thinning behavior. Rheological properties of MR grease under rotational and oscillatory shear have been investigated by a number of researchers. Mohamad et al prepared a series of MR grease with different content of carbonyl iron particles. The highest dynamic yield stress and the relative MR effect of MR grease in that work can reach about 52.7 kPa and 952.38%, respectively [18].

Kwon et al studied rheological properties of MR grease composed of Carbonyl Iron, grease and CrO2. The yield stress of the fabricated MR grease varied as $B^{3/2}$ and has a linear relationship with particle volume fraction [19]. Park et al. investigated the dependence of the storage modulus (G') and loss modulus (G'') on angular frequency (ω). The results showed that both the storage and loss modulus values remain constant as the frequency increases at a fixed magnetic field, implying MR grease formed a strong solid-like structure [20].

(C) EFFECT OF PARTICLE VOLUME FRACTION (PERCENTAGE OF MAGNETIC PARTICLES):

It has been reported in literature that MR effect of MR fluids strongly depends on magnetic particle volume [21]. In case of MR grease M. Hari Prasad and K V Gangadharan [16] in their study prepared different composition of Mangnetorheological grease using, carbonyl iron, silicone oil and grease and reported that Iron content >70% by weight and < 50% by weight did not show any promising results. Higher percentage of iron results nonlinear behavior whereas lower percentage is not showing significant MR property. MR Grease with 60% iron powder revealed good MR Effect. Sukhwani et al in their study [22] reported More variation in consistency of MR grease on application of magnetic field i.e. more MR effect was observed for MR grease with more Iron particles loading.

(D) EFFECT OF PARTICLE SHAPE:

To determine the effect of particle shape on MR grease performance, N Mohamad et al [15] experimentally investigated the principal characteristics of magnetorheological greases (MRGs) which have two different particle shapes. One was conventional spherical shaped carbonyl ions (CI) particles, while the other was plate-like CI particles prepared using high energy rotary ball mill from spherical CI particles. A set of bidisperse MRG samples were prepared by adjusting the weight percentage of plate-like CI particles and mixing with spherical CI particles. Subsequently three important properties of MRGs were compared between the two particle shapes. The field- dependent apparent viscoelastic properties, field-dependent storage and loss moduli and transient response time were measured using an oscillatory shear rheometer. Study concluded that bidisperse MRG with plate-like CI particles exhibits an increase in initial apparent viscosity as well as stiffness property compared with MRG with spherical particles only.

(E) EFFECT OF TEMPERATURE

The thickener forms the basic skeleton structure of the grease. Lithium12-hydroxystearate is the most widely thickening agent used in soap-based grease which forms an entanglement fiber network trapping the oil and conferring appropriate rheological to the grease. Changes in the structure of the entanglement fiber will inevitably cause changes in the rheological properties of the grease. Temperature is one of the important factors affecting the change of entanglement fiber structure. Sanchez et al investigated the rheological characterization of lubricating greases under different temperature by using the atomic force microscopy. The results showed that the overall entanglement degree of the soap fiber decreased with the increase of temperature, resulting in the decrease of viscosity of grease [23].

Gordaninejad et al investigated the viscosity and shear stress responses of MR grease in the temperature range from 10℃ to 70℃.They found that the field-induced viscosity and yield stress of MR grease are more sensitive to temperature compared to MR fluids. In addition, they proposed a new model including temperature parameter T to characterize the rheological behavior of MR grease under different temperatures. The result shows that the proposed model agrees well with experimental data [24].

In another study Huixing Wang et al [14] investigated the effect of temperature on the rheological properties of Magnetorhelogical (MR) grease containing carbonyl iron suspended in lithium-based grease with 70% weight fraction of carbonyl iron in the same temperature range of 10^{o}C to 70^{o}C. The apparent viscosity and shear stress as a function of shear rate under different temperatures and magnetic field strengths were measured. It was found that the influence of temperature on apparent viscosity reduces with the increase of magnetic field strength. Besides, unlike the decrease in the maximum yield stress of MR fluid with increasing temperature, in the presence of magnetic field, maximum yield stress in MR grease exhibits an increase trend as temperature increase from 50℃ to 60℃, and the trend is more pronounced at higher magnetic field compared to lower field. The results demonstrate that the enhancement of temperature leads to the increase of storage modulus and the reduction of the loss factor which indicates that increase of

temperature enhances the MR performance. This is because MR grease becomes more liquid-like as temperature increased, which allows the migration of the particles under the presence of a magnetic field. The initial storage modulus, maximum magneto-induced modulus and maximum MR effect of MR grease under different temperature has been shown in table-2. Here Magneto-induced modulus, oG, is defined as the difference between storage modulus, G′, and initial storage modulus, G_0'. MR effect is the ratio of magneto-induced modulus to initial storage modulus. It was observed that both magneto-induced modulus and MR effect are increased with increasing temperature and magnetic field strength.

Table 2: Initial storage modulus, maximum magneto-induced modulus and maximum MR effect of MR grease under different temperatures

Temperature T(℃)	Initial storage modulus $G_0^{'}(KPa)$	*Maximum* magneto-induced modulus $\Delta G_{\max}^{'}(KPa)$	*Maximum MR effect* $\Delta G_{max}^{'} / G_0^{'} \times 100\%$
10	5.9	1786.5	30280%
20	4.91	1945.8	39629%
30	3.96	2057.1	51947%
40	3.63	2245.7	61865%
50	3.28	2274.6	69348%
60	3.12	2462.1	78913%
70	2.93	2646.6	90328%

(F) EXPERIMENTAL STUDIES RELATED TO MR DEVICES USING MR GREASE:

Many studies have been conducted to evaluate performance of MR Grease and to compare its performance with MR Fluid performance, when they are used in MR Devices. Gordaninejad et al [25] in their study related to Magnetorheological (MR) clutch, reported 75% increase in torque controlling capacity in MRG-based clutch as compared to commercial MR fluid based clutch. It is also brought out that the off-state condition the torque capacity of MRG is constant regardless of operating speed, whereas the torque capacity of MRF exhibited much dependence on the operating speed. It is concluded that MRG samples are applicable in torque transfer applications where a high-speed, constant torque output and low off-state torque clutch is desired.

Similarly Gordaninejad et al [26] examined the performance of MR damper using MR grease and reported that MR grease offers similar or superior controllability as compared to MR fluid with the added benefit of absolutely no particle settling. It was also reported by them that MRG Damper provides lower dynamic force range (between 1 to 2) than MR fluid damper.

However in a study conducted by Sukhwani and Hirani [27], performance of MR Fluid and MR Grease for brake application was compared and it was found that MR Grease brake yields low amplification of brake power output in comparison to MR Fluid brake but change in amplification factor with magnetic field is more linear in case of MR grease brake in comparison to MR fluid brake and both the MR suspensions show shear thinning behavior. In conclusion to this study use of MR Fluid has been recommended for use in brakes rather than MR Grease because of the more importance of requirement of MR effect rather than achieving sedimentation stability.

(G) PATENT GRANTED FOR MR GREASE COMPOSITION:

Many patents related to MR technology i.e. MR Fluids, MR Dampers, MR Transmission devices, MR Clutch, MR polishing devices, MR actuated prosthetic Knee etc, have been granted all over the

world. Some Patents have also been granted for MR Grease compositions. **United States Patent No 6547986** was granted in 2003 for Magnetorheological grease composition to inventors Kintz, K. Andrew; Carlson, J. David; Munoz, Beth C and Sessoms, Julia D [28]. In this invention, inventors claimed magnetorheological grease compositions, which shows variable consistency. The invention provides a Magnetorhelogical grease compositions which contains magnetic responsive particles, a carrier fluid and a thickening agent. The composition according to the invention contains an effective amount of thickening agent to provide a composition of proper consistency with good properties and little settling of the magnetic responsive particles.

Another Patent for Magneto-rheological grease composition **(United States Patent 10377964)** was granted [29] for the invention which provides a magneto-rheological grease composition containing (a) a base oil including at least 30% by mass of an ether type synthetic oil; (b) an aliphatic diurea thickener; and (c) magnetic particles in an amount of 45 to 95% by mass based on the total mass of the composition. This magneto-rheological grease composition claimed superior thermal stability, dispersion stability and magneto-rheological properties.

(H) AVAILABILITY OF COMMERCIAL MR GREASE:

Today a number of MR devices and Commercial MR Fluids are available in the Market. Main supplier of MR Fluids is Lord Corporation USA. Commercial MR fluids available in the market are i.e. MRF-132 AD, MRF-241 ES and MRF-336 AG. But no commercial MR Grease has been made available by any manufacturer in the market so far.

(I) PERFORMANCE EVALUATION OF MAGNETORHEOLOGICAL (MR) GREASE [22]

To evaluate the performance of synthesized MR grease, an experimental study was conducted by Sukhwani et al [22]. MR Grease has been synthesized using economical Electrolytic Iron. The electrolytic Iron powder of 300 Mesh size was ball milled to reduce its size to only few microns. Milled magnetic particles were characterized for their size distribution by PSD analyzer, for magnetic properties by VSM and for their morphology using SEM.

In this synthesis, an additive package consists of anti wear, anti oxidant, anti friction and anti corrosion additives and for prevention of sedimentation a natural additive, polysaccharide guar gum was used. Guar gum is used as thickening agent, emulsifier and suspension stabilizer [30].Two different types of MR greases were prepared. In first preparation (MR Grease-1), Iron particles with coating of guar gum have been used. In the second preparation (MR Grease-2 and MR Grease-3) Iron particles without guar gum have been used. Ingredients are same in MR grease-2 and MR grease-3 but they have different weight percentage of ingredients.

Synthesis Route: Fig-1 shows flow chart for synthesis route of MR Grease and Fig-2 and Fig-3 show the photographs of MR grease ingredients and prepared MR grease.

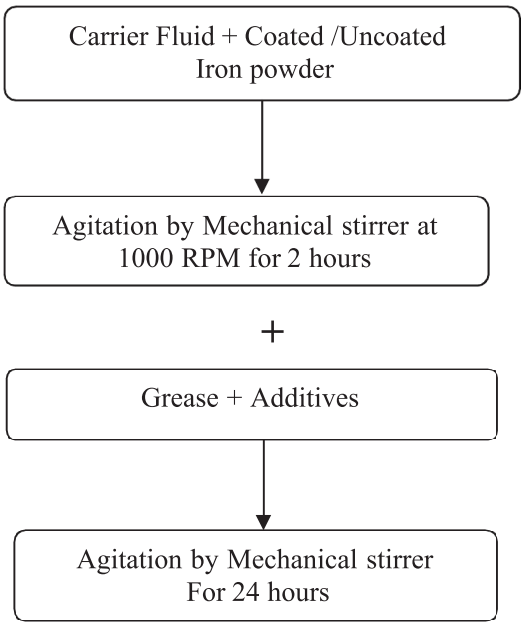

Fig-1: Flow chart for Synthesis route of MR Grease

Fig-2: Different Ingredients of MR Grease

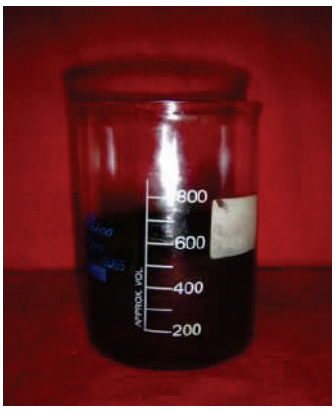

Fig-3: Photograph of Prepared MR Grease

Table-3 provides the compositions of three MR greases prepared in the present work.

Table-3, Composition of Prepared MR Greases

Ingredient	MR Grease-1		MR Grease-2		MR Grease-3	
	Weight (Gram)	Weight %	Weight (Gram)	Weight %	Weight (Gram)	Weight %
Grease	246	24.6	246	24.6	396	39.6
Oil	250	25	250	25	250	25
Iron Powder	480	48	500	50	350	35
Guar Gum	20	2	--	--	--	--
Additive package	4	0.40	4	0.40	4	0.40

Testing Procedure:

Performance of 1 three prepared MR greases was examined for their sedimentation stability (i.e. oil separation from grease during storage), oil separation from grease at elevated temperature and MR effect produced (i.e. change in their consistency in response to magnetic field). The standard test methods for measurement of consistency of lubricating grease by cone penetration (ASTM D217 and D1403) have been used Grease Penetrometer (PNR-10 Petrotest Germany) was used for measurement. To make the penetrometer suitable for consistency measurement at different magnetic fields, a specially designed electromagnet was provided on the grease cup to generate magnetic field inside the cup to influence the MR grease .Figure-4 shows the photographs of the test apparatus. Magnetic field was varied by applying the desired electric current using a DC power supply (0-60Volts).Tests to measure the consistency were conducted at five different currents 0.0 A, 0.5 A, 1.0 A, 1.5 A and 2.0 A. At the center of the cup with a position, x=0 (at center of the solenoid) Magnetic field (H_0) generated perpendicular to the shear flow generated by the solenoid surrounding the cup is given by [10].

$$H_0 = \frac{4\pi n i}{10 L}\left[\frac{L}{\sqrt{L^2 + D^2}}\right] \quad (2)$$

Here designed solenoid has inner diameter which is actually outer diameter of grease cup as 77.5 mm and length of solenoid is equal to 63.5 mm with turnover number of coil =1000 . Therefore when a current of 2 A is applied to the electromagnet, the magnetic field at the measuring point within the solenoid is 250 Oe.

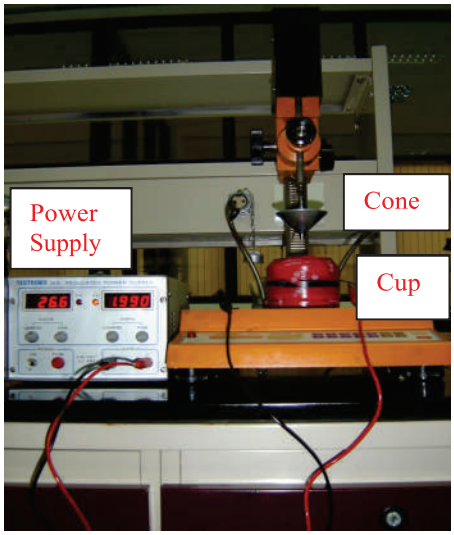

Fig-4: Photographs of Test setup

In this study sedimentation tendency of prepared MR greases was determined by two approaches. First they were put in three similar graduated cylindrical flasks and observed for their sedimentation behavior over period of time. In second approach standard method of determination of oil separation from lubricating grease "Pressure filtration method" (IP121) was conducted for MR greases to determine their tendency to separate oil during storage. This oil separation test was conducted for 42 hours at 40 ^{0}C using 100 gram sample. To determine separation of oil from grease at elevated temperature "conical sieve method" (ASTM D6184) was used. This test was conducted with 10 gram sample of each MR grease for 30 hours at 100 ^{0}C. The separated oil is weighed and has been reported as percentage of the mass of the test sample. It has been clarified in this study that though both the above mentioned separation tests are not generally used for soft greases with penetration greater than 340 (measured by ASTM D217) i.e. grease softer than NLGI No.1 grade, but have been used here for MR greases as MR grease is a new concept and standard tests do not exist for this kind of grease. Therefore these existing tests have been conducted get an idea about the tendency of the MR grease to separate oil during storage as well as at elevated temperature.

Variation in Consistency of MR grease:

Variation in NLGI consistency number with change of magnetic field applied was recorded using fullscale equipment is listed in table-4.

Table-4, Variation in NLGI number using full scale equipment

Applied Current (Amp)	Magnetic Field (Oe)	(MR Grease-1)		(MR Grease-2)		(MR Grease-3)	
		Penetration	NLGI Number	Penetration	NLGI Number	Penetration	NLGI Number
00	00	395	00	392	00	372	0
0.5	62.5	372	0	378	0	362	0
1.0	125	362	0	365	0	355	0
1.5	187.5	338	1	335	1	334	1
2.0	250	329	1	323	1	322	1

Results indicated that NLGI number of all three samples increased with increment of current i.e. magnetic field. However MR effect produced (increment in consistency) was not as large as expected by authors. This may be due to the large diameter of grease cup (77.5 mm), as equation-2 shows that intensity of magnetic field produced will be low at the center of cup where tip of the cone penetrates in case of large diameter cup. Therefore it was decided to select the small cup and cone, 1/2 scale cup and cone (ASTM D 1403) as an alternative to full scale cup and cone (ASTM D 217). Tests were repeated for same input currents 0.0 A, 0.5 A, 1.0 A, 1.5 A and 2.0 A with 1/2 scale cup and cone. However corresponding values of magnetic fields are different for 1/2 scale cup as length and diameter of the solenoid as well as number of turns of coil are different for this cup. Here designed solenoid has inner diameter, which is also outer diameter of small cup is 40 mm and length of solenoid is equal to 32.5 mm with turnover number of coils =750. Values of penetration obtained using 1/2 scale cup and cone have been converted in the corresponding full scale cup readings by equation-3 [31]. Original and converted penetrations values obtained are shown in table-5.

$$p = 2r + 5 \quad (3)$$

Where, p = Cone penetration by Test method D217
r = Cone penetration by1/2 scale equipment

Table-5, Variation in NLGI number obtained using 1/2 scale equipment

Applied Current (Amp)	Magnetic Field (Oe)	(MR Grease-1)			(MR Grease-2)			(MR Grease-3)		
		½ scale Penetration	Converted full scale Penetration	NLGI Number	½ scale Penetration	Converted full scale Penetration	NLGI Number	½ scale Penetration	Converted full scale Penetration	NLGI Number
00	00	198	401	00	201	407	00	181	367	0
0.5	91.38	185	375	0	187	379	0	168	341	1
1.0	182.76	163	331	1	164	333	1	157	319	1
1.5	274.16	140	285	2	143	291	2	144	293	2
2.0	365.54	115	235	3	121	247	3	130	265	2

As expected reducing the cup size results in greater variation in consistency of MR grease. Also consistency has been found function of particle loading and amount of grease. MR Grease-1 and MR Grease-2 has almost same weight % (48 % and 50 %) of Iron particles. But MR grease-3 has less weight % (35 %) Iron particles. This is reflected in the change in consistency number with magnetic field. MR Grease-1 and MR Grease-2 show greater variation in NLGI number (NLGI 00 to NLGI 3) as compared to MR grease -3 (NLGI 0 to NLGI 2). Change in consistency of MR grease-1(grease with guar gum coated particles) and MR grease-2 (grease with particles without guar gum) with change of magnetic field has almost been same i.e. NLGI 00 to NLGI 3 for same magnetic field variation from 0 to 365.5 Oe. This shows that guar gum does not affect the MR effect produced by MR grease .This finding matches well with the VSM results which showed equal values of saturation magnetization for guar gum coated and uncoated Iron particles and therefore same expected MR effect. Off state consistency (consistency without magnetic field) of MR grease-3 was found greater than MR Grease-1 and MR Grease-2. This is due to more weight percentage of grease (39.6 %) in MR grease-3 then MR Grease-1and MR Grease-2 (24.6 % for both).

Separation of oil from grease during storage (Sedimentation Stability):
All three MR greases remain in well dispersed and stable state without significant settling as thickening agent grease has a yield stress large enough to prevent particles sedimentation in the suspension. Highest sedimentation stability was observed for MR grease-3(i.e. MR grease with highest % of grease 39.6 %). Sedimentation stability of MR Grease-1 and MR Grease-2 were found comparable as both had same percentage of grease (24.6 %). However sedimentation was found somewhat lower for MR Grease- 1(MR grease containing guar gum coated Iron particles) than MR greae-2 which does not have guar gum coated particles. This shows that guar gum plays important role in improving the sedimentation stability of MR grease. The guar gum shows a lot of hydroxyl group stretching outside. The hydroxyl groups may interact with oil molecules by strong hydrogen bonding, forming a three-dimensional network structure with the particles and preventing the particles from conglomeration and sedimentation quickly [20].
Test conducted for determination of oil separation during storage (IP121) shows the similar results. Separation of oil from MR grease during storage is reasonably low for all three MR greases keeping in view the low off state consistency of these MR greases. However, no standards are available regarding maximum permissible limit of oil separation for MR grease as this is a new concept. Separation of oil was found lowest for MR Grease-3 (i.e. MR grease containing maximum percentage of thickening agent
i.e. grease). Out of other two MR greases, separation of oil for MR Grease-1 (MR grease containing guar gum coated Iron particles) is somewhat lower than MR Grease-2 (MR grease with uncoated Iron particles).

Table-6, Results of test for oil separation during storage

MR Grease	% Oil Separation
MR Grease-1	4.08
MR Grease-2	5.10
MR Grease-3	3.12

Separation of oil from grease from grease at elevated temperature:
Results of test ASTM D6184 conducted to determine the separation of oil at elevated temperature is shown in table-7. Results indicated that all the MR greases follow the same trend for separation of oil at elevated temperature (100 ^{0}C) as shown by them for separation of oil from grease under storage.

Table-7, Results of oil separation at Elevated Temperature (100 ^{0}C)

MR Grease	% Oil Separation
MR Grease-1	6.21
MR Grease-2	7.55
MR Grease-3	5.03

It is evident from results that the oil separation under storage and at elevated temperature can be reduced by increasing the grease content and using guar gum as additional thickening agent in the MR grease.
Some important observation from this study is:

I. Significant variation in NLGI number i.e. consistency of MR grease on application magnetic field was observed which shows the usefulness of MR grease in applications demanding variable consistency. More variation in consistency i.e. more MR effect was observed for MR grease with more Iron particles loading.

II. Sedimentation stability was found maximum for MR Grease containing highest percentage of grease. However sedimentation stability of MR grease containing guar gum coated Iron particles is better than MR grease containing uncoated particles, which shows the contribution of guar gum additive in preventing sedimentation of particles.

III. Separation of oil from MR grease during storage and separation of oil from grease at elevated temperature for all three MR greases are reasonably low keeping in view the low off state consistency of all three MR greases.

IV. Lowest separation of oil during storage as well as separation of oil at elevated temperature was observed for MR grease containing maximum percentage of grease. Also, separation of oil was found less for MR grease containing guar gum coated Iron particles

CONCLUSIONS:

The MR technology has very good potential for various engineering applications demanding controllability in operation. To solve the existing limitations and problems related to this technology and to enhance its engineering application, many studies have been done by researchers on different types of Magnetorhelogical compositions. In recent years many research studies works have been conducted on MR grease. It has attracted the interest of many researches as MR grease produces significant MR effect and overcomes the limitation of MR fluids. Study of available research work related to MR grease shows that MR grease offers solution to the two important problems of MR fluids. It can mitigate the sedimentation problem of magnetic particles and solves the leakage problem of MR devices. Some studies have reported that MR grease offers similar or superior controllability as compared to MR fluid with the added benefit of absolutely no particle settling and no leakage problem and therefore can beused as more effective substitute of Magnetorhelogical fluids in engineering applications. Various studies showthat performance of MR grease is function of type of magnetic material, particle volume, particle shape and size, type and amount of thickening agent used, temperature etc. Shear thinning behavior of MR grease has also been reported in literature. Though more research is required to optimize MR grease composition and accurately model its behavior, it is expected that this review article can provide useful guidelines for commercial production and applications of MR grease as well as accelerate more innovative research activity in the field of MR materials.

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