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Alternatives to Lithium Soap Greases for Automotive Applications

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NLGI Lubricating grease survey for the year 2021 published recently indicates that 69% of the greases sold world over are based on Lithium Soap. In India approximately 83% share of greases sold are Lithium soap based. Lithium soap greases have been work horse for many decades with industrial and automotive segment. The automotive grease segment stands at 56% of total volume of greases sold in India.

In past one year there has been a spike of 80 to 120% in the prices of Lithium containing products due to more than 250% increase in prices of viz. Lithium Carbonate used in making batteries and Lithium Hydroxide used in making grease worldwide.

The increased price of lithium soap greases and inconsistent availability in future has led to a debate on use of alternates for the soap bases in greases. Many customers are evaluating alternates not only as cheaper options only but also as equivalent of better performance alternatives.

The presentation provides detailed comparison of aluminium complex and calcium sulphonate complex greases versus currently used lithium and lithium complex greases in automotive wheel bearing grease applications. The properties of various grease formulations have been compared in laboratory tests. The results of field trials for automotive applications have also been presented.

Aluminium complex greases though exhibit reversibility, require additives for sustained load carrying capacity, heat stability, mechanical stability and water handling, where as calcium sulphonate complex greases provides holistic solution for high mechanical stability, high load carrying ability, inherent corrosion protection with excellent heat, load and handling wet environments.

Wheel bearing applications in automotive application for calcium sulphonate complex greases also saw some enhanced drain intervals in city buses.

Keywords: Grease, Aluminium, Calcium, Lithium, Automotive Wheel Bearing.

Introduction

NLGI Lubricating grease survey for the year 2021 published recently indicates that 69% of the greases sold world over are based on Lithium Soap. In India approximately 83% share of greases sold are Lithium soap based. Lithium soap greases have been work horse for many decades with industrial and automotive segment. The automotive grease segment stands at 56% of total volume of greases sold in India.

In past one year there has been a spike of 80 to 120% in the prices of Lithium containing products due to more than 250% increase in prices of viz. Lithium Carbonate used in making batteries and Lithium Hydroxide used in making grease worldwide.

The increased price of lithium soap greases and inconsistent availability in future has led to a debate on use of alternates for the soap bases in greases. Many customers are evaluating alternates not only as cheaper options only but also as equivalent of better performance alternatives.

The choice of base oil, thickener and performance-enhancing additives mainly defines the performance properties of a grease, but also the grease production process significantly impacts some of the parameters. Significance of parameters on performance can be summarized as under

PERFORMANCE PROPERTY	BASE OIL	THICKENER	ADDITIVES	PRODUCTION PROCESS
Consistency	■	■ ■ ■		
Cold temperature behaviour	■ ■ ■	■ ■		
Oxidation stability	■		■ ■ ■	
Pumpability	■ ■ ■	■ ■		
Corrosion resistance		■	■ ■ ■	
Mechanical/ shear stability	■	■ ■		■ ■ ■
Oil separation	■ ■ ■	■ ■		■ ■ ■
Seal compatibility	■ ■ ■	■	■	
Water wash-out and spray-off resistance	■	■ ■ ■		
Dropping point		■ ■ ■		

There isn't one perfect grease that suits all applications, but some thickeners are particularly suited for some applications. The grease chosen will depend on which are the most important characteristics needed for particular application.

Automotive wheel bearing grease is one such application requiring adhesiveness, load carrying ability, high temperature, etc.. Lithium greases have been in use for more than 5 decades in these applications, but currently more due to reasons of cost impact and inconsistency of supply, alternates are being looked at for future. Calcium complex, Calcium sulphonate complex and aluminum complex greases very well fit the requirement of application and are considered for this study.

Experimental

Lithium, Lithium complex, Calcium complex, Calcium sulphonate complex and aluminum complex greases commercially available in range prepared by the ingredients as shown below for carrying out the on road field trials in Heavy duty vehicles were selected.

Lithium Grease Formulation Ingredients	**Lithium complex Grease Formulation Ingredients**
Lithium Hydroxide	Lithium Hydroxide
12 – Hydroxy stearic acid	12 – Hydroxy stearic acid
Hydrogenated castor oil	Hydrogenated castor oil
Calcium Oxide	Borated complexing agent / di basic acid complexing agent
Performance Additives	Performance Additives

Aluminium Grease Formulation Ingredients	**Aluminium complex Grease Formulation Ingredients**
Aluminium Iso propoxide	Preformed Aluminium complex Half soap
12 – Hydroxy stearic acid	Benzoic Acid
Benzoic Acid	Performance Additives
Performance Additives	

Calcium complex Grease Formulation Ingredients (Drop point ~ 200)	Calcium complex Grease Formulation Ingredients (Drop point > 300)
Calcium Oxide	Calcium Oxide
12 – Hydroxy stearic acid oil	12 – Hydroxy stearic acid
Hydrogenated castor	Hydrogenated castor
Borated ester	C2 – C3 organic acid
Performance Additives	Performance Additives

Calcium Sulfonate complex Grease Formulation Ingredients	Calcium Sulfonate complex Grease Formulation Ingredients	Calcium Sulfonate complex Grease Formulation Ingredients
Sulfonate pre-mix	Sulfonate pre-mix	> 400 BN Calcium Sulfonate
500N + 150 BS Group I base oil	500N + 150 BS Group I base oil	500N + 150 BS Group I base oil
Water	Water	Water
	12 Hydroxy Stearic acid	12 Hydroxy Stearic acid
	Acetic acid	Acetic acid
	Calcium Hydroxide	Calcium Hydroxide
		Sulfonic Acid
		Coupler

The results of common test parameters are as under for each type of grease. Lithium and Lithium complex grease properties

Property	Method	Unit	40K - 60 K	80K - 100 K	> 120 K
Appearence	Visual		Smooth, Shiny & slightly Tacky	Smooth & Tacky	Smooth & Tacky
Colour	Visual		Amber	Red	Green
Soap / Thickener			Lithium	Lithium Complex	Lithium Complex
Worked Penetration@25°C (60x)	ASTM D217	0.1mm	235	236	236
Roll Stability % change, Max.	ASTM D1831	%	20	16	16
Drop Point, °C	ASTM D2265	°C	200	>265	>265
Viscosity of base Oil @100°C, cSt	ASTM D445	mm^2/s	14 - 16	18	18
Viscosity of base Oil @40°C, cSt	ASTM D445	mm^2/s	150 - 160	220	220
Timken OK Load, LBS	ASTM D2509	Kg	-	50	60
Four-Ball Weld Load, KG	ASTM D2596	Kg	200	315	400
Four-Ball wear scar diameter, mm	ASTM D2256	mm	0.6	0.48	0.48
Copper Strip Corrosion Rating	ASTM D4048		1A	1A	1A
Water Washout@79°C, wt%	ASTM D1264	% wt	<10	<7.5	<5

Aluminium Complex grease properties

Property	Method	Unit	40K - 60 K	80K - 100 K	> 120 K
Appearence	Visual		Smooth, Shiny & slightly Tacky	Smooth & Tacky	Smooth & Tacky
Colour	Visual		TAN	TAN	TAN
Soap / Thickener			Aluminium Complex	Aluminium Complex	Aluminium Complex
Worked Penetration@25°C (60x)	ASTM D217	0.1mm	237	235	230
Roll Stability % change, Max.	ASTM D1831	%	12	12	12
Drop Point, °C	ASTM D2265	°C	>265	>265	>265
Viscosity of base Oil @100°C, cSt	ASTM D445	mm²/s	18	18	18
Viscosity of base Oil @40°C, cSt	ASTM D445	mm²/s	220	220	220
Timken OK Load, LBS	ASTM D2509	Kg	35	50	60
Four-Ball Weld Load, KG	ASTM D2596	Kg	230	315	400
Four-Ball wear scar diameter, mm	ASTM D2256	mm	0.55	0.44	0.4
Copper Strip Corrosion Rating	ASTM D4048		1A	1A	1A
Water Washout@79°C, wt%	ASTM D1264	% wt	<5	<5	<5

Calcium complex and Calcium sulphonate complex grease properties

Property	Method	Unit	40K - 60 K	> 120 K	> 120 K
Appearence	Visual		Smooth, Shiny & slightly Tacky	Smooth & Tacky	Smooth & Tacky
Colour	Visual		TAN	TAN	TAN
Soap / Thickener			Calcium Complex	Calcium Sulphonate complex (conventional)	Calcium Sulphonate complex (Low soap)
Worked Penetration@25°C (60x)	ASTM D217	0.1mm	240	237	240
Roll Stability % change, Max.	ASTM D1831	%	10	5	5
Drop Point, °C	ASTM D2265	°C	>300	>300	>300
Viscosity of base Oil @100°C, cSt	ASTM D445	mm²/s	18	18	18
Viscosity of base Oil @40°C, cSt	ASTM D445	mm²/s	220	220	220
Timken OK Load, LBS	ASTM D2509	Kg	35	50	60
Four-Ball Weld Load, KG	ASTM D2596	Kg	400	500	500
Four-Ball wear scar diameter, mm	ASTM D2256	mm	0.6	0.4	0.4
Copper Strip Corrosion Rating	ASTM D4048		1A	1A	1A
Water Washout@79°C, wt%	ASTM D1264	% wt	<5	<5	<5

As the performance of Lithium and lithium complex greases are already well established, only aluminum and calcium based greases were run to establish the performance in actual field conditions. For evaluating the performance of a grease in all 20 - 24 sets of bearings were considered

Results and Discussion

The wheel bearing of a vehicle provides low friction bearing surface for free rotation of wheel. It not only supports the weight of the vehicle but also transfers the lateral loads of cornering from the wheel and tires into the body / frame. Weight of vehicle is the largest radial load acting on the bearings at right angle to the axis of rotation. Jounce and rebound forces are also encountered on the bearing when vehicle encounters bumps in the road. Acceleration and braking also applies additional radial loads on the bearing. Cornering force or tire hitting the curbs are other additional forces acting on bearings. The bearings are supposed to last through out the life of vehicle but the conditions in which most of the Indian transport vehicles operate don't allow such a great life of the bearings if not re-greased at certain time intervals.

The most failures are seen in the rear drive wheel hubs of all vehicles and left hand side front wheel hubs of public transport vehicles barring those running on bus rapid transport pathways.

Normally the greases in India are sold as greases for 40000 – 60000, kms, 80000 – 100000 kms and greater than 120000 kms of greasing intervals for heavy commercial vehicles. Lithium and lithium complex greases have been well established over the years and are differentiated by colours for drain intervals in the markets.

Aluminum Complex Grease

Performance-wise, aluminum-complex grease performed just as well as lithium-complex grease in many aspects and even surpassed it in a few key areas, but it was more expensive to produce.

Typically, aluminum-complex grease resisted water washout and had better oxidation stability. Aluminum grease was a bit tougher to clean up when found its way onto skin or clothing.

One major international OEM has been recommending use of Aluminum complex grease in bearings wherever disk brakes are used because of its reversibility characteristics.

The one drawback that aluminum-complex grease had when pitted against lithium-complex grease was its work or shear stability in wheel bearing applications of heavy commercial vehicle. Aluminum-complex grease broke down to lower consistencies in many cases. The bearing performance was not hampered in-spite of this loss of consistency for the drain interval of planned trials.

Calcium Complex Grease

Calcium complex grease being the cheapest grease produced in the series has exhibited excellent water resistance and adhesion properties, good oxidation stability and rust protection. Mechanical stability at higher temperature was not as good as that of Aluminum or Lithium greases. Shear stability has shown some hardening of grease. The keeping quality over a period of time resulted in hardening of the grease. The bearings could survive upto 80000 kms with the grease when 12 hydroxy stearic acid and hydrogenated castor oil were used in the ratio of 11.9 : 2.1. Further experimentation needs to be done with only 12 hydroxy stearic acid based grease as this combination works out as the cheapest.

Calcium sulfonate Complex Grease

This grease has shown inherent EP performance, as demonstrated in the four-ball EP test, and in the Timken test. Mechanical stability, thermal stability water resistance properties were excellent but certain formulations had very poor water spray off characteristics. During production process, initially, reaching the right calcite particle formation / concentration was a challenge and thus consistent quality was somehow not achieved without incremental time consumption in manufacturing. However the production time were shortened by use of preformed soaps available.

It is understood through literature that calcite particles form a wafer or scale like structure which creates shear planes that trap between the metal surfaces for load carrying properties and this being a sacrificial layer on the metal that is constantly sheared away, the prepared grease formulations worked very well beyond 120000 kms in all hubs.

Conclusion

High mechanical stability, inherent load carrying ability, corrosion resistance and tolerance to wet environment, heat and load, the consideration of cost, performance and availability make us believe that calcium sulfonate complex greases will be the holistic solution for lithium base greases in the application discussed.

Acknowledgement

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Can Calcium 12-hydroxy stearate soaps replace Lithium 12-hydroxy soapsin greases?

Sachin Kumbhar[1], Amar Dhopte[2], Komal Ghadi[3], Joel Kandathil and Vikas Nirala

Abstract:

Lithium 12-hydroxy stearate-based greases are the most popular and widely used greases. Oneof the critical factors behind Lithium Grease becoming the preferred grease was its competitivepricing versus other greases. However, due to the steep increase in Lithium HydroxideMonohydrate prices in the last year, there was an immediate need to find some alternates to this popular grease chemistry that would be economical and perform equally well, if not better. In this paper, the authors focus on Calcium 12-hydroxy stearate greases. Various Sulfurbased EP additive response was studied in Calcium 12-hydroxy stearate greases. It was concluded that, besides being economical, Calcium 12-hydroxy stearate-based greases poses better and inherent antiwear, anti-rust and mild-EP properties, which help reduce additive treatrates. Further, it was also seen that improving the dropping point of Calcium 12-hydroxy stearate greases to 180^0C from 150^0C was possible with mixed Alkyl Borate Ester.

Keywords: Lithium 12-hydroxy stearate, Calcium 12-hydroxy stearate, EP additives, AlkylBorate Ester.

Introduction:

Lithium based greases are most widely used greases because they fit in diverse application arrays. It can withstand temperature upto 120°C and have excellent mechanical and roll stability. Its soap structure is very robust which helps in pumpability, and it is also economical. However, lithium is emerging as a soil contaminant and environmental pollutant. Also there hasbeen a steep price increase in the main ingredient of the lithium grease which is lithium hydroxide monohydrate giving exhorbitant price increase for the finished grease. There are various papers that propose Polyurea, Aluminium complex and Calcium sulfonate as an alternative system for lithium base grease. Though polyurea grease is a nonmetallic grease witha very high dropping point but it has certain limitations such as use of toxic isocyanates like MDI (diphenylmethane diisocyanate) and TDI (toluenediisocyanate) and hazardous amines asraw materials, poor compatibility with other thickener system. Aluminum Grease shows excellent pumpability and chemical resistance properties but has disadvantages such as less thermal stability compared to lithium base grease and produces Isopropanol during saponification. Calcium Sulfonate grease has poor low temperature properties and pumpability.All the three proposed thickeners are expensive than lithium in the current scenario. In this paper calcium 12-hydroxystearate grease is proposed as an alternative for lithium 12- hydroxystearate grease, which are environmentally acceptable and having superior properties compared to lithium base grease.

Synthesis of Calcium 12-hydroxystearate grease:

Saponification process for Calcium 12-hydroxystearate grease is similar to that of Lithium12-hydroxystearate grease. It is prepared by reacting fatty acid/s (most commonly 12-HSA), a small amount of water, with calcium hydroxide in mineral oil. Typically, 10-16 % of soap will be required to make NLGI grade 2 grease. Dehydration process takes place between 105°C to 125°C. Maximum temperature during production of grease is 150°C.

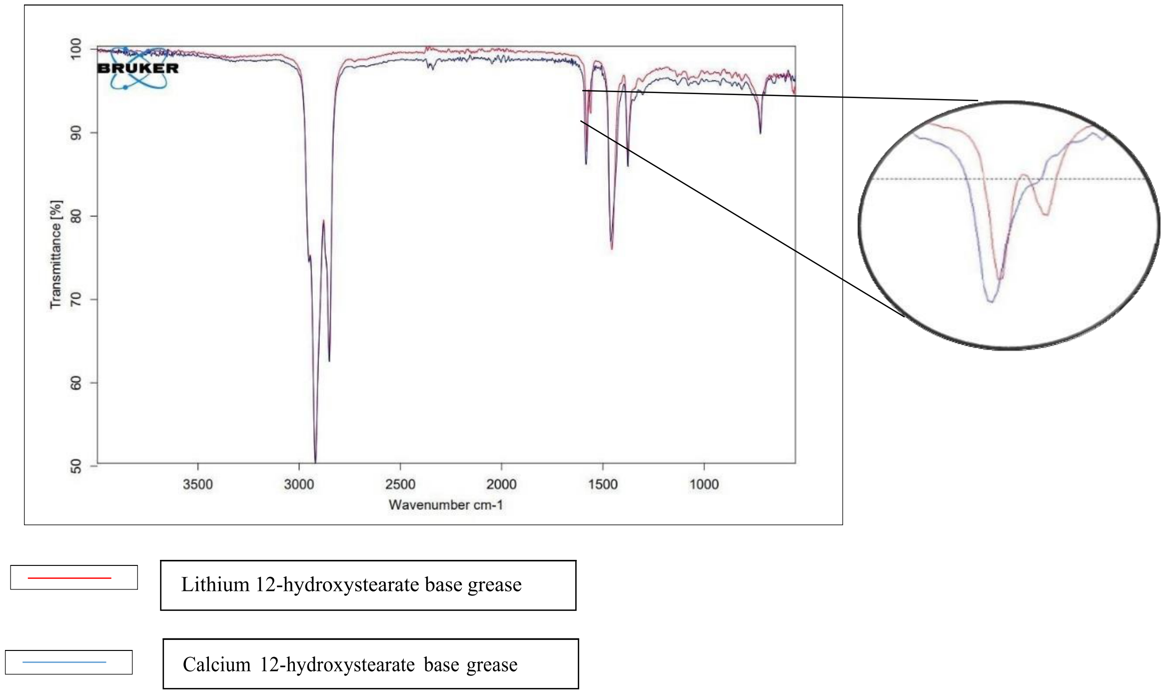


Fig 1. ATR of Lithium 12-hydroxystearate base grease and calcium 12-hydroxystearate base grease

Challenges in manufacturing calcium 12-hydroxystearate greases

Large scale production of calcium 12-hydroxystearate grease is a very tedious and challengingprocess. During saponification excessive foaming is observed and at dehydration stage more oiladdition is required leaving less room for oil to be added at cooling stage. If simple lithium grease's kettles are used, then it will lead to reduction in output. Due to grainy structure additional milling and homogenization process is required. Deaeration process is required dueto lot of entrapped air in the grease.

Overcoming the manufacturing challenges

To avoid foaming during saponification process, less diluent oil is required. To increasethe production yield, bigger reaction kettles like that of cooling kettle must be used. Goodmilling machine or homogenizer followed by vacuum deaerator gives ease in the production and getting smoother grease structure.

Simple Lithium Grease

Calcium 12-hydroxystearate Grease

In Table.1, Comparison results of Lithium 12-hydroxystearate grease and calcium 12- hydroxystearate greaseis given. All the performance results of calcium 12-hydroxystearate grease is better than Lithium 12- hydroxystearate grease. The only limitation of calcium 12- hydroxystearate grease is dropping point.

PARAMETERS	Li 12-HSA BaseGrease	Ca-12HSA Base Grease
Unwork Penetration, (0.1mm)	288 mm	271 mm
Penetration (60 strokes), (0.1mm)	280 mm	273 mm
Penetration (100K strokes), (0.1mm)	333 mm	294 mm
Roll Stability, (% change)	16.9 %	1.53 %
Copper Corrosion, (rating)	1B	1B
Dropping Point, (°C) (ASTM D 556)	208°C	153°C

Table.1 Comparison results of Lithium 12-hydroxystearate grease and calcium 12-hydroxystearate grease.

Methods to increase the dropping point of calcium 12-hydroxystearate grease:

There are two different methods to increase the dropping point of calcium 12-hydroxystearate grease. One alternative method is by complexing calcium grease with different acids. Complexing acids, generally used to increase dropping point in Lithium greases. In Fig 2 and 3 Postulate complexing mechanism of Lithium 12 hydroxystearate soap with Lithium azealate and Lithium borate is shown respectively. [1,2]

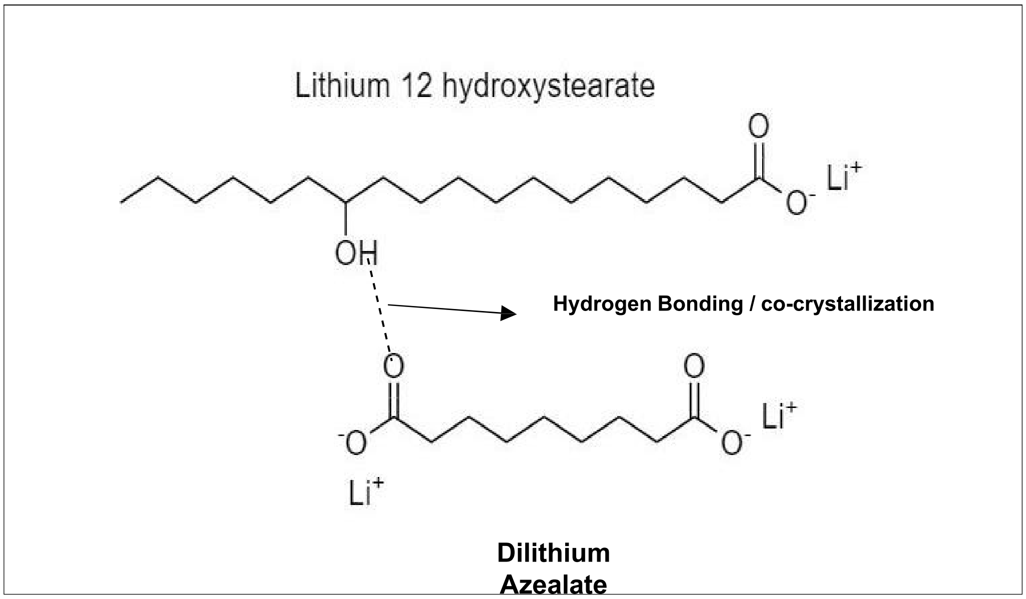


Fig 2: Postulate Complexing mechanism of simple lithium soap with azelaic acid.

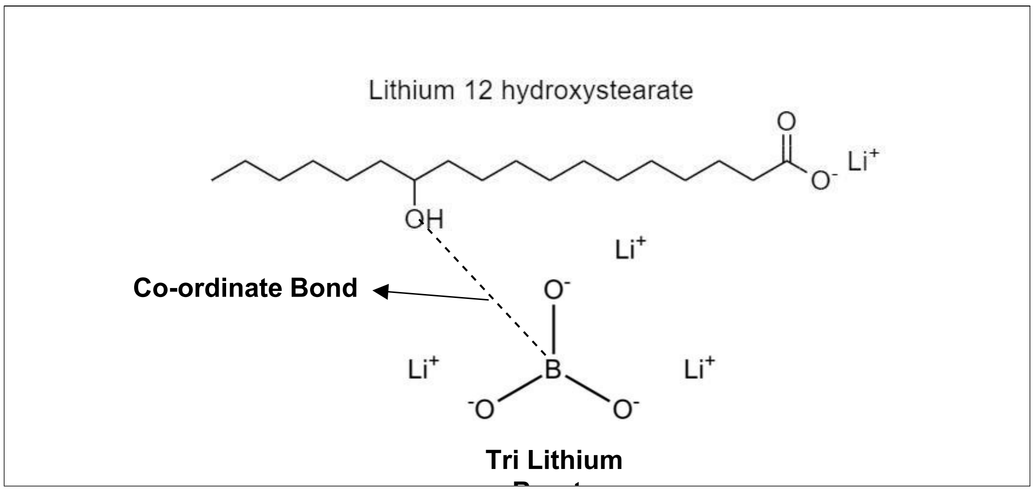


Fig 3: Postulate Complexing mechanism of simple lithium soap with Tri Lithium Borate.

In Table.2 parameters of complexing calcium grease with different acids is given. Complexing with acetic acid [1], boric acid, sebacic acid and azealic acid is carried out. From the detailed study it can be concluded that complexing with different acids can lead to age-hardening after exposing at 120° for 12 hours. Also, these grease as much more expensive than Lithium 12-hydroxystearate grease. Thus, it can be concluded that complexing of calcium grease with different acids is not an appropriate way according to the current scenario.

Parameters	**Acetic Acid (3%)**	**Sebacic Acid (4%)**	**Azealic Acid (4%)**	**Boric Acid (1%)**
Dropping Point (•C) (ASTM D 556)	250°C+	168°C	165°C	169°C
Penetration (0.1 mm)	285	285	289	288
Penetration after exposing at 120°C for 12 hours	237	256	259	290
Penetration change (%)	- 16.84 %	-10.17 %	- 10.38 %	0.69 %

Table. 2 Complexing calcium grease with different acids

Fig 4: Caking effect of grease after 12 hours at 120°C (Complexing calcium grease with different acids)

Another alternative method to increase the dropping point of calcium 12-hydroxystearate grease is by using alkyl borate ester [3] as an additive. Different alkyl chain borate ester with different treat levels is studied (Table.3). But it is concluded that mixed alkyl borate ester with $C3 - C12$ give appropriate increase in dropping point without any alteration in the performance of the base grease. Significant changes in fiber structure are evident in fig. 5. [4]

According to Siegart and Henry [5], the boron atom of the borate ester forms a coordinate bond by sharing electrons with the hydroxyl group of the hydroxy fatty acid soap. These coordinated interactions between soap and complexing agent helps to hold oil intact within the thickener structure at high temperatures, which leads to a high dropping point.

According to Joe Kaperick, Greases additized with borate esters were found to show either similar or superior physical and chemical properties to the base grease. Also concluded that the borate ester-additized greases retained their structure and their high-temperature properties. No significant change in dropping point, mechanical stability and other properties was observed while storing the greases for one year.[4]

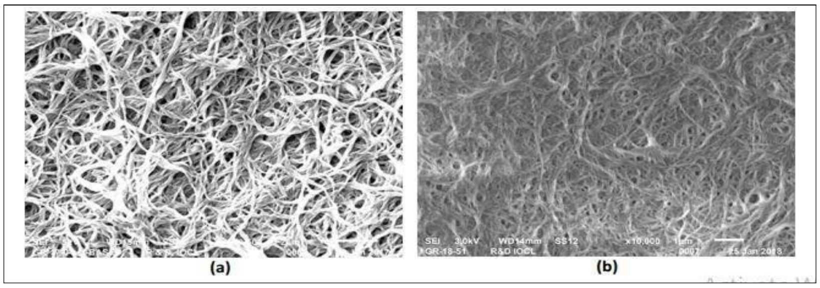


Fig.5 SEM images of grease (a) without and (b) with borate complexation (Adopted from NLGI Spokesman,May/June 2019, Joe Kaperick)

When borate ester is added as an additive in grease, lower activation energy is required to form a coordinate complex between the boron atom and the hydroxyl group of the hydroxy fatty acid soap. The cumulative/synergic effect of borate ester and ZDDP is very commonly used by grease formulators to enhance the dropping point [6].

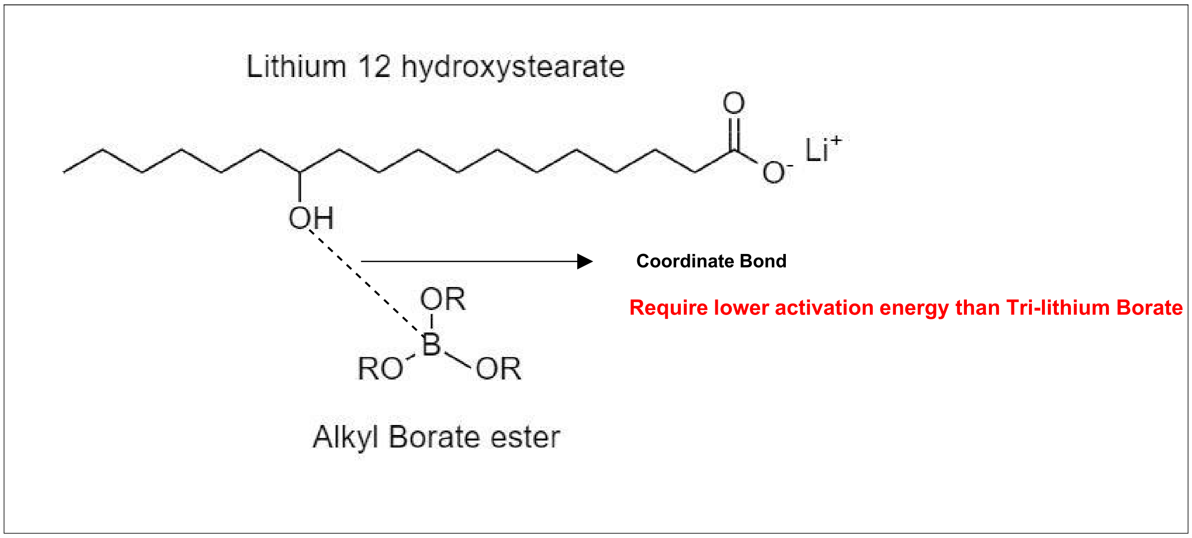


Fig 6: Postulate mechanism of simple lithium soap with Alkyl borate ester.

Parameters	**Ca-12HSA Base Grease**	**Ca-12HSA Base Grease + Alkyl Borateester (C4)**		**Ca-12HSA Base Grease + Alkyl Borate ester (C8)**		**Ca-12HSA Base Grease + Alkyl Borateester (C12)**		**Ca-12HSA Base Grease + Mixed Alkyl Borate ester (C3 to C12)**	
		2%	3%	2%	3%	2%	3%	2%	3%
Dropping Point (ASTM D 556)	153°C	162°C	167°C	158°C	160°C	155°C	157°C	172°C	185°C

Table.3 Dropping point of Ca-12HSA Base Grease with different alkyl chain borate ester with differenttreat levels.

Calcium 12-hydroxystearate grease with 3% mixed alkyl borate ester was exposed to 120°C for 12 hours to observe the penetration change (%). From the below table it can be concluded that alkyl borate ester do not affect the penetration grade and do not lead to age hardening as observed in greases complexed with different acids.

Parameters	**Ca-12HSA Base Grease + Mixed Alkyl Borate Ester (3% w/w)**
Penetration (0.1 mm)	280
Penetration after exposing at 120°C for 12 hours (0.1 mm)	285
Penetration change (%)	1.78%

Table 4: Penetration change (%) after exposing grease to 120°C for 12 hours

Properties of Ca- 12 HSA grease with mixed alkyl borate ester:

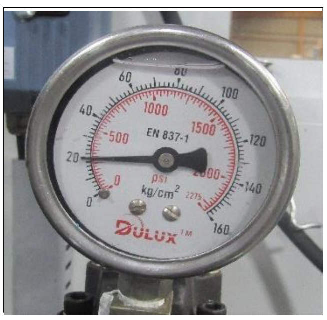
1. **Mechanical stability:**
   Ca-12HSA base grease with mixed alkyl borate ester has excellent mechanical stability than lithium base grease

Parameters	**-12HSA Base Grease**	**-12HSA Base Grease**	**Ca-12HSA Base Grease + Mixed Alkyl Borate Ester (3% w/w)**
Unwork Penetration, mm	288 mm	271 mm	275 mm
Penetration (60 strokes) mm	280 mm	273 mm	281 mm
Penetration (100K strokes) mm	333 mm	294 mm	310 mm
Roll Stability, %	16.9%	1.53%	2.06%

Table 5: Mechanical stability properties

2. **Pumpability (Centralized Lubrication System):**

   Minimum Pressure required to pump the grease is mentioned in the below table

Parameters	**Li-12HSA Base Grease (NLGI Grade 2)**	**Ca-12HSA Base Grease (NLGI Grade 2) + 3% w/w Mixed Alkyl Borate ester**
Pressure at Pumpability *(Minimum Pressure required for pumping the grease)*	20-22 kg/cm^2	22-24 kg/cm2
Image of Pressure Gauge during Pumpability		

Pumpability Instrument

Table 6: Pumpability properties

3. **Rust and corrosion properties:**

Ca-12HSA base grease with mixed alkyl borate ester has good rust and corrosion preventive properties. Below are the results of EMCOR RUST test (ASTM D 6138) andCorrosion preventive test (ASTM D 1743) conducted in-house.

Parameters	Li-12HSA BaseGrease	Ca-12HSA Base Grease	Ca-12HSA Base Grease + Mixed Alkyl Borate Ester (3% w/w)
EMCOR Rust test (ASTM D 6138)	3,4	1,1	0,1
Corrosion Preventive Test (ASTM D 1743)	Fail	Pass	Pass

Table 7: Rust and corrosion properties

4. **Water resistance properties:**
Compared to simple lithium base grease, Ca-12 HSA with mixed alkyl borate ester hasbetter water resistance properties.

Parameters	Li-12HSA BaseGrease	Ca-12HSA Base Grease + Mixed Alkyl Borate Ester (3% w/w)
Water washout	6.68%	5.06 %

Table 8: Water resistance properties

5. **Tribological Properties:**
Calcium grease has excellent tribological properties compared to simple lithium grease. Also 3% of mixed alkyl borate ester in calcium base grease enhance these properties.

Parameters	Li-12HSA Base Grease	Ca-12HSA Base Grease	Ca-12HSA Base Grease + Mixed Alkyl Borate Ester (3% w/w)
Four Ball Weld Load(ASTM D 2596) OK load Welding Load	100 Kg 126 Kg	126 Kg 160 Kg	160 Kg 200 Kg
Four Ball Wear Scar (ASTM D 2266)	0.987 mm	0.65 mm	0.478 mm

Table 9: Tribological Properties

6. **Extreme Pressure and Anti-wear additives' response:**
In this paper, effect of Extreme Pressure and Anti-wear additives on Ca-12HSA base grease with 3 % mixed alkyl borate ester is studied. 1% w/w Sulfurized Isobutylene, Dialkyl trisulfide and Zinc Dialkyl Dithiophosphate responses have been studied. From this study (Table10,11 and 12) it can be concluded that commonly used extreme pressure additive and anti-wear additive do not show effective responses in calcium grease as compared with lithium base grease. But overall performances of calcium 12-hydroxystearate grease

with 3% mixed alkyl borate ester is better and can be a replacement for lithium 12-hydroxy stearate in certain applications. Also, it is economical and thus becomes an alternative for lithium base grease.

Parameters	**Li-12HSA Base Grease + 1% SIB**	**Ca-12HSA Base Grease + 1% SIB**	**Ca-12HSA Base Grease + Mixed Alkyl Borate ester + 1% SIB**
Four Ball Weld Load (ASTM D 2596) *OK load* *Welding Load*	200Kg 250Kg	250 Kg 315Kg	200 Kg 250 Kg
Four Ball Machine Wear Scar (ASTM D 2266)	0.652 mm	0.601 mm	0.512 mm
Roll Stability, % (ASTM D 1831) Room Temperature for 2hours	14.49 %	21.31 %	1.58 % (Repeated twice)
Copper Corrosion (ASTM D-4048)	2e	2e	2c
Dropping Point, °C (ASTM D 556)	210°C	153°C	178°C

Table 10: Effect of 1% w/w sulfurised Isobutylene

Parameters	**Li-12HSA Base Grease + 1% Dialkyl trisulfide (Inactive Sulfur)**	**Ca-12HSA Base Grease + 1% Dialkyl trisulfide (Inactive Sulfur)**	**Ca-12HSA Base Grease + Mixed Alkyl Borate ester + 1% Dialkyl trisulfide (Inactive Sulfur)**
Four Ball Weld Load (ASTM D 2596) *OK load* *Welding Load*	160 Kg 200 Kg	160 Kg 200 Kg	200 Kg 250 Kg
Four Ball Machine Wear Scar (ASTM D 2266)	0.658 mm	0.564 mm	0.523 mm
Roll Stability, % (ASTM D 1831) Room Temperature for 2 hours	14.28%	2.94 %	4.83%
Copper Corrosion (ASTM D-4048)	1b	1b	2c
Dropping Point, °C (ASTM D 556)	207°C	154°C	183°C

Table 11: Effect of 1% w/w Dialkyl trisulfide (Inactive sulfur)

Parameters	Li-12HSA Base Grease + 1% Zinc Dialkyl Dithiophosphate	Ca-12HSA Base Grease + 1% Zinc Dialkyl Dithiophosphate	Ca-12HSA Base Grease + Mixed Alkyl Borate Ester + 1% Zinc Dialkyl Dithiophosphate
Four Ball Weld Load (ASTM D 2596) *OK load* *Welding Load*	126 Kg 160 Kg	126 Kg 160 Kg	200 Kg 250 Kg
Four Ball Machine Wear Scar (ASTM D 2266)	0.487 mm	0.482 mm	0.548 mm
Roll Stability, % (ASTM D 1831) Room Temperature for 2 hours	17.64%	0 %	2.68%
Copper Corrosion (ASTM D-4048)	1a	1a	1a
Dropping Point, °C (ASTM D 556)	208°C	154°C	177°C

Table 12. Effect of 1% w/w Zinc Dialkyl Dithiophosphate

Applications:

Calcium 12-hydroxystearate grease with 3% mixed alkyl borate ester field trial was successful at application areassuch as Automotive (Chassis/ Wheel Bearing), General Industrial (Stone Crusher Bearings), Paper mill bearings, Automotive window regulators and Stainless-Steel sheet (Paata) roll bearings

Future Study:

1. Studying possibilities for making Calcium 12-hydroxystearate grease in synthetic oils (PAO, Esters, AlkylatedNaphthalene, PAG and Silicone Oil)
2. Studying antioxidants' response in Calcium 12-hydroxystearate grease
3. Studying other EP additives' response in Ca 12-HSA greases and target to build formulation to achieve 500 Kg weldload

Summary and Conclusion:

Calcium 12-hydroxystearate with mixed alkyl borate ester is a most economical alternative for Simple Lithium greases with Good Mechanical Stability, Fair Pumpability, Inherent water resistance, Anti-wear and Mild EP property, Good Corrosion resistance, Fair dropping point and Economical than simple lithium grease. Manufacturing Calcium 12- hydroxystearate grease with mixed alkyl borate ester is little tricky but not hazardous as seen in case of Aluminum or Polyurea. Complexing acids is generally used for lithium greases but does not show similar performance in Calcium 12-HSA greases. Mixed Alkyl borate ester is used as dropping point enhancer in calcium 12-HAS grease. Commonly used EP and AW additives' response are not very good and often show antagonism in Ca 12-HSA soap

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A Unique Shear Captive Grease For High End Applications

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ABSTRACT:
Consistency of a lubricating grease would change if it is subjected to mechanical shear in any suitable device. The ability of the greases to maintain its consistency under mechanical shear is called shear stability or mechanical stability. Working Stability (ASTM D217) and Roll Stability (ASTM D1831) are the two standard test methods that are widely referred for checking shear stability of lubricating greases. Roll stability test appears to be more significant compared to mechanical stability test as the shearing action in bearing races is nearly identical to rolling. Lower the change in consistency the better is the product considered in shear stability.
The standard roll stability test depicts the change in grease consistency at ambient temperatures after two hours. Many grease developers modify the standard test method by a lot of variations in the test temperature and duration. Normal operating temperature of bearing is in the range of 80^{o}C while under the extreme conditions the bearing temperature may go further high. It is anticipated that greases may further excel in performance if lower values in both mechanical and roll stability tests are obtained.
Many functional polymer suppliers claim improved performance in mechanical stability and roll stability tests at ambient temperatures but in the present paper we aimed to improve the performance by altering the chemistry of thickener not by doping any polymer.
Based on the industry requirement, we at Siddharth Grease & Lubes Pvt Ltd have developed "**A New Shear Stable Grease Using No Polymer"** having excellent mechanical and roll stability even at elevated temperatures. The new greases have been extensively evaluated for life in FAG FE9 & HTWB Life Tester. Important properties of the newly developed grease like dropping point, mechanical stability, and roll stability at ambient and elevated temperatures even on increasing test duration and are discussed in this paper.
Key Words: Shear Stability, Roll Stability, FAG FE9 test, HT WB Life Test, polymers.

INTRODUCTION:
A grease consists of a physical matrix containing a fluid base oil, a thickener which provides its gel structure. When a grease is worked (subjected to mechanical stresses), its consistency or hardness will change. The reason for the change is that the soap fibers are being modified by the mechanical actions. In general, a grease will soften or become more fluid when worked. If a grease softens when worked it is referred to as thixotropic; however, if the grease hardens, it is called rheopectic. A good grease must have good shear stability implying that it exhibits a little change in penetration after undergoing mechanical stress (1). Mechanical stability is an essential performance characteristic of lubricating grease as it is a measure of how the grease consistency will change in service when it is subjected to mechanical stress (shear) resulting from the churning action caused by moving elements or vibrations generated by, or external to, the application (2&5).

Excessive grease softening in a bearing may eventually cause grease to leak out from the housing, requiring more maintenance and frequent grease replenishment to avoid premature failure resulting from lack of lubricant in the rolling elements. Shear stability varies from grease to grease. A grease with poor mechanical stability is not preferable because it may experience large changes in consistency that can cause a grease to leave its optimal operation range after being semifluid and allow an element to fail. The soap used as thickener plays the major role in grease stability. To have good mechanical stability, greases are developed through careful selection of the thickener composition and optimization of the manufacturing process. Though mechanical stability test as per ASTM D217 depicts if a grease show <40 units change in 100,000 strokes, it is rated as good.

Another test is Roll Stability which holds equal significance to evaluate shear stability of greases. The test is normally conducted at room temperature for two hours as per standard ASTM D1831 test, but the specification designers have made the test conditions more stringent by varying the standard test conditions like increase in operating temperature from ambient to 80^{0}C, conducting test in presence of water and enhancing duration of test. Due to the fibre instability of the thickener above 60°C, considerable shortening of the thickener fibres and increasing penetration values after shearing of the grease in a roll stability tester at 75°C, as well as transformation from shear thinning to shear thickening at the shear rate of 1800 s^{-1} and 80°C, were observed (3).

In real field application and use, ingress of environmental contaminants sometimes is unfortunately a common reality which often adversely affects the mechanical stability of the greases. It is important that grease not only be developed to provide excellent structural stability in a perfect state, but also in the presence of environmental contaminants such as water, process fluids, or other contaminants. This can be assessed by means of laboratory bench tests operating in a variety of conditions with presence of water (4). In order to bring the above environmental contaminants into tests conditions researchers try to conduct mechanical and roll stability in presence 5-10% of water and is considered OK if the structure is not much deteriorated indicating that the thickener is capable of sustaining stress and strain. Thus, a good grease must also be capable of depicting low to moderate changes in terms of penetration if the above tests are conducted in presence of water.

EXPERIMENTATION:

Four batches (A-D) were prepared using different thickener chemistries initiating development work from simple lithium base to Li-Ca then further shifting over to Li- complex doping different complexing agents like boric acid and di-basic acids using VG 150 base oil. All these batches were evaluated for mechanical stability and roll stability at 80^{o}C for 50 hrs. Test data is indicated in Table-1.

Candidate	Type
A	Lithium Grease in VG 150
B	Li-Ca Grease in VG 150
C	LC Grease with Boric Acid as complexing agent in VG 150
D	LC Grease with Azelaic acid as complexing Agent in VG 150
E	Li Grease with **(ASSCT) technology**
F	LC EP Grease with **(ASSCT) technology**

Table-1 : Mechanical Stability & Roll Stability Test Data

Candidate	Type	Mechanical Stability 10^5 X	Roll Stability	
		Penetration Change		
			Room Temp, 2 Hrs.	80^{o}C 50 Hrs
A	Lithium Grease in VG 150	+30		102
B	Li-Ca Grease in VG 150	+22	+18	85
C	LC Grease with boric acid as complexing agent in VG 150	+27		68
D	LC Grease with Azelaic as complexing agent in VG 150	+29		62

DEVELOPMENT OF SHEAR STABLE GREASE:

Mixed soap **greases** were initially developed to improve the short comings of individual simple soap-based greases. The most preferred thickener choice is mixed soap **grease** i.e., **lithium-calcium** as **lithium** improves the high temperature resistance of the resulting **grease** while the **calcium** explores the possibility of developing a grease having better mechanical stability and roll stability. Work was initiated in different direction using our own **Advanced Soap Salt Complex Technology (ASSCT)** on Li thickener chemistry. This approach was having limitation in dropping point around 208^{o}C. The **grease E** was finally evaluated, and the test results are shown in Table-2. The developed product was tested extensively in mechanical stability up to 5 X 10^5 strokes (Table-3). Similarly Roll Stability test was studied at ambient and elevated temperatures with increased test duration (Table-4 & 5). To further improve dropping point further complexing of thickener was done and could achieve DP > 260 ^{o}C. Based on best results obtained on a candidate batch dosage of dibasic acid was further optimized to meet other characteristics also. After observing repeated improvements in test results manufacturing process was finally optimized based on better results and yield. Additive studies were also carried out after evaluation of base greases. Finally, a wonderful product has been developed which was completely evaluated for various characteristics (Table-6) and christened the grease as Wonder Grease.

PERFORMANCE TEST:

FAG FE8 & FE9 tests are mainly used to evaluate the friction & wear characteristics of rolling element bearing. It can simulate different operating conditions, and the test results can be used to simulate the practical application of bearing, and study the friction of grease, lubrication, rolling bearing material under different working conditions.

FE 9 TEST: DIN 51821

The test rig with its test units is intended exclusively for examining the service life of grease in Angular Contact Ball Bearings.

Angular contact ball bearings type FAG Z-No. 529689 are installed in the 5 units of the test rig. They are loaded axially with a force of F = 1.5/3/4.5 kN and are operated at the specified test -1 speed of n = 3000/6000 min. The required temperature of q = 120 - 200°C is achieved by means of the resistance heating unit. The test is continued until the bearings require at least the double steady-state moment for operation due to insufficient lubricity of the grease.

The FAG FE9 test as per DIN 51821 uses five angular ball bearings, rotating at 6000 rpm, under an axial load (usually 1500N). Test temperature is selected (120 to 200^{O}C), and time to failure is based on a two-fold increase in the power requirement to rotate the bearing. The times at which the bearings have a failure probability of 10% and 50% (denoted by L10 and L50) are calculated from the data by using Weibull analysis. This method is the basis for upper operating temperature claims in the DIN (Deutsches Institut für Normung) 51825 grease classification system.
The Greases E& F were extensively evaluated for life tests at some renowned overseas independent laboratories.

RESULTS & DISCUSSION:
It is a well-known fact that >80% of the bearings are lubricated with greases, though the percentage of greases is <5. Mechanical stability & roll stability are of immense importance when dealing with the long-term service-length of grease-lubricated bearings. Poor stability will lead to consistency degradation of the grease, because of mechanical forces between the rolling parts of the bearing. Higher change in penetration numbers either in working or in rolling show greater grease thinning and, therefore, less stability. Leakage of grease through seals, or at worst a total failure of the bearing may be experienced in operation. Similarly, if roll stability at elevated temperature is good, grease will not lose its structure and can work consistently resulting in increased life of bearings.
The test data of mechanical stability and roll stability of developed grease with a dropping point of 208 C is indicated in Tables 1-4 clearly depict that the product is excellent in both mechanical stability and roll stability. This newly developed grease has shown +20 units change in 1 Lakh strokes and 30-34 units' changes in 2 to 5 Lakhs strokes working indicating that grease is not undergoing mechanical degradation even after 5 lakhs double strokes. Similar trend is visible in roll stability at ambient and in elevated roll stability test. Change in penetration is very abysmal i.e., 12 to 25 units even after prolonged rolling at 80^{O}C These two properties have contributed to achieve long life of 130 hrs in High Temperature Wheel Bearing (HTWB) Life test as per ASTM D3527. Though test data has been generated on grease made with 150 cSt base oil at 40 ^{O}C, however, product with higher base oil viscosities have also been designed and evaluated.
Another semi-synthetic product was developed in higher viscosity base oil using the above similar chemistry, but the thickener molecule was further complexed to boost the dropping point around 262^{O}C.The EP, AW, AO and other additives were also incorporated into the developed grease. Tests data has been given in Table-5. Besides physio chemical tests, test data of roll stability at different temperatures like ambient, 50 & 100^{O}C is having similar trend with little change in penetration number in working and that too on prolonged rolling. Both the working stabilities have shown a quantum jump of 390 hrs in ASTM D3527 HTWB life test. Based on the tests data indicated in Table-5, it is evident that the grease is expected to perform exceptionally good in field.
The grease E was also tested for FE 8 TEST and passes the test. This product is commercialised by one reputed company and is being supplied regularly.
The grease F was tested for FE 9 TEST at 140 & 160^{O}C.
Recommended Applications:
Based on the extraordinary life tests data, we embarked upon field trials of this grease in long life applications. The grease has shown promising results in the field for 300K mileage and is being evaluated for 500K and EV application also. It has also found to be a problem solver for many critical industrial applications, where good high temperature stay put property is required. This grease can be true high-performance grease for important industrial applications, where no unwanted breakdowns are warranted. Based on the evaluation data obtained in FE 8 & FE 9 TEST Rigs including HTWB Life tester, we strongly recommend the developed products in the

following applications:

- Greases for heavy duty automobiles for long GDI.
- Railroad Greases
- Electrical Vehicles
- Critical Steel Plant & other critical areas.

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Table-2 : **GREASE E**

S. No.	Test Parameter	Test Method	Test Results
1	Penetration, Worked 60X Change in penetration after 10^5X	ASTM D 217	245 +20
2	Dropping Point, ºC	ASTM D 2265	208
3	Copper Corrosion at 100^0C, Rating	ASTM D 4048	1b
4	Base Oil KV 40ºC, cSt	Formula	150
5	Roll Stability ,80 ºC ,50 Hrs., Change in penetration	ASTM D 1831	+ 20
6	WB Life	ASTM D 3527	130 Hrs
7	Low Temp Torque, Nm At -10ºC At -20ºC	IP 186	 0.04/0.02 0.12/0.07
8	Heat Stability, % wt.	ASTM D 6184	0.90

The above developed grease was extensively studied for extended mechanical stability for 1X 10^5X; 2 X10^5X; 3 X10^5X; 4 X10^5X and 5 X10^5X. The test data of mechanical working are indicated in the Table (III)

Table-3

S. No	Test Parameter	Test Method	Test Results
1	**Penetration, Worked 60X** Change in penetration after 1x 10^5X Change in penetration after 2x 10^5X Change in penetration after 3x 10^5X Change in penetration after 4x 10^5X Change in penetration after 5x 10^5X	ASTM D 217	245 +20 +30 + 32 + 33 + 34

The developed grease was studied for roll stability at ambient temperature for 2 hrs and 16 hrs. The test data of roll stability are indicated in the Table (III).

Table-4

1	**Roll Stability at ambient temperature** Change in penetration after 2 Hrs. Change in penetration after 16 Hrs.	ASTM D 1831	-10 +9

Table-5

1	**Roll Stability ,80^{O}C** Change in penetration after 24 Hrs. Change in penetration after 50 Hrs. Change in penetration after 100 Hrs. Change in penetration after 150 Hrs.	ASTM D 1831 (Modified)	+12 +20 +25 +23

Table-6

GREASE F

S. No	Test Parameters	Test Method	Test Results
1	Colour	-	Brown
3	VI	ASTM D2270	110
4	Thickener Type	-	Proprietary
5	Base oil viscosity at 100^{o}C in cSt	ASTM D445	18.5
6	Worked Penetration (1/10 mm) at 25℃ 60 Double strokes 100,000 Double strokes	ASTM D217	284 (+18)
7	Drop Point, ℃	ASTM D566	262
8	Shell 4 ball OK Load, kgf	ASTM D2596	315
9	Four ball wear scar diameter, mm	ASTM D2266	0.52
10	Fretting Wear, mg	ASTM D4170	8
	Roll Stability, change in penetration- **a)** For 2 h at room temperature **b)** For 16 h at 50 ℃ d) For 100 hrs at 100	ASTM D1831	a) + 14 b) + 16 c) + 15
12	Water washout, % mass	ASTM D1264	1.9
13	Oil separation during storage, % mass	ASTM D1742	1.4
14	Oxidation Stability. Pressure drop at 100 h ,100^{o}C, Drop in pressure in psi	ASTM D942	1.5
15	Rust preventive properties	ASTM D 1743	Pass
16	EMCOR Test (DW)	ASTM D 6138	0,0
17	Copper Corrosion	ASTM D 4048	1a
18	WB Leakage Test, **1)** Leakage in mass, g **2)** Other observations	ASTM D1263	1). 0.80 g 2). No deposits in the WB races & rollers no abnormal changes in consistency or structure of the material indication of dry running of races
19	High temperature wheel bearing life test	ASTM D 3527	390
20	FAG FE 9 (h),6000 rpm/1500N **a)** 120 ^{o}C **b)** 140 ^{o}C **c)** 160 ^{o}C		Actual data given in presentation

A Study on Effect of Pre-formed Li-12HSA Thickener on the Properties of Lithium Grease

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KEY WORDS – Grease, Lithium hydroxide, Lithium 12- HSA, Preformed soap, in-situ process

Abstract

Thickening agent or gellant or thickener is the most important component of lubricating greases. Many characteristics of greases such as high temperature behavior, flow properties, water resistances etc depend upon these thickeners. Typical thickeners used in lubricating greases include the alkali/alkaline metal soaps, clays, polymers, asbestos, carbon black, silica gels and aluminum complexes. Soap thickened greases constitute the largest segment by far of the commercially available greases. Among soap based thickeners, lithium 12-hydroxystearate (Li-12HSA) is most widely used thickener. These soap based thickeners are made in-situ reacting long chain fatty acids with neutralizing agents such as alkali/alkaline metal hydroxides and this process is called saponification. Grease manufacturing is highly energy intensive as saponification is done in an open and a pressurized vessel at high temperature for long duration. Energy efficient processes and superior grease compositions are being preferred these days in grease industry for better suitability. With the use of pre-formed soap thickeners, saponification step can be omitted leading to energy savings. Many pre-formed metal soaps of fatty acids are availablein market for grease making and other applications. Present study deals with use of pre-formed Li- 12HSA powder for grease making. The effect of Li-12 HSA when used in different ratios in grease compositions has been studied and compared with normal Lithium grease manufactured by conventional method.

Introduction

There are several thickener types and grades available in market. However, Lithium soap has majorityshare (85-90%) of grease market [1]. These lithium greases are made by reacting fatty acids such as 12-hydroxystearic acid (12-HSA), stearic acid, hydrogenated castor oil (HCO) and vegetable oils with lithiumhydroxide monohydrate. Grease soap manufacturing can be done by following two types of processes [2]. **Continuous Process**: Continuous flow of raw materials to the system during the production cycle.Production output is also very constant. High productivity, energy efficient, minimal batch to batchvariations, limited products. It is suitable for high volume greases.

Batch Process: Total amount of raw material is introduced to the system at the beginning of the process. Output process is obtained after certain time**.** Low productivity, high energy consumption, large batch to batch variations, multiple products. Batch process is most widely used manufacturing process. It is suitable for low volume and variety of grease products.

A typical grease making process using fat and alkali is shown in the Fig. 1(a) [3]:

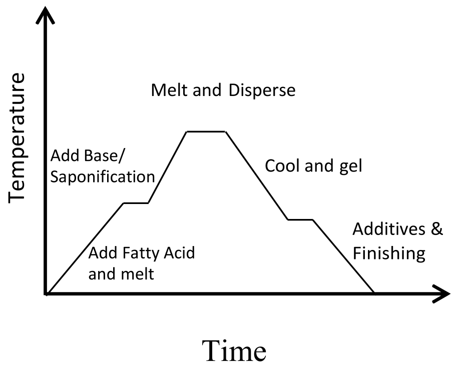

Fig. 1(a) Typical grease making process using Fat and Base

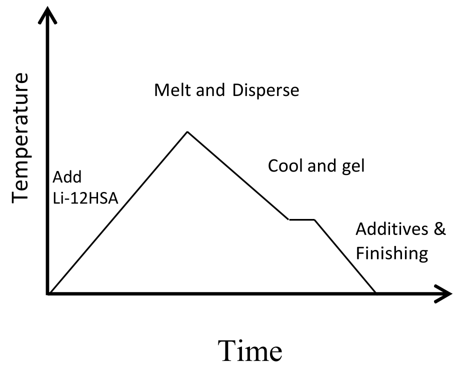

Fig. 1(b) Typical grease making process using Pre-formed Soap

number of pre-formed metal soaps such as Calcium Stearate, Aluminum Stearate, Sodium Stearate, Lithium 12-Hydroxystearate (Li-12HSA) and Calcium 12-Hydroxystearateare are commercially available for grease manufacturing. A typical grease making process using pre-formed soaps is shown in Fig. 1(b). Details and general properties of these preformed thickeners are given below in Table-1.

Table 1: Typical Test Data of Commonly Used Pre-formed Thickeners

S. No .	**Properties**	**Calcium Stearate**	**Sodium Stearate**	**Lithium 12-HSA**	**Lithium Stearate**	**Calcium 12-HSA**
1.	CAS no	1592-23-0	822-16-2	7620-77-1	4485-12-5	3159-62-4
2.	Mol wt. g/mol	607.02	306.47	306.41	290.42	639.00
3.	Texture & Color	White powder	Off-white powder	Off white powder	Off white powder	Off white powder
4.	Melting point, °C	145-148	205-207	210-212	220-223	142-146

Key advantages of pre-formed grease thickeners over conventional soap making are as follows:

- Superior batch uniformity: with use of pre-formed grease thickeners, batch to batch variations in grease characteristics such as color, texture, consistency etc can be minimized in comparison to conventional in-situ grease making.
- Reduction in processing time: with removal of grease soap making and subsequent dehydration, grease processing time can be reduced significantly in comparison to conventional soap making. Finally, this will lead to increase in overall production and productivity.

- No water to remove: Water is produced as by-product in-situ grease making. Specially designed high pressure reactors which can handle high steam pressure. Special systems such as vacuum suctions

  etc are also required for dehydration of soap. So issues associated with water generation can be eliminated.
- Smaller raw material inventory: with use of pre-formed thickeners, inventory requirements for fats, fatty acid and neutralizing agents can be eliminated.
- Improper chemical stoichiometry: In-situ grease making requires exact mole calculations of all reactants. Improper chemical stoichiometry due to calculation, measurement and manual errors can leave excess free acidity or free alkalinity in greases. Excessive free acidity or free alkalinity can be detrimental for grease performance.
- Greatly Improved safety of plant personnel: With elimination of high pressure step and corrosive alkali/alkaline hydroxides, safety of plant personnel can be increased significantly.

Lithium soap greases are gels comprising a major portion of normally liquid lubricating oil held within the interstices of a mat of twisted microscopic fibers of the lithium soap [4]. According to widely accepted theories, fiber geometry (expressed as fiber length in microns, or as the ratio of fiber length to fiber width "L/W") controls the properties of a grease [5]. A short fiber length or small L/W ratio makes the grease softer in consistency. The temperature fluctuation near the molten stage of grease is found to influence the growth of soap fiber. This fluctuation causes fusion and solidification of the soap fiber leading to the growth of long fibers [6, 7]. Mechanical or shear stability, that is the ability of a grease to resist hardening upon ageing and permanent softening after physical working, is normally associated with greases of relatively long fiber length. On the other hand, the ability of a grease to retain the lubricant oil in gel form or 'oil bleed' depends on the size of spaces between soap fibers, and for greases of a given soap concentration, resistance to oil bleed is found in grease with shorter fibers[8]. A balance of both the parameters could lead to superior properties in grease.

Structure of thickeners will also have an effect on other physical properties of the grease such as lubricity and frictional behavior. Greases with same composition but different thickener structure are reported to show different friction coefficients. Boundary lubrication properties of greases with different soap fiber structures have also been studied. It has been observed that strength of soap fiber structure againstshear force dominated the boundary friction properties of greases. Studies carried out using ball-on-disk type point-contact sliding test apparatus show that grease with long soap fibers shows better frictional resistance properties and offers greater protection against friction at the rubbing surface than grease with short soap fibers [9]. Numerous studies have also shown the effect of thickener fiber size on film thickness and eventually friction coefficient especially under low speed conditions [10-14].

Lithium greases are selected for this study as these accounts for 80-85% of total grease volume[1]. In the light of previously discussed theories and results, a study was planned to evaluate pre-formed Lithium - soap for grease making. Ltihium grease was also manufactured in conventional way by making Lithium in-situ soap (Li in-situ). During study total thickener weight % was kept constant and Lithium in-situ soap/Li-PFT ratio was changed to evaluate the effect on resulting grease properties.

Experimental
Material &
Methods

Pre-formed Li-12HSA powder was sourced from its manufacturer. All greases were made through batch process (~4 kg) in auto-clave type grease kettle (M/s Sotelem make) having hot oil thermic fluid re- circulation system and finally finished with milling machine (M/s Frigmaires Engineers make, Stator-rotor type model). Finished greases were tested in details by following standard ASTM test methods. Group I 500 N mineral base oil was sourced from CPCL refinery of M/s Indian Oil Corporation Ltd.

Seven different Lithium grease batches were freshly prepared in mineral base oil in laboratory in a greasekettle by batch process and were finished by milling keeping gap constant. The greases contained different proportions of in-situ Li soap and Pre-formed Li-12 HSA thickener (Li-PFT). The base oil and thickener content were adjusted to get NLGI Grade 3 grease. The greases were designated as Li-1 to Li-

7. Grease Li-1 contained 100% Li-in situ soap and manufactured by standard procedure. The greases Li- 2, Li-3, Li-4 and Li-7 contained Li in-situ: Li-PFT in following ratios 90:10, 80:20, 70:30 and 50:50 respectively. In these greases the Li-PFT thickener was added to the molten grease at 200 °C and stirred followed by cutback, cooling and milling. The grease Li-5 contained 100% Li-PFT thickener which was added to the kettle at charging stage and usual process was carried out. The grease Li-6 contained Li in- situ: Li-PFT in the ratio of 90:10 but in this case the Li-PFT was added during the charging stage unlike grease Li-2. The grease batches were tested for different parameters viz., dropping point, penetration, shear stability, roll stability and water washout characteristics. To investigate the grease soap fiber structure, size and morphology, SEM studies were performed on the grease samples using JEOL, (JSM- 6610 LV Model) from JAPAN at room temperature. Film of a speck of grease sample was made on a micro-slide by means of a spatula and this film was rinsed gently with Hexane to remove the oil from the soap fiber matrix. The slide was then dried at ambient temperature for few hours to evaporate hexane. Film was then mounted on a carbon tape and was sputter coated with Pt film and examined by SEM at 5kV.

The test results of these greases is summarized in the following tables 2, 3 and 4.Table 2 shows the test data of greases containing 100% of single type of thickener. Table 3 shows the effect of change in greaseproperties with change in Li-PFT concentration and Table 4 displays the effect of impact of addition timeof Li-PFT on grease properties.

Table 2: Test Data of Lithium greases containing 100% Single type of Li thickener

Batch Name		**Li-1**	**Li-5**
Thickener Content (Wt.%)		10.0	10.0
Li-PFT Content in Thickener (Wt. %)		0	100
Addition stage of Li-PFT		None	Charging stage
Testing Parameter	Test Method		
Dropping Point, °C	ASTM D 566	203.0	199.0
Penetration	ASTM D 217		
Unworked		237	235
Worked		236	230
100000 strokes		262 (+26)	260 (+30)
Texture		Smooth	Smooth, Glossy, Transparent
Color	Visual	Brown	Brown
Roll Stability, Penetration Change units, 16 hr, RT	ASTM D1831	259 (+23)	259 (+29)
Roll Stability, Penetration Change units, 16 hr, 80°C	ASTM D1831	333 (+97)	305 (+75)
Water washout (%)	ASTM D1264	2.11	2.18
Oxidation Stability (kPa)	ASTM D942	20.0	19.5
Weld Load (kg)	IP 239	160	160
Wear Scar Diameter (mm)	ASTM2266	0.7	0.7

Table 3: Test Data of Lithium greases containing different ratios of Li in-situ and Li-PFT thickener

Batch Name		Li-1	Li-2	Li-3	Li-4	Li-7
Thickener Content (Wt.%)		10.0	10.0	10.0	10.0	10.0
Li PFT Content in Thickener (Wt. %)		0	10	20	30	50
Addition stage of Li-PFT		None	Molten stage (at 200 °C)	Molten stage (at 200 °C)	Molten stage (at 200 °C)	Molten stage (at 200 °C)
Testing Parameter	Test Method					
Dropping Point, °C	ASTM D 566	203.0	202.0	201.0	197.0	204.7
Penetration	ASTM D 217					
Unworked		236	228	231	232	248
Worked		236	224	230	227	239
100000 strokes		262 (+26)	264 (+40)	267 (+37)	259 (+32)	266 (+27)
Texture		Smooth, Opaque	Smooth, Glossy, Translucent	Smooth, Glossy, Translucent	Smooth, Glossy, Translucent	Smooth, Glossy, Transparent
Color	Visual	Brown	Brown	Brown	Brown	Brown
Roll Stability, Penetration Change units, 16 hr, RT	ASTM D1831	259 (+23)	262 (+38)	267 (+37)	257 (+30)	267 (+28)
Roll Stability, Penetration Change units, 16 hr, 80°C	ASTM D1831	333 (+97)	325 (+101)	329 (+99)	315 (+88)	313 (+74)
Water washout (%)	ASTM D1264	2.11	1.87	2.1	1.82	2.84
Oxidation Stability (kPa)	ASTM D942	20.5	20.0	19.5	19.5	20.0

Weld Load (kg)	IP239	160	160	160	160	160
Wear Scar Diameter (mm)	ASTM2266	0.7	0.7	0.7	0.7	0.7

Table 3: Test Data of Lithium greases containing 90:10 ratio of Li in-situ: Li-PFT with differentaddition stage of Li-PFT

Batch Name		Li-2	Li-6
Li PFT Content in Thickener (Wt. %)		10	10
Addition stage of Li-PFT		Molten stage (at 200 °C)	Charging stage
Testing Parameter	Test Method		
Dropping Point, °C	ASTM D 566	202	206
Penetration	ASTM D 217		
Unworked		228	237
Worked		224	224
100000 strokes		264 (+40)	253 (+29)
Texture		Smooth, Glossy, Translucent	Smooth, Glossy, Translucent
Color	Visual	Brown	Brown
Roll Stability, Penetration Change units, 16 hr, RT	ASTM D1831	262 (+38)	251 (+27)
Roll Stability, Penetration Change units, 16 hr, 80°C	ASTM D1831	325 (+101)	309 (+85)
Water washout (%)	ASTM D 1264	1.87	1.96
Oxidation Stability (kPa)	ASTM D942	20.5	20.0
Weld Load (kg)	IP239	160	160
Wear Scar Diameter (mm)	ASTM2266	0.7	0.7

Results and Discussion

Seven different Lithium grease batches were prepared with different ratios of Li-in-situ soap: Li-PFT thickener. As already proven that the properties of grease formed by In-situ Saponification process and that by pre-formed thickener are significantly different, it was considered worthwhile to try out combinations of both the In-situ and pre-formed thickener in different ratios. The effect of replacing a certain quantity of Li in-situ with Li-12HSA pre-formed soap is studied in detail in different ratios. The test data of these greases is shown in Tables 2, 3 and 4. Each test parameter result is discussed in the following paragraphs.

All the greases were brown coloured and had a smooth homogeneous texture. The greases with higher concentration of Li-PFT were found to have a more transparent and glossy appearance. This is because of the formation of thinner fibers and a denser fibrous network of Li-PFT (Fig. 3). The dropping points ofall the greases were in the range of 195- 206 °C which is characteristic of Lithium greases.

SEM analysis of the three base greases was carried out to study the grease microstructure. All the greases were found to have dense entangled fibrous structure. However the greases where Li-PFT is present have a very fine and even more dense fibrous network than regular Li in-situ soap grease. This may be correlated with the high optical clarity very smooth texture, and relative stiffness for a given soap content. As already known that fiber size is crucial for light transmission through the medium therefore, shorter the fiber length higher the transparency. The fibers themselves are too small to scatter light but allow it to transmit through the medium resulting in transparency [15, 16]. The SEM images (Fig 2-8) are aligned to this fact.

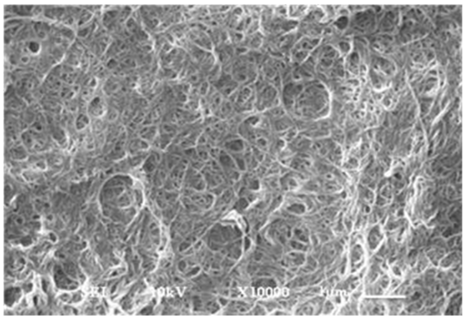

Fig. 2 Grease Li-1 with 100% In-situ Li 12HSA

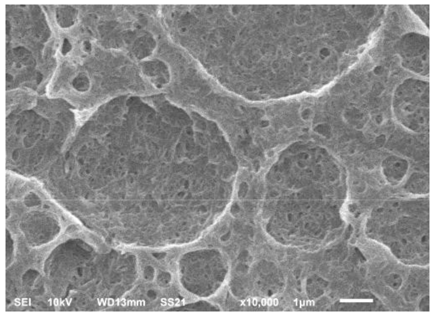

Fig. 3 Grease Li-5 with 100% Li-PFT

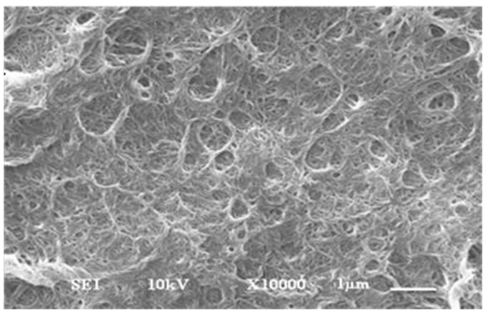

Fig. 4 Grease Li-2 with 10% Li-PFT

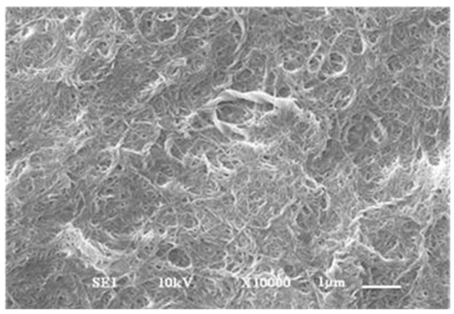

Fig. 5 Grease Li-3 with 20% Li-PFT

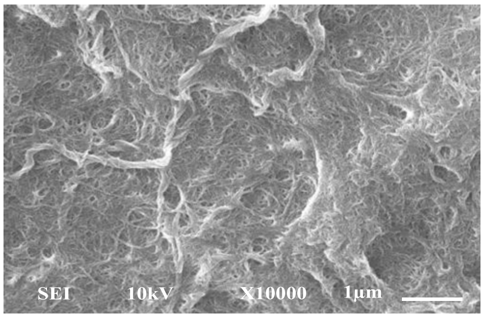

Fig. 6 Grease Li-4 with 30% Li-PFT

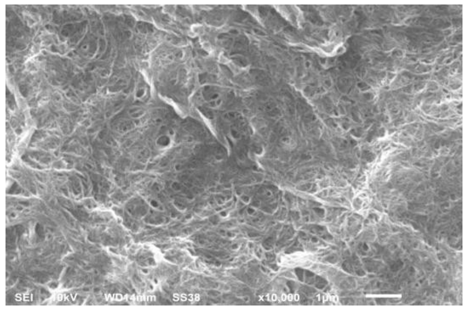

Fig. 7 Grease Li-7 with 50% Li-PFT

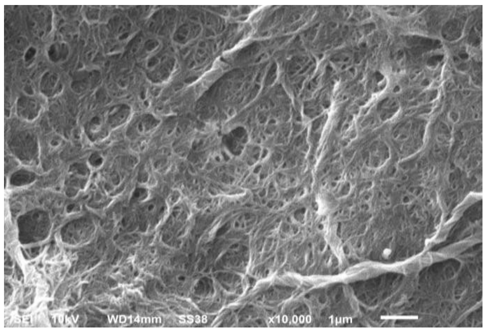

Fig. 8 Grease Li-6 with 10% Li-PFT (added during charging)

In Fig. 2 grease Li-1, thick dense soap fibers are observed. But when we analyze the grease Li-5 (Fig. 3) where the thickener matrix is 100% Li-PFT, we observe a very fine and extremely dense fibrous network of thickener. This definitely impacts the properties of the finished grease.

On observing the SEM images 4 -7 we observe that as the concentration of Li-PFT increases the fibers become comparatively thinner and the structure becomes a very dense fibrous network. On comparing the structures of Li-2 and Li-6 (Fig. 4 & 8) we observe that the grease Li-6 has a similarity with Grease Li-

1. The role of addition stage of Li-PFT thus makes an impact on fibrous network formation.

The worked penetration of all the greases was found to be between 220-240 ie. NLGI Grade 3. With the introduction of Li-PFT product yield may be higher probably because there is no chemical reaction involved while using Li-PFT. However, in case of Li in-situ soap there are chances of raw material remaining unreacted that may lower the yield. Variation of worked penetration and shear stability of greases prepared is shown in Fig. 9.

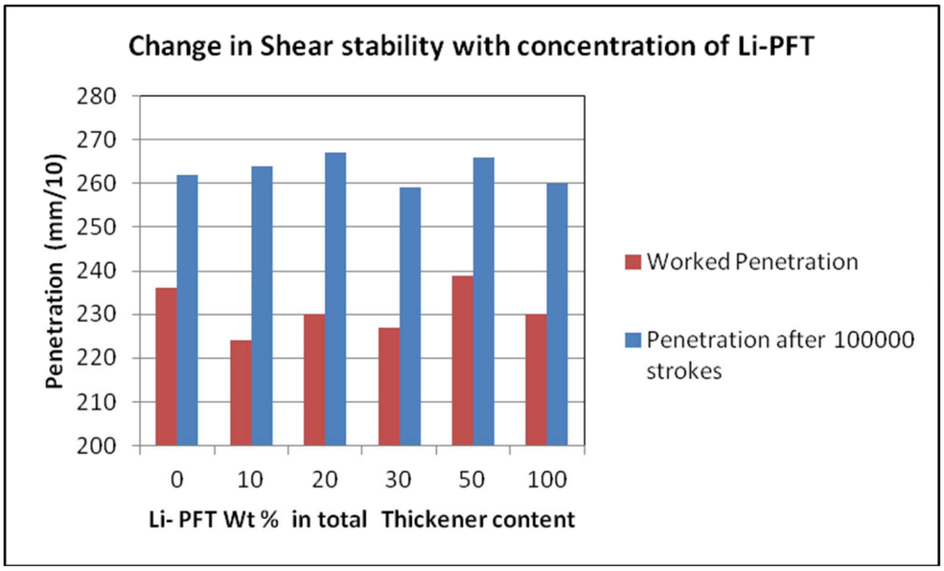

Fig. 9 Graph showing change in Shear stability with concentration of Li-PFT

On observing the data of penetration after 10^{5x} strokes it was observed that the shear stability of grease becomes poor after introduction of Li-PFT in grease matrix. However, the grease Li-7 with 50:50 ratio of Li in-situ: Li-PFT is found to be more shear stable than others and comparable to grease Li-1 with 100%Li in-situ soap. The 50:50 ratio of two different fiber sizes might help to balance the grease thickener network. The stage of addition of Li-PFT seems to have an influence on shear stability. When we compare the greases Li-2 and Li-6, both these greases have the same ratio of thickeners Li-in-situ soap: Li-PFT thickener ie. 90:10, however the grease Li-6 is found to be more shear stable than Li-2. It could be a possibility that the addition of Li-PFT during charging stage leads to a better co-crystallization of thickeners and therefore a better fiber network formation than when it is added at molten stage. In case of Grease Li-2, the addition of Li-PFT at 200 °C leads to the melting of the Li-PFT instantly and creating nucleation sites which leads to the formation of long fibers. This could be a reason of relatively poor shearstability [5-7]. The effect of Li-PFT concentration on grease consistency and its shear stability is shown in the bar graph in Fig. 9.

When we look at the Roll stability test data at room temperature the Li-1 grease with 100% Li in-situ soap appears more stable than others. Introduction of Li-PFT at 10% concentration makes the grease poor wrt Roll stability, however when the Li-PFT content is further increased to 50% the roll stability appears to improve. Here the time of addition of Li-PFT seems to influence the roll stability. Addition of Li-PFT (10%) at charging stage in case of grease Li-6 appears to perform better than grease Li-2 where the Li-PFT is added at molten stage [6-8]. The effect is shown in Fig. 10 below.

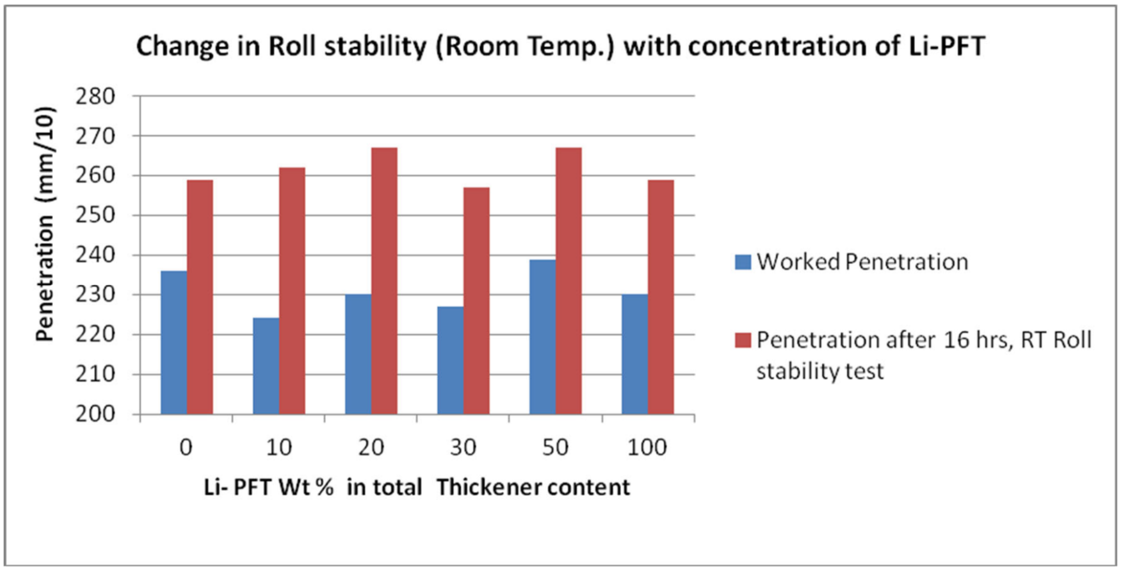

Fig. 10 Graph showing change in Roll stability (Room Temp.) with concentration of Li-PFT

When we go through the high temperature Roll stability data at 80 °C, it was found that the Grease Li-7 with 50:50 ratio of both thickeners fares better than the other greases. At high temperature with an increase in the concentration of Li-PFT the performance of grease appears to improve. For the greases Li-5 and Li-7 with 100% and 50% Li-PFT respectively the high temperature roll stability test data is somewhat similar. Here again the order of addition makes an influence. When we compare the greases Li-2 and Li-6, both these greases have the same ratio of thickeners Li-in-situ soap: Li-PFT thickener ie. 90:10, however the grease Li-6 is found to be perform better than Li-2. The thickener co-crytallization and fiber size probably has a role to play in this case [6-8]. This data has be summarized as a bar graph in Fig. 11 shown below.

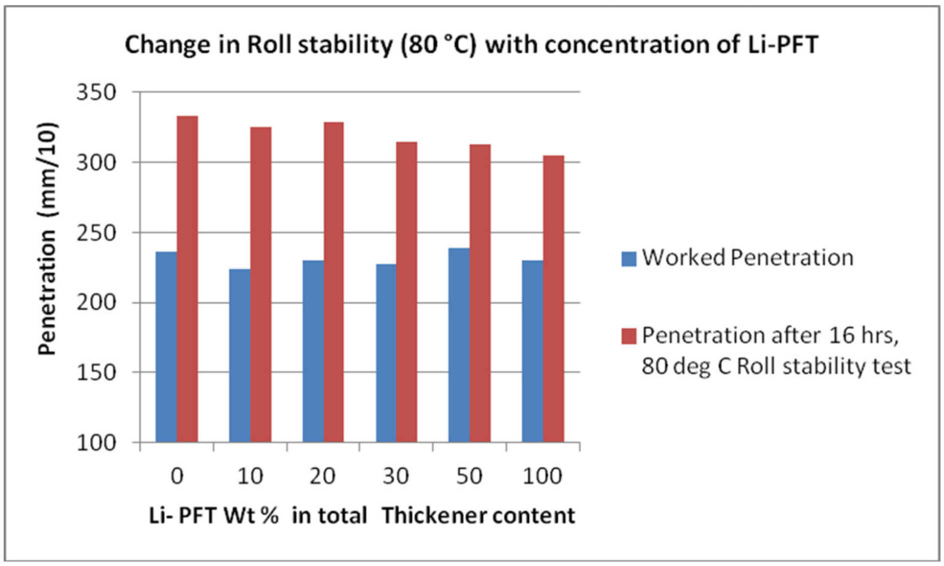

Fig.11 Graph showing change in Roll stability (80 °C) with concentration of Li-PFT

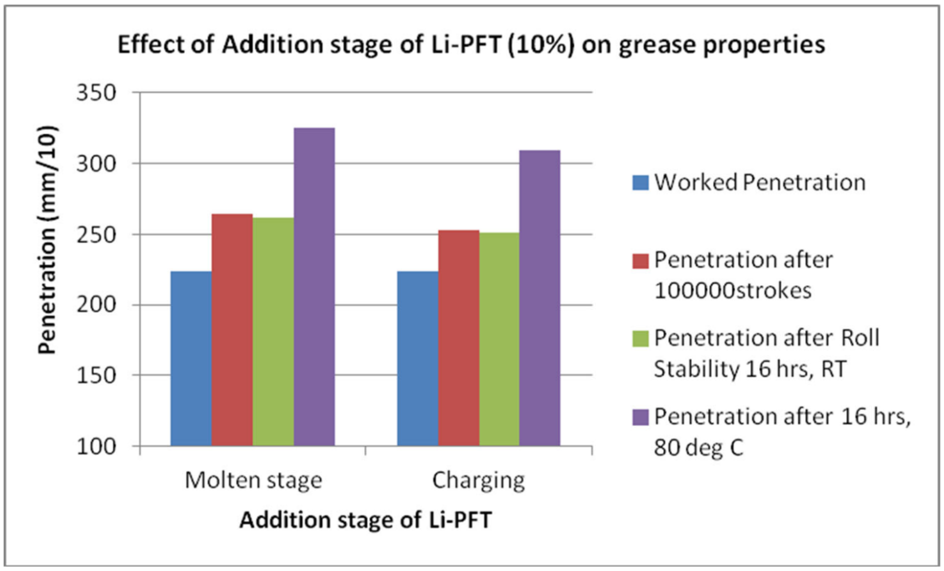

Fig. 12 Graph showing change in different properties with change of addition time of Li-PFT

A comparison of all the properties which are influenced by changing the addition stage of Li-PFT (10% in total thickener) is presented in graphical plot in Fig. 12. The results have been discussed in the above paragraphs.

On comparing the water washout characteristics all the greases were found to be more or less similar in performance. The water washout value was found to be between 1.8- 3.0 % typical for Lithium greases. There doesn't seem to be much effect of concentration of Li-PFT on water washout characteristics of these greases.

Conclusions

This study provides insights in the grease manufacturing aspect of Lithium greases where Li-PFT is used either purely or in combination with in-situ Lithium soap. An approach to use Pre-formed Li-12 HSA thickener in place of Lithium hydroxide was explored.

Some of the advantages of using Pre-formed Li-12 HSA are that production time and energy would be saved as there would be no chemical reaction rather only physical mixing where the thickener would be melted and blended with hot oil. The cooking process would be simplified or rather eliminated. As a result lesser time, pressure, energy would be required for batch production. Resulting in no or less pressure would make cooking process much safer. Also since the raw material is not undergoing any chemical reaction and no water is involved in the manufacturing process so dehydration time would not be needed and therefore saved. There might be lesser incidents of batch to batch variation.

With increase in Li- PFT thickener in the grease shorter fibers are formed resulting in a more dense thickener fibrous network. This leads to a smoother texture and the grease has a more glossy and transparent appearance providing an aesthetic appeal to the product.

On observing the test data some of the disadvantages of Pre-formed thickener could be identified. With increase in Li-12 PFT in grease the resulting product is not as much shear stable as the grease formed by Li in-situ soap and penetration change of +6 to + 14 units is observed. Also there are significant changes observed during the roll stability test at both room temperature and higher temperature. This may have an impact on the grease performance for applications where excessive mechanical shearing is present. The fiber length or fiber structure of lithium soap grease will also have an influence on tribological properties such as friction because soap fibers provide a protective function by intervening at the rubbing surface area. Although the two types of grease had the same composition, their different soap fiber structures resulted in a different extent of protective ability against friction. It is considered that the factors involving different degrees of protection ability at the rubbing surface area are (1) the resistance against friction of soap itself intervening at the rubbing surface area differs according to the strength of the fiber structure; and (2) since the grease entraining ability into the rubbing area differs according to the soap fiber structure, the amount of grease that is entrained into the rubbing surface area resulted in different degrees of protection.
After studies on Li-PFT and its effect on grease properties we can conclude that the properties of grease could be fine tuned to suit our requirements by changing the various manufacturing conditions viz., concentration of Li-PFT, addition time and temperature of Li-PFT and reaction time.

Future Plan

Further studies are being planned by authors to study the other aspects of Li-PFT greases such as EP, Friction and high temperature life.

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