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High Performance Greases For Long-Life And Sustainability

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ABSTRACT

Sustainability is the ability to exist and develop without reducing natural resources for the future generations. The United Nations defined sustainable development as the development that meets the current needs without compromising the ability of future generations to meet their own needs. As the resources are finite, we should try to use them conservatively and carefully to ensure that these are enough for future generations, without hampering present quality of life. We should focus on environmental protection by reducing the usage of lubricants and greases which are pilfering into the environment in many total loss systems. So, efforts should be made to develop high performance greases to reduce the overall consumption so that natural resources are conserved, and pilferages are minimized.

We at Siddharth Technology Centre of Siddharth Grease & Lubes Pvt Ltd, developed a series of long-life greases for automotive, industrial and mining applications. These new greases have manifold performance levels over the current greases thus meeting the undefined sustainability targets in the industry. This paper describes the development and evaluation of long life greases showing the benefits accrued by these greases to the industry and environment.

Keywords: Thickener, Lithium Complex, Life performance, base oil, field trial, GCLB /HPM Core specification & ASTM D 3527, FAG FE9 Tests.

INTRODUCTION

Sustainability is the ability to exist and develop without depleting natural resources for the future generations. The United Nations defined sustainable development in the Brundtland Report as development that meets the needs of the present without compromising the ability of future generations to meet their own needs while ensuring a balance between economic growth, environmental care and social well-being. Sustainability and environment are inter-related and so lubricants are required to be sustainable and at the same time protect the environment.

Lubricants are essentially used in moving machinery to smoothen the operation by reducing friction and wear of the moving parts so that life of machine components is extended and trouble-free operation is achieved. Lubricating grease is one of the basic requirements of industrial and automobile sectors to cater to the durability, reliability, service efficiency of moving mechanisms, machines and equipment. Automotive segment is the dominating end user industry of greases globally. World grease market for automotive sector is of prime importance and accounts for 35-40% of total grease usage. India's developing economy, fast developing infrastructure and rising status of working class keep on demanding long life greases. This would further demand the automotive lubricant market to grow in positive direction. The automotive industry in India is the fourth-largest in the world as per 2021 statistics. In 2022, India became fourth largest country in the world by valuation of automotive industry. As of 2022, India is the 3rd largest automobile market in the world, surpassing Japan and Germany in terms of sales.

In automotive industry, the passenger vehicles and commercial vehicles are driving the demand for high performance greases. Lubricating greases are extensively used in various auto parts such as wheel bearings, chassis points, universal joints, CV joints, suspensions, gears, connectors, etc due to their well-established properties such as mechanical stability, high temperature operability, corrosion resistance, and oxidation resistance characteristics. The need for high performance grease is rising due to innovative technological approaches advances in machinery and equipment. The global grease market was valued at USD 2.04 billion in 2015, and is projected to reach USD 2.28 billion by 2021 at a CAGR of 2.0% between 2016 and 2021.

Motor vehicles are categorized into light vehicles, buses and heavy-duty trucks. Life of the grease is very important and greases with increased life will be preferred. Conventionally automotive greases were based on Calcium and Sodium thickener but now both are replaced by Li/Li-complex greases. Sodium base greases are being phased out slowly but still sold in Indian market.

AUTOMOTIVE LONG-LIFE GREASES

The heavy duty motor vehicles like trucks and buses consume a major portion of high performance greases. Keeping the longer drain period, down time and service cost in consideration, the specifications are framed more and more stringent. The benefits include longer grease life, enhanced bearing protection & longevity, wide temperature range of application and the potential for improved mechanical efficiency and finally energy savings.

For the last few years, grease manufacturing companies including MNCs have adopted GC-LB as the most stringent specification for performance rating of automotive greases. Grease suppliers used to claim changeover of grease after 80,000 Km run as maximum life of grease but now the grease formulators are under pressure and they are required to develop grease life

>120,000 Km and above. It is rather difficult to monitor trials in heavy duty trucks for over 200,000 Km or more. There is no standard test exactly simulates or predict life of grease in field. It is, therefore, felt necessary to extrapolate lab test data with actual field data to draw some correlation. As ASTM D 3527 is a standard test method for evaluation of life of wheel bearing commonly used in heavy duty trucks and this test is also included in GCLB specification, it was therefore thought to generate life data of all developed greases using this standard test method. As given in the Table 1 GC-LB specification has been further upgraded in HPM Core by increasing EP & AW and incorporating oxidation stability which is essential for long life property.

We presented a paper in ELGI AGM in 2018 at London disclosing the methodology of attributing grease life & mileage claims based on ASTM D3527 data, actual field trials and data generated on an in-house life tester of bearing company. We developed a series of long life greases up to 500,000 kms as given in the Table 2 and commercialized. These greases are currently in use mostly by heavy duty long haul multi axle trucks. The long life automotive greases give many advantages and help in sustainability and environment protection.

TABLE-1: COMBINED GC-LB / HPM CORE SPECIIFICATION

S. No	Test	Test Method	Spec. Limit
1	Consistency	ASTM D217	220-340
2	Dropping Point, ^{O}C	ASTM D566/2265	220 Min
3	Rust protection, Rating	ASTM D1743	Pass
4	Low Temperature performance at -40 °C, Nm	ASTM D4693	15.5 Max
5	Water Resistance at 80°C,% loss	ASTM D1264	10 Max
6	Oil Separation ,% mass	ASTM D1742	6 Max
7	Emcor Rust Test, rating	ASM D6138	0,1 Max
8	Wear scar diameter, mm	ASTM D2266	0.6 Max
9	Weld Load, kgf	ASTM D2596	250 Min
10	Elastomer (NBR) compatibility: % Volume change, % Hardness change	ASTM D4289	−5 to + 30 −15 to + 2
11	Leakage tendencies, g	ASTM D4290	10 Max
12	High temperature life, hours	ASTM D3527	80 Min
13	Fretting protection, mass loss, mg	ASTM D4170	10 Max
14	Oxidn. stability, pressure drop in psi 100 hrs	ASTM D942	5.1
15	Heat Stability, %wt	ASTTM D6184	7 Max
16	Oil Separation on storage, %wt	ASTM D1742	5 Max

TABLE-2: COMPARATIVE DATA OF LONG LIFE GREASES 80000 / 100000 / 120000 / 200000 / 500000 KMs

S. No	Test Parameters	Test Method	Long Life Greases in km				
			80K	100K	120 K	200K	300 K
1	NLGI Grade	ASTM D217	3	3	3	3	3
2	Penetration 60X		220-250				
3	Wheel bearing leakage test, g	ASTM D1263	5 max				
4	Base oil, KV @ 40° C, cSt	ASTM D445	160-200	180-240			
5	Dropping Point,° C	ASTM D2265/ D566	230 min.	250 Min.	260 Min.		
6	Copper strip corrosion	AST M D4048	1b max				
7	Water washout, %wt	ASTM	10 max	5 max	3 max		

		D1264					
8	Oil separation, mass % loss	ASTM D1742	5 max	5 Max		2 Max	
9	4 Ball Weld load (Kgf)	ASTM D2596/ IP239	250 Min.		315 Min.		
10	4 Ball wear scar diameter, mm	ASTM D 2266	0.6 max	0.6Max			
11	Corrosion prevention Properties	ASTM D1743	Pass				
12	Dynamic Rust test in D/W	ASTM D6138	0,0				
13	Wheel Bearing Life Performance test, hrs.	ASTM D3527	90 min.	120 min.	135 min.	225 min.	350 min.
14	Roll stability after 50 hrs. at 80 °C , Δ in %	ASTM D1831 (Modified)	25 Max				
15	Mileage claim under ideal test conditions, Km, Min	Based on our co related study of Rig Data's & Field trials	80K	100K	120K	200K	500K

MINING & CONSTRUCTION EQUIPMENT GREASES

Mining and construction segment is another sector, where huge quantities of lubricants and greases are used. The infrastructure projects are increasing in developing countries in a big number. Currently the infrastructure projects are in boom in India due to the ambitious plans of the current government. As per the data available on the Indian government website.

Excavating, processing and transporting material within a mining operation requires dedicated, specialised equipment. A key element in ensuring the reliability and cost effectiveness of such equipment is the appropriate selection, application, and management of the correct lubricating grease technology. Before selecting or indeed developing grease technology for any given application, it is first essential that the operational demands of the equipment and the environment are fully understood. Mining equipment can be split into two distinct categories; namely mobile and fixed plant. As the name suggests, mobile plant is equipment that is frequently relocated within a mine for the purposes of extracting and transporting overburden.

The infrastructure projects involve both stationary and mobile equipment like Backhoe Loaders, Excavators, Drag liners, Shovels, Dozers, Large Mining Trucks, Motor Graders, etc. These equipment are the backbone of the mining and construction industry and they work under extremely drastic environment of dust, dirt, water, stones, etc and pose very tribological challenge to the lubricant industry. In terms of both cost and size, the scale of the equipment required to extract product effectively and efficiently can be matched by the large cost implications of equipment failure and downtime.

In this paper we are focussing on the mobile equipment particularly the excavators and backhoe loaders, which are the major equipment in Indian infrastructure projects. There are different capacity excavators in the industry. The most common lubrication mechanism is pin-bush, where hydrodynamic and boundary lubrication regimes are prevalent. The capability and productivity of the equipment relies on a wide range of components and mechanisms for drive and movement.

For the maximum machine operability and durability for use under such harsh operating conditions, correct lubrication of the moving components becomes imperative to deliver to their full potential in terms of machine availability and expected life. We developed custom made greases after thoroughly studying the tribological and lubrication requirements of the pin-bush available in the excavator in multiple numbers.

In pin-bush mechanism, as speeds decrease and loads increase, the base oil viscosities typically seen in traditional multipurpose EP 2 greases would cease to be sufficiently effective. Therefore, in the interests of creating a liquid lubricant phase with enhanced film strength that is better able to keep surfaces apart and thus contribute to extending the capability of the grease to lubricate better for longer, base oil viscosities are typically required to increase.

Sometimes polymer additives are incorporated not only boost base oil viscosity but more commonly they are used to increase both the adhesive and cohesive properties of the grease, thereby enhancing resistance to water as well as a barrier to other external contaminants. Such features are particularly beneficial in those exposed applications where the primary function of the lubricant is to cling on and act as a robust protective barrier between the metal component and the elements.

Another aspect we brought into the new grease is to increase the consistency of the grease seeing the leakage of the grease in NLGI 2 consistency. This will not only increase the stay-put property of the grease but reduces the leakage into the environment as these are total loss systems. Since the excavation and loading operations experience heavy loads and shock loads we added EP additives for achieving a weld load of 250 kgs minimum.

With the above technological improvements in the grease, there are multiple advantages like increase in the lubrication interval from 2-3 hours with local non-EP greases to 15-20 hours with the new grease. Consequently, the volumes of greases required got reduced by 6-7 times. Thus it is considered to be an excellent approach not only for the sustainability but also helps in environment protection and carbon foot print. The following Table 3 shows a typical grease saving per year per machine.

TABLE-3: COMARISON OF LOCAL & CUSTOM MADE GREASE

S No	Attributes	Local Greases	New Grease
1	Grease NLGI Grade	2	2.5
2	Dropping Point, ^{O}C	100-140	190
3	Weld Load, Kg	0-160	250
4	Grease Interval, hrs	2-3	15-20
5	Quantity per charge per machine, gms	500	500
6	Quantity per 12 hours, kg	3.0	0.4
7	Quantity per month, kg	90.0	12.0
8	Quantity for 30,000 machines, MTs	2700	360
9	Quantity of Approx. 300,000 machines, MTS	27000	3600
10	Reduction in grease consumption	86.7 %	

UNIQUE SHEAR STABLE GREASE FOR HIGH END APPLICATIONS

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 we aimed to improve the performance by altering the chemistry of thickener not by doping any polymer. We at Siddharth Grease & Lubes Pvt Ltd have developed "A New Shear Stable Grease without any polymer" adopted a different process technology using our own **Advanced Soap Salt Complex Technology (ASSCT)** on Lithium thickener chemistry with 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 were discussed in the last NLGI India Chapter Grease Conference held during August 26-28, 2022 at Visakhapatnam. The test of the wonder grease are given in the following table.

TABLE- 4: TEST DATA OF THE SHEAR STABLE GREASE

S. No	Test Parameters	Test Method	Test Results
1	Thickener Type	-	Proprietary
2	Worked Penetration (1/10 mm) at 25℃		
	60 Double strokes		284
	100,000 Double strokes	ASTM D217	+18
	100,000 Double strokes with 10 % water	ASTM D7342	+26
3	Drop Point ,℃	ASTM D2265	262
4	Shell 4 ball OK Load , kgf	ASTM D2596	315
5	Four ball wear scar diameter ,mm	ASTM D2266	0.52
6	Fretting Wear, mg	ASTM D4170	8
7	Roll Stability, Δ penetration		
	For 2 h at room temperature		+ 10
	For 16 h at 50 ℃		+ 16
	For 100 hrs at 100 ℃	ASTM D1831	+ 15
8	Water washout, % mass	ASTM D1264	1.9
9	Oil separation during storage, % mass	ASTM D1742	1.4
10	Oxidation Stability. 100 h ,100 ^{o}C drop in pressure in psi	ASTM D942	1.5
11	Rust preventive properties	ASTM D 1743	Pass
12	EMCOR Test (DW)	ASTM D 6138	0,0
13	Copper Corrosion	ASTM D 4048	1a
14	WB Leakage Test		
	Leakage in mass , g		< 1.0 g
	Other observations	ASTM D1263	No deposits & no abnormal changes
15	High temperature wheel bearing life test	ASTM D 3527	390

16	FAG FE 9: 6000 rpm /1500N at 140°C		
	F10/hrs		448.5
	F50/Hrs.	DIN 51821	565.4

It has been observed that the new unique shear stable grease has extremely long service life and can replace many conventional greases both in industrial and automotive applications. We have already positioned this grease as a long life grease for 500,000 kms in automotive applications including the EVs. This has also been found to solve the grease related problems in the steel rolling mills in the lubrication of back- up rolls and work roll bearings.

OTHER CONCEIVABLE STEPS TOWARDS SUSTAINABILITY:

1. Re-refining of Waste Lubricating Oil & its use in Greases shall help towards sustainability by reducing the use of Virgin Base Oil which are sourced from gradually depleting natural Petroleum resources.
2. Developing greases based on Polymer Thickener using an alternate to Lithium, an essential and important metal for many applications including EVs. These greases may have lower dropping point compared to lithium but similar or better in operating temperature.
3. Use of semi-synthetic or fully synthetic greases designed for Long Service Life will definitely reduce the grease consumption 5-10 times, thus help sustainability.
4. Use of Fire Resistant greases in Steel & Mining Industry shall also help to save costly bearings resulting in a step towards sustainability.
5. Use of high performing Polyurea greases in heavy industries will save not only minerals of lithium, aluminum, calcium & fat but also extend life of machinery saving lot of energy and revenue.

All the above points will definitely contribute significantly towards Carbon Neutral Effort by minimizing the hazardous wastes to the environment.

CONCLUSIONS:

Sustainability is a global phenomenon bothering the world about the wellbeing of our future generations. Many countries are taking measures to minimize the use of natural resources. Environmental protection is also an integral part of the sustainability to keep the flora and fauna in its natural abundance and integrity. Unfortunately, many countries have not mandated the use of biodegradable greases, food-grade greases and lubricants, without which the sustainability may not be meaningful. We have discussed and presented our efforts in developing high performance greases helpful towards sustainability and environment protection.

Formulating High Performance Multi-Purpose EP Greases

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Abstract

This paper discusses performance trends for Extreme Pressure (EP) greases and formulation considerations in meeting performance balances for load carrying capacity, wear and yellow metal corrosion. Current sourcing demands for key raw materials used in thickeners will be highlighted along with a brief overview on the attributes of the various common greases used. Original Equipment Manufacturers' (OEM) requirements and current global supply chains require an introspective view of possible changes in providing alternative greases and supporting new approvals. Supply of key raw materials and future OEM requirements are driving grease formulations and manufacturers to consider alternative chemistries to ensure long term sustainability in industrial and automotive markets.

Introduction

OEM trends, to continuously strive for energy efficiency, are driving gear box designs to higher power densities, lower sump capacities, lower speeds for reduced churning or traction losses, reduced grease and lubricant levels, and longer drain intervals. These drivers are placing higher performance demands on greases and lubricants. Greases and lubricants must inherently be able to provide lubrication under high loads and low speeds, possess improved thermal and oxidative stability, and able to operate in wide temperature ranges and harsher environments.

In meeting these higher performance trends in multipurpose EP greases, careful consideration is needed to the type and functionality of key EP, anti-wear and corrosion additives used. Typical additives used for load carrying capacity are metal dithiocarbamates, sulfurised olefins, polysulfides, sulfurised esters and metal sulfides, for example molybdenum disulfide. In recent years, increasing use of ashless multifunctional additives in thiadiazoles and alkyl dithiocarbamates have gained popularity. These additives collectively can achieve higher load carrying capacity, but typically deteriorate wear and corrosion performance. Test results on formulation options with select additives will be discussed to attain high load carrying capacity while improving anti-wear and corrosion performances.

Grease Classifications and Specifications

Grease Properties

Lubricating greases are made of a thickening agent such as metallic soap, urea, carbon black or clay and a base fluid made of either synthetic and/or mineral base oil, rheology modifiers, tackifiers and performance additives. This unique composition allows greases to stay in place in applications where continuous lubrication is required. Greases also assist in preventing contaminants from entering critical mechanisms such as bearings, constant velocity joints and gear boxes.

There are various typical tests that qualify the properties of greases. The viscosity of a grease is dependent on the shear rate. Due to its thickening constituents, the grease acts as a solid or semi-solid at low shear rates. As the shear rate increases, the viscosity of the grease decreases to the limit of the base blends viscosity. This term called apparent viscosity is affected by the type and amount of thickener and cannot be lower than the base blend's viscosity. This property is important for determining the flow through dispensing lines and can be measured by ASTM D1092.

Another key property of the grease is its consistency measured by the depth to which a cone will penetrate into a prescribed sample of grease. The NLGI consistency number (sometimes referred to as "NLGI Grade") expresses a measure of the relative hardness of a grease used for lubrication, as specified by the standard classification of lubricating grease established by NLGI. NLGI has designated consistency numbers depending on the depth of penetration as described in ASTM D217. Table 1 shows these Consistency Numbers as defined by NLGI.

Table 1. NLGI Consistency Numbers for Grease According to ASTM D217.

NLGI number	ASTM worked penetration (60 strokes) at 25°C (77°F) in tenths of a millimeter
000	445–475
00	400–430
0	355–385
1	310–340
2	265–295
3	220–250
4	175–205
5	130–160
6	85–115

Source: National Lubricating Grease Institute.

Elastomer compatibility of greases is important to ensure seals maintain their sealing ability. Any grease leakage or contaminants can lead to premature failure. ASTM D4289 measures the hardness and volume changes after immersion in the grease for a specified temperature and duration. Another important grease property is corrosion as measured by ASTM D1743. The temperature at which the grease becomes a liquid is called its dropping point. This is measured by ASTM D566 and subjects the grease to temperatures as high as 260^0C. For higher dropping points ASTM D2265 can be used for temperatures up to 330^0C. ASTM D972 and ASTM D2595 can be used to measure evaporative weight loss up to 316^0C. Other key functional tests are the effective lubrication of bearings by greases. These are measured by ASTM D1263, ASTM D 1264, ASTM D1741, ASTM D3527, and ASTM D4290. The mechanical stability of a grease can be determined by measuring changes in consistency post working or shearing for two hours at room temperature as described by ASTM D1831. Another key test for greases is the measurement of the oxidative stability in ASTM D942, but has limited correlation to predict field performance. Other oxidation tests available for consideration are the Penn State Micro-Oxidation and Pressure Differential Scanning Calorimetry (PDSC) in ASTM D5483. Measurement of oil separation in grease is described by ASTM D1742, during storage. This method is a static test and does not simulate oil separation during dynamic applications. Measuring fretting wear of ball bearings installed in machinery during shipment is described by ASTM D4170, under a prescribed oscillation and load. Table 2 provides the summary list of key ASTM Test methods for qualifying greases.

Table 2. List of Common Key Grease Property Tests

Test Method	Property of Grease	Function Tested
ASTM D1092	Apparent Viscosity	Measures viscosity as function of shear rate
ASTM D217	Consistency	Measures hardness with cone penetration
ASTM D4289	Elastomer Compatibility	Immersion tests for hardness and volume change with Elastomers
ASTM D1743	Corrosion Test	Measures corrosion at specified temperature & humidity
ASTM D566 ADTM D2265	Dropping Point	Temperature at which grease transitions to liquid state
ASTM D972 ASTM D2595	Evaporation	Weight loss after evaporation at specified temperature & duration
ASTM D3232	Flow	Flow properties at high temperature & low shear
ASTM D1263	Leakage	Measures leakage from unseal wheel assembly
ASTM D1264	Water Washout	Measures resistance to water washout in rotating bearing
ASTM D1741	Grease Life	Measures grease life in steel ball bearings
ASTM D3527	Grease Life	Measures high temperature life of wheel bearing
ASTM D4290	Leakage	Measures leakage of unsealed wheel bearings at high temperatures
ASTM D2509	Load Carrying	Determines load carrying using the Timken Test
ASTM D2596	Load Carrying	Determines load carrying using Four Ball Test
ASTM D1478	Low Temperature Torque	Measures retardation of ball bearings
ASTM D4693	Low Temperature Torque	Measures retardation of wheel bearing assembly
ASTM D1831	Mechanical Stability	Determines consistency change after working
ASTM D942	Oxidative Stability	Static test that measures oxygen consumption
ASTM D1742	Oil Separation	Measures tendency of oil to separate from grease
ASTM D2266	Wear Resistance	Measures wear resistance using Four Ball Test
ASTM D4170	Fretting Wear	Measures fretting wear resistance

ASTM D4950 Standard Classification and Specification for Automotive Service Grease (1,2)
The corroboration between American Society for Testing and Materials (ASTM), National Lubricating Grease Institute (NLGI) and Society of Automotive Engineers (SAE) led to the development and release of ASTM D4950, Standard Classification and Specification for Automotive Service Grease in 1989. This standard was collectively accepted by OEMs for automotive applications. The early success of adopting this standard with the listed grease tests was made possible with the development and testing of methods for automotive applications. Specific key tests for automotive applications include:

ASTM D3527 – Test Method for Life Performance of Automotive Wheel Bearing Grease

ASTM D4170 – Test Method for Fretting Wear Protection by Lubricating Grease

ASTM D4289 – Test Method for Compatibility of Lubricating Grease with Elastomers

ASTM D4290 – Test Method for Determining the Leakage Tendencies of Automotive Wheel Bearing Under Accelerated Conditions

ASTM D4693 – Test Method for Low Temperature Torque of Grease Lubricated Wheel Bearing

ASTM D4950 was written to classify automotive service greases into chassis and wheel bearing categories. These two categories are further classified pending on the severity of the application, two and three sub-categories for chassis and wheel bearing, respectively. Table 3 describes the performance requirements for the two chassis (LA, LB) and three wheel bearing (GA, GB, GC) grease categories, respectively.

Table 3: Guide to Requirements for ASTM D4950 Grease Categories (2)

ASTM Test	Description	LA	LB	GA	GB	GC
D217	Penetration		✓	✓	✓	✓
D566[A]	Dropping Point	✓	✓	✓	✓	✓
D1264	Water Washout				✓	✓
D1742	Oil Separation		✓		✓	✓
D1743	Rust Protection		✓		✓	✓
D2266	Four Ball Wear	✓	✓		✓	✓
D2596	Four Ball EP		✓			✓
D3527	High Temperature Life				✓	✓
D4170	Fretting Wear		✓			
D4289	Elastomer Compatibility	✓	✓		✓	✓
D4290	Leakage				✓	✓
D4693	Low Temperature Torque		✓	✓	✓	✓

[A] ASTM D2265 may be substituted.

A licensing procedure for greases qualifying for ASTM D4950 was instituted by NLGI (1). This applies to only to the highest performance level categories for wheel bearing grease (GC) and for chassis grease (LB). The NLGI allows the use of three compliance symbols that can be applied to packaging and product literature, the greases having these symbols must be registered with NLGI and meet one or both highest-level categories (Fig. 3). NLGI does not offer symbols for the lesser performance categories, and they specifically prohibit the creation and use of such symbols. Industry acceptance to the licensing system has grown and now the NLGI compliance symbols are commonly seen on product packaging and literature. Presently, most U.S. automakers still recommend the use of NLGI Service Greases GC, LB, and GC-LB for scheduled maintenance of chassis and wheel bearings of passenger cars and light-duty trucks (2). The GC-LB certification is not being replaced by the new High-Performance Multiuse (HPM) specification. The new HPM specifications will be certified in parallel to GC-LB. NLGI will continue to support GC-LB certification and the use of the mark on finished products as long as there is a market for these greases.

Figure 3. NLGI Service Grease Illustrations (1)

SAE J310

This SAE Recommended Practice was developed by SAE, and the section "Standard Classification and Specification for Service Greases" cooperatively with ASTM, and NLGI. It is intended to assist those concerned with the design of automotive components, and with the selection and marketing of greases for the lubrication of certain of those components on passenger cars, trucks, and buses. SAE J310 provides an understanding of the terms related to properties, designations, and service applications of automotive greases.

Table 4. Relative Importance of Lubricating Grease Properties for Automotive Use (3)

Property	Wheel bearings	Universal joints	Chasis	Extended lubrication, internal chassis	Multi-purpose applications
Structural stability (including mechanical stability)	H	M	L	H	H
High dropping point (high-temp. service)	H	M	L	M	H
Oxidation resistance	H	M	L	M	H
Protection against friction and wear	M	H	M	H	H
Protection against corrosion	M	M	L	H	M
Protection against washout	M	M	M	H	M

H = Highest; M = moderate; L = least.
Source: Society of Automotive Engineers (SAE J310).

ISO Standards
ISO 6743 was established as a general system of classification for lubricants, industrial oils and related products. Within this classification, greases are also categorised (ISO 6743-9) and it is stiputed that any given grease cannot have more than one symbol. The symbol corresponds to the most severe conditions of temperature, water contamination, and loads.

ISO 12924 specifies the requirements of greases used for the lubrication of equipment, components of machinery and vehicles. This standard provides guidance to suppliers, end users and OEMs taking into consideration climatic conditions world wide and requirements for greases at the time of delivery. ISO 12924 is intended to complement ISO 6743-9.

DIN 51825
The German standard allows for the classification of Industrial Greases. The most common are as follows:

- DIN 51825 K – grease made from high viscosity mineral and/or synthetic oil with a thickener.
- DIN 51825 KP-K – grease made from additional additives that reduce friction and protect against wear in mixed friction locations.
- DIN 51825 KF – K grease with additional solid additives (graphite, molybdenum disulfide).
- DIN 51825 KPF – K grease with additional additives that reduce friction and protect against wear in mixed friction locations, plus additional solid additives (graphite, molybdenum disulfide).

Japan JIS K2220

This standard specifies lubricating greases and gear compounds to be used as lubricants for distinct types of machine parts. There are several test methods and ISO standards that are cited. Key tests are ISO 2137 – Determination of Cone Penetration of Lubricating Greases and Petroleum; ISO 2176 – Determination of Dropping Point; ISO 11009 – Determination of Water Washout Characteristics of Lubricating Grease; ISO 12924 and ISO 6743-9.

High-Performance Multiuse Specification (4)
The High-Performance Multiuse Grease (HPM) certification offers a core specification and four additional performance tiers/tags. Greases must meet the core specifications in order to be approved against the additional performance tiers.

HPM Core Specification
In the HPM core Specification, seven tests are common to the GC-LB specification, have more restrictive limits: Cone Penetration (ASTM D217), Elastomer Compatibility (ASTM D4289), Water Washout (ASTM D1264), Oil Separation (ASTM D1742), 4-Ball Wear (ASTM D2266), 4-Ball EP (ASTM D2596), and Corrosion Prevention (ASTM D1743). Two tests, not required for GC-LB specification are: Extended Worker Penetration (100,000 strokes by ASTM D217) and Roll Stability (ASTM D1831). Also, additional tests added are: EMCOR Rust Test (distilled water by ASTM D6138), Copper Corrosion (ASTM D4048), Oxidation Stability (ASTM D942), and High Temperature Oil Bleed (ASTM D6184) and Low Temperature Torque of Wheel Bearing Grease (ASTM D4693). The incorporation of these tests are intended to raise the level of performance for relevant use in industrial applications.

HPM + WR (Water Resistance)
The HPM+WR Specification includes three tests intended to demonstrate an increased level of performance over the HPM core Specification in wet or water wash environments. Keys tests required are: Water Washout (ASTM D1264) with restrictive limits, Water Spray Off (ASTM D4049) and Wet Roll Stability (ASTM D8022).

HPM + CR (Salt-Water Corrosion Resistance)
The HPM+CR Specification includes three tests intended to demonstrate improved corrosion resistance over the HPM core Specification in saltwater environments. Key tests required are: Saltwater Rust (ASTM D5969 10% Synthetic Seawater), EMCOR Rust (ASTM D6138) in 100% synthetic sea water and 0.5 N sodium chloride solution.

HPM + HL (High Load)
The HPM+HL Specification includes five tests intended to demonstrate improved load carrying capability over the HPM core Specification. Key required tests with restrictive limits are: 4-Ball Wear (ASTM D2266), 4-Ball EP (ASTM D2596), Extreme Pressure Properties by SRV (ASTM D5706), Fretting Wear by SRV (ASTM D7594), and Bearing Fretting Wear (ASTM D4170).

HPM + LT (Low Temperature)
The HPM+LT Specification includes three tests intended to demonstrate improved low temperature performance over the HPM core Specification. Key required tests are: Low Temperature Torque of Ball Bearing Grease (ASTM D1478), Grease Mobility (U.S. Steel method) demonstrates grease resistance to flow at low temperatures, and Flow Pressure by Kesternich method DIN 51805.
More details on the test conditions and restrictive limits for the additional four performance tags and how they compare against GC-LB are provided in NLGI's website (4)

Grease Market Drivers & Trends
Legislature and Original Equipment Manufacturer (OEM) drivers are leading to the development of greases that are environmentally safe and targeted for extended service. Environmental factors are reduced water hazard classification, no heavy metals, no chlorinated compounds and increasing degree of biodegradability. OEMs are developing smaller components in bearings, and constant velocity joints in cars, where improved reliability and less frequent re-greasing or extended life are creating increased performance demands on greases. These trends are already placing demands on changes in the type of chemistries used in greases. Selection of soap and thickener types, base oil types and their viscosities, improved thermal stability, washout and bleed rates are key parameters for consideration. The performance additives used in greases need also to be re-evaluated for their type and function in order to enhance the overall performance of greases.

The typical composition of grease includes up to 15% of performance additives, up to 20% of the soap and or thickener and the remainder of up to 95% is the base oil (6). The performance additives include Extreme Pressure, anti-wear, corrosion inhibitors, metal deactivators, antioxidants, and polymers for enhanced grease structure.

Some common examples of Extreme Pressure additives are metal based dithiocarbamates, sulfurized olefins, alkyl polysulfides, zinc dialkyldithiophosphates and solid additives like molybdenum disulfide. Typical anti-wear additives are zinc dialkyldithiophosphates, alkyl phosphates. Corrosion inhibitors and metal deactivators are amine phosphate salts, imidazoline derivatives and triazoles, respectively. Common antioxidants used are radical scavengers and peroxide decomposers. Table (5) provides the key additive types and their function in greases.

Table 5. Common Performance Additives and their Function in Greases

Additive Type	Purpose	Function
Extreme Pressure	Prevent scuffing, scoring and seizure	Prevents metal to metal adhesion with sacrificial boundary film of low shear strength
Anti-wear	Reduce friction and wear	Reduces wear through boundary films
Corrosion Inhibitor	Prevent corrosion and rust	Forms protective film on surface to prevent or react with corrosive acids
Metal deactivators	Prevents catalytic activity of metal surface for oxidation	Forms protective film on metal surface
Antioxidants	Provides oxidative stability	Terminates free radicals and decomposes peroxides

Properties of Greases and Additives Used in Studies (See Table 6)

There were three greases that were used in this study. Two were Lithium Complex Greases (BG1 & 3) and one Calcium Sulfonate (BG2). All these greases were compounded with their respective soaps, thickeners and base oils with no performance additives. They all meet NLGI 2 Grade for consistency. This was done to study and compare performance additives type and concentration in several thickener types for their functional performances. The performance additives' interaction amongst each other were then quantified in several key performance tests next.

Table 6. Unadditized Base Grease and Performance Additives Used in Study

Type	Description	Typical Concentration used in Study
BG1	Unadditized Lithium Complex Grease; Meets NLGI 2 Grade	Up to 97%
BG2	Unadditized Calcium Sulfonate Grease Meets NLGI 2 Grade	Up to 97%
BG3	Unadditized Lithium Complex Grease; Meets NLGI 2 Grade	Up to 97%
EP1 & EP2	Ashless EP additive	Up to 4%
EP3	Ash based RP additive	Up to 4%
CI1 – CI3	Corrosion or Metal Deactivator	Up to 2%
AW1 – AW4	Anti-wear	Up to 1%

Blends using these base greases BG1-3, with various levels of the performance additives EP1-3, CI1-3, and AW1-4, were then tested using the following tests designated as:

ASTM D2596 - Standard Test Method for Measurement of Extreme-Pressure Properties of Lubricating Grease (Four-Ball Method)

ASTM D2266 – Standard Test Method for Wear Preventive Characteristics of Lubricating Grease (Four- Ball Method)

ASTM D4048 – Standard Test Method for Detection of Copper Corrosion from Lubricating Grease.

Results and Discussion

Study 1: Effect of Extreme Pressure (EP 1-2) and Corrosion Inhibitors (CI 1-2) in Lithium Complex Grease BG1.

In the first study, the interaction between Extreme Pressure additives in EP 1 & 2 were blended with corrosion inhibitors in CI1 & 2. Figure 4 summarizes the weld load results from ASTM D2596. The base grease provided a weld of 400 Kgf. The Extreme Pressure additives in EP1 & 2 were able to improve weld substantially to 800 Kgf. The effect of EP1 was more severe than EP2 for copper corrosion performance (See Fig. 5). The Extreme Pressure additive in EP2 was able to show no change in copper corrosion when compared to the base grease. This result is atypical for Extreme Pressure additives. Subsequent tests were then performed using the Extreme Pressure additive in EP2 in combination with corrosion inhibitors CI1 & CI2. The effect of CI1 did deteriorate both weld load and copper corrosion. The weld and copper corrosion results were not affected with the addition of CI2. Figure 6 summarizes the wear scars from ASTM D2266. The addition of EP1 & 2 in combination with CI1 & 2, all marginally increased the wear scars. This suggest that the optimization of weld and corrosion inhibition will affect wear performance. In a later study, the effect of anti-wear additives will be discussed.

Figure 4: Effect of EP & CI Additives on Weld Loads in Lithium Complex Grease BG1

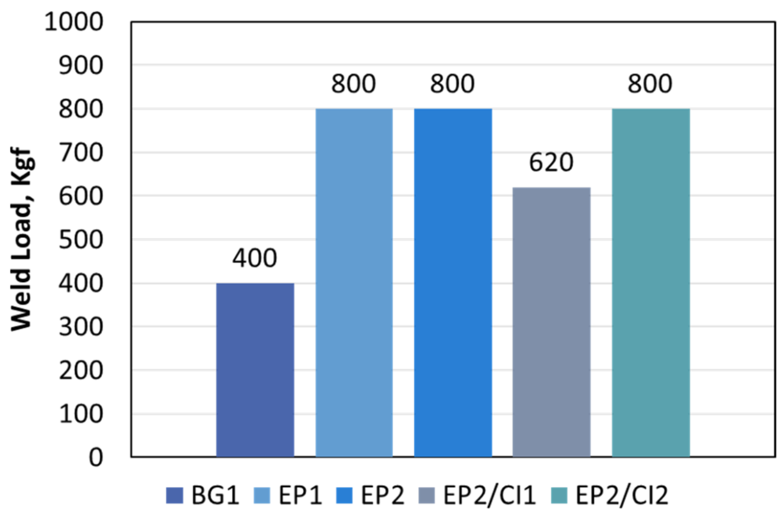


Figure 5: Effect of EP & CI Additives on Copper Corrosion in Lithium Complex Grease BG1

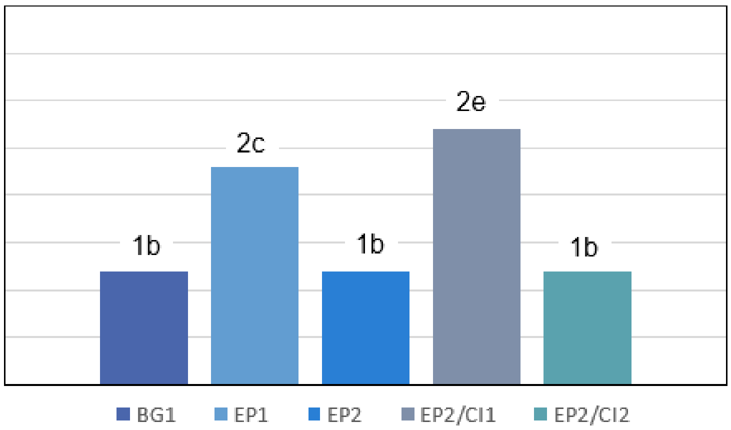
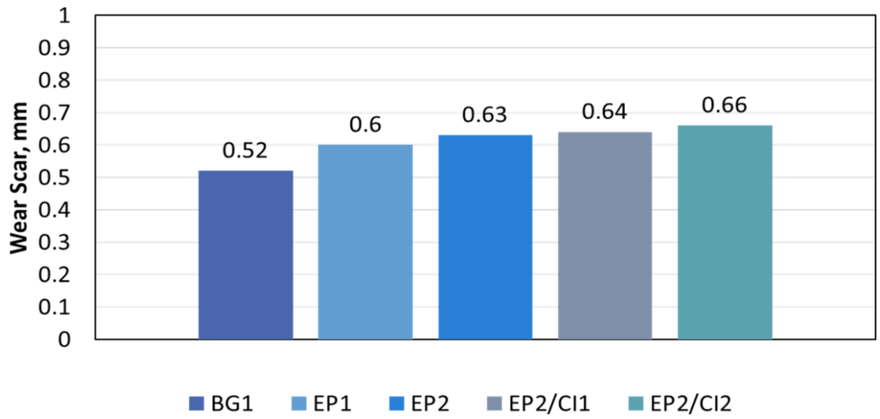


Figure 6: Effect of EP & CI Additives on Wear Scar in Lithium Complex Grease BG1



Study 2: Effect of Extreme Pressure (EP2), Corrosion Inhibitor (CI2) and Anti-wear (AW1-4) in Calcium Sulfonate Grease BG2.

In the second study, the effect of Extreme Pressure additive EP2 and combinations with corrosion inhibitor CI2 were initially evaluated for weld load, copper corrosion, and wear scar. The weld loads were affected by increasing the level of EP2. The wear scars were deteriorated with increasing levels of EP2. The effect of CI1 on weld and wear was minimal. This suggest that the choice of Extreme Pressure additive can be critical for initial weld and wear performance. The copper corrosion results were not affected by the choice of EP2 & CI2. The effect of anti-wear additives was then studied next, added as top-treats to the EP2 & CI2. Except for AW3, the addition of AWs deteriorate weld loads. The wear scars results show that the choice of AW can improve wear scar while maintaining high welds. The copper corrosion results were all favorable with ratings of 1b. These results collectively show that it is possible to optimize performance for weld loads, wear scar and copper corrosion with the proper choice of EP, AW and CI additives.

Figure 7: Effect of EP, CI and AW Additives on Weld Loads in Calcium Sulfonate Grease BG2.

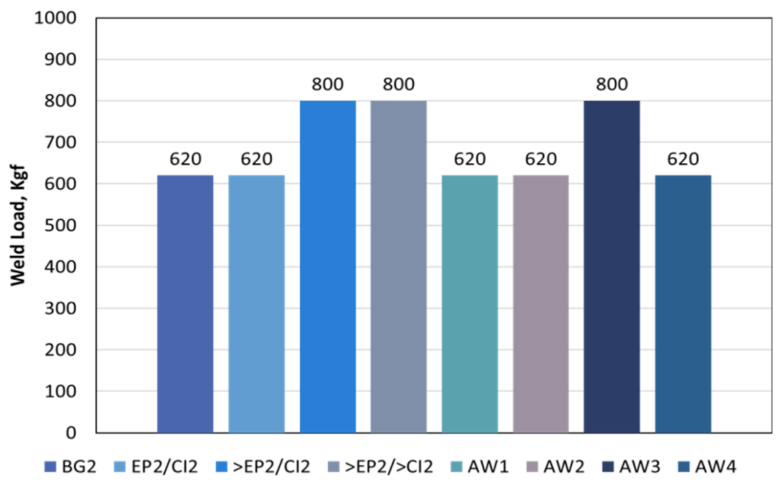


Figure 8: Effect of EP, CI and AW Additives on Wear Scars in Calcium Sulfonate Grease BG2.

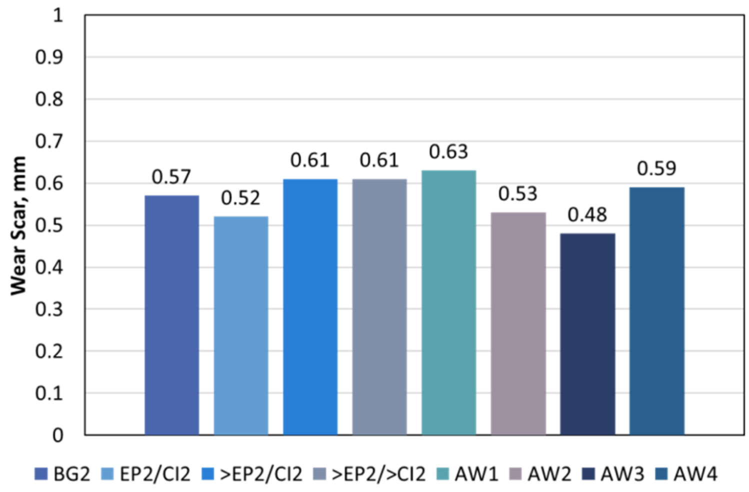
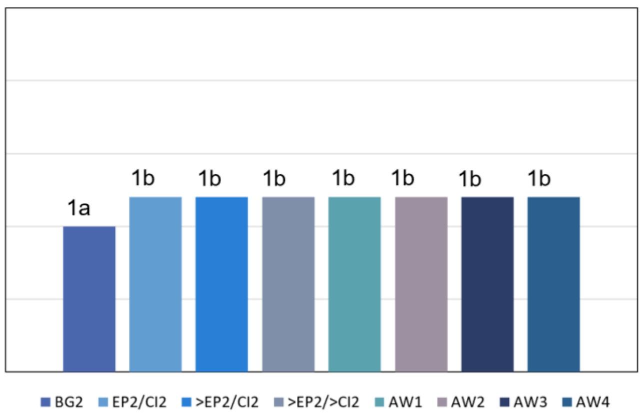


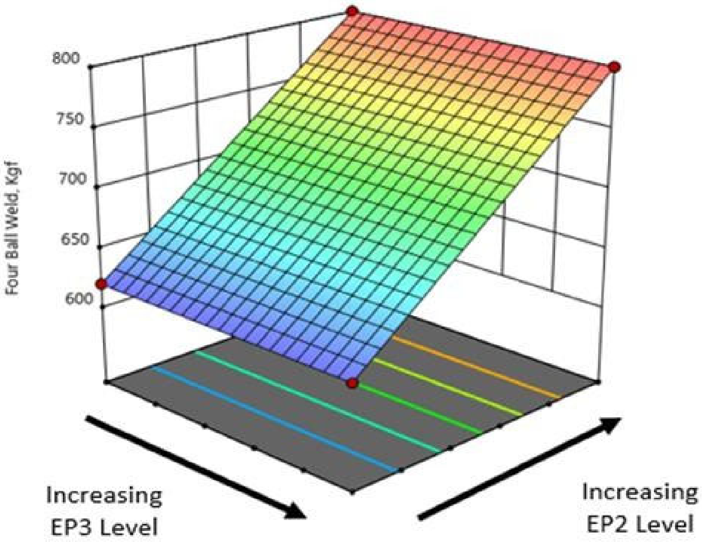
Figure 9: Effect of EP, CI and AW Additives on Copper Corrosion in Calcium Sulfonate Grease BG2.



Study 3: Effect of Extreme Pressure (EP2 & 3) and Corrosion Inhibitor (CI3) in Lithium Complex Grease BG3.

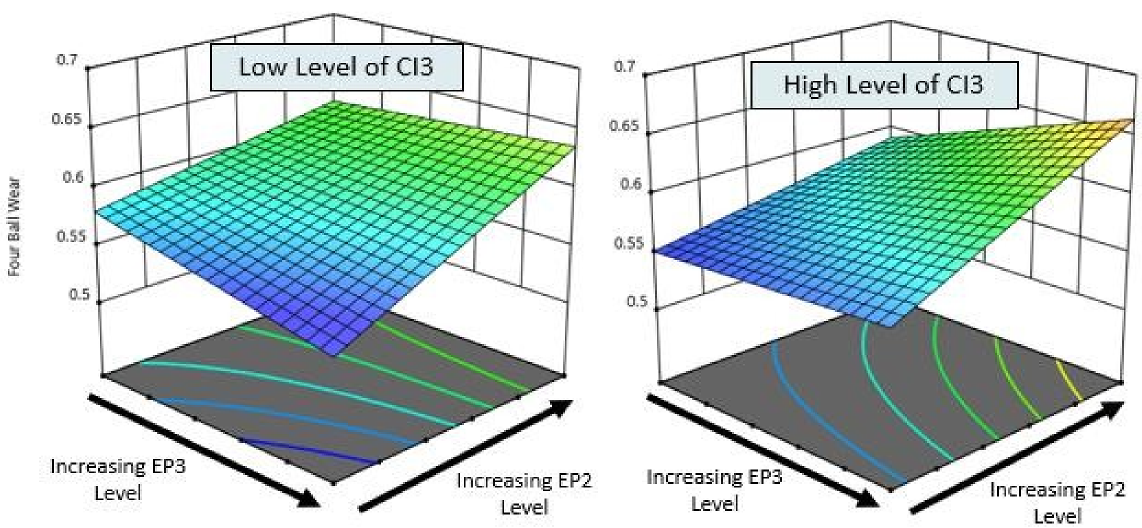
In the third study, the effect of Extreme Pressure additives EP2 & 3 and combinations with corrosion inhibitor CI3 were evaluated for weld load, and wear scar. The data for weld loads and wear scars were regressionally fitted to the levels of additives tested. The weld loads were affected by combinations of EP2 and EP3 (see Fig. 10).

Figure 10: Effect of EP Additives on Weld Loads in Lithium Complex Grease BG 3



Either Extreme Pressure additives can be used to target a wide range in weld loads. The interaction with the level of CI3 did not affect the weld loads. Figure 11 plots the wear scars at low and high levels of the corrosion inhibitor CI3. The data suggest that the wear scars are affected by the level of CI3. The combinations for lowering wear scars are increasing level of EP3, lowering EP2 in combination with low level of CI3. Alternatively, another combination for reducing wear scars is the combination of low levels of EP2 & EP3, if higher level of CI3 is used. The copper corrosion results for these combinations did not change in ratings from the base grease BG3. This study shows that a wide range of weld loads, and wear scar can be affected pending on the choice of EP additives and choice of CI.

Figure 11: Effect of Corrosion Inhibition on Wear Scars in Lithium Complex Grease BG3



Conclusions

In summary, based on the three studies conducted in lithium complex and calcium sulfonate greases, it is recommended that the base greases be base lined against targeted performance for weld loads, wear scar and copper corrosion. The initial selection of EP, AW and CI is critical and does rely on the base grease used. Optimization with performance additives can be done but caution should be taken to confirm grease performance traits such as consistency, oxidation, oil separation and washout. These performance parameters although not discussed in this paper, are still important to evaluate for overall performance of the finished grease. The results from these studies have shown that it is possible to target high weld loads and mitigate wear scars while maintaining good copper corrosion. The studies also show that synergies can be exploited between EP, AW and CI with the careful selection of these additives.

Acknowledgements

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A study on the New Approach towards making of Sulphonated Complex Grease

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ABSTRACT
The global arrival of EVs and the shift to e-mobility is prompting reconsideration of the role of lithium in Lubricating Grease market. There is a constant surge in the rise in prices of lithium hydroxide and potential instability in future for the lithium greases market supply to industry.. In this context, several alternative lubricating greases based on low and non-lithium such as purely calcium based, calcium sulphonates to low lithium with mixed lubricating greases, aluminium complex, polyurea greases etc. were explored and manufactured to meet the application requirement as a alternative replacement.

In the present study, a new approach has been adopted to make better yield of Sulphonate Complex grease with the influence on the thickening with co-aids having varying degree of carboxylic groups were studied. In this work, an attempt has been made to study the shear stability, droppingpoints, EP properties, of greases with above processing methods. The surface hardening of typical calcium sulphonate grease has been reduced with the proper choice of carboxylic acids. The information obtained will be used selecting the right type of co-aid agents to produce better thickening / yield of sulphonate complex greases, enhance the mechanical properties and pumpability of these greases.

Introduction

Calcium sulfonate greases are made by converting a fluid detergent Sulphonic acid form based that contains amorphous calcium carbonate to a grease containing calcite particles. Because of thecalcite particles contribute lubricating properties, performance additives containing sulfur, phosphorous or zinc may not be needed. Calcium sulfonates are used in engine oil, metalworking, automatic transmission fluid, industrial and automotive gear oil additives as well as other applications.

Calcium Sulfonate Grease are dispersions in oil of amorphous calcium carbonate (with a size of 1.5 to 10 nm[1]) that is stabilized by a surfactant (molecule with a polar head group, usually alkyl benzene sulfonic acid as shown in **Fig. 1**). In the grease-making process, the amorphous carbonateis converted into a crystalline carbonate (mostly calcite). A description of the manufacturing process can be found in Denis and Sivak [2]. The grease had the desirable characteristics of high dropping point and good extreme pressure and antiwear characteristics but also had negative properties such as high thickener concentration, surface hardening complex manufacturing, and high costs[3]. The complex calcium sulfonate was then invented, where anhydrous calcium 12- hydroxystearate was used as a complexing agent [4].

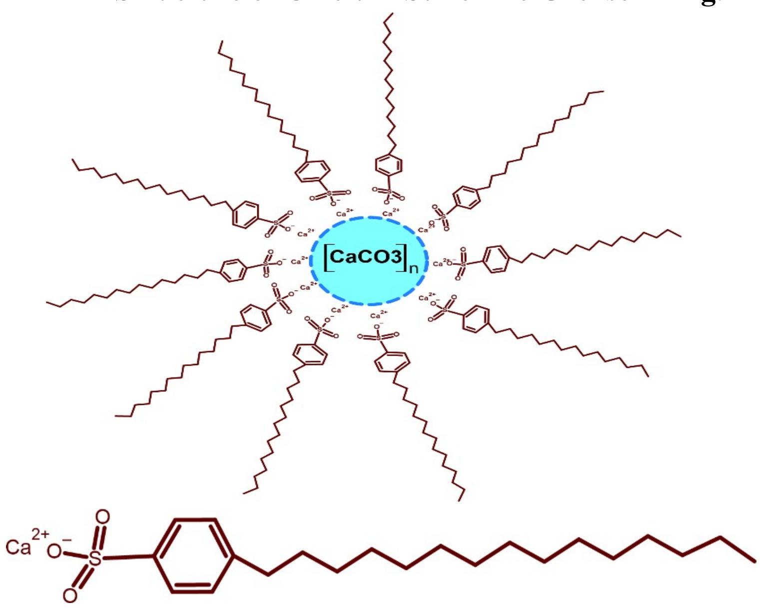
This grease excels in EP performance, Dropping point, Mechanical properties and Rollingstability. Some formulations also excel in salt spray performance. Applications that fit this category include marine environments, suspension bridges, automotive or other applications exposed to salt conditions. General applications for calcium sulfonate greases include automotive, agricultural, construction, food, industry, mining, paper manufacturing and steel mills. Specific automotive applications include chassis, ball joints, universal joints, and wheel bearings. Industrial applications include continuous casters, conveyors, ball mills, crushers, offshore and underwater applications.

Another literature reference[5], supports that the calcite particles, inherent in calcium sulfonate greases, make them a good choice for high-temperature applications. Calcium sulfonate greases are generally beneficial for rust performance, with oxidation stability considered good or excellent. In the case of the four-ball weld test, a weld load test of 315 kg, 400 kg or even higher is common with a calcium sulfonate grease. Calcite particles have been described as forming a wafer- or scale- like structure which creates shear planes that trap between the metal surfaces. This forms a sacrificial layer on the metal that is constantly sheared away. After all, it is better to shear the calcite particles than the metal on the equipment.

Structure of Calcium Sulfonate Grease In the process, a fluid detergent that contains over based calcium sulfonate based on amorphous calcium carbonate is converted to a grease containing over based calcium sulfonate where the calcium carbonate consists of calcite particles[6]. This is done by treating the liquid with an active compound such as water, alcohol, or lower carboxylic acid[4]. Its rheology is caused by the high degree of association between the wafer-like calcite particles[4]. Fluid over based calcium sulfonate is a colloidal dispersion of inverse micelles formed by amorphous CaCO3 in oil stabilized by a surfactant.

The term over based is used to describe the excess of metal (Ca) over that required to neutralize the sulfonic acid. Calcium-12-hydroxystearate is used as a complexing agent. In many patented versions, boric acid is used as a complexing agent. Grease-like sulfonate contains predominantly crystalline calcite (wafer-like platelets) with a much larger particle size (15–500 nm[4]). The crystalline calcite consists of ultrathin calcite layers/slices of calcium carbonate with a large surface-to-volume ratio, have a great surface activity and cover the surface, forming a tribolayer/ferrite(oxide) structure on the surface[7]. The thickener makes a viscous on deposit of calcium carbonate[8].

Structure of Calcium Sulfonate Grease in Fig. 1



The main purpose of this study is to reduce the surface hardening characteristics of calcium sulphonate grease on ageing. This is ascribed to the fact that calcium sulfonate greases are gels (and therefore do not separate much oil)[9] and high thickener content also reduces pumpability[10].

Experimental:
The Calcium sulphonate grease is added to the grease making kettle. It is heated to 100^0C. Different processing aids like mono, di, tri and long chain carboxylic acids with 3% parts by weight are added with 100 ml water. It is heated up to 180^0C (slow heating through 1.5 - 2 hours) and maintained for2 hours @ 180^0C.The heating is stopped and kept for cooling over night with covering the top of the kettle.

Chemicals: All carboxylic acids employed for the analysis are of Analytical Reagent Grades. The list of carboxylic acids with mono, di, tri, hydroxyl, long chains, and their carboxylic groups per mole are listed below in Table -1

Table -1: List of Carboxylic acids used as processing aids.

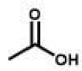
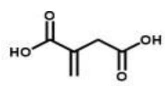
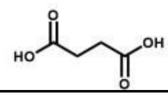
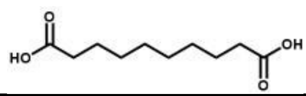
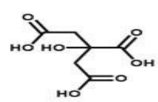
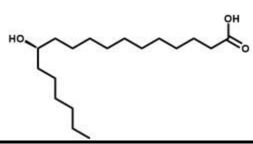
SI	Processing Acids	Structu re	Molecular Weight	COOH eq./mol
1.	Acetic acid		60	0.75
2.	Itaconic acid		13 0	0.70
3.	Succinic acid		118	0.76
4.	Sebacic acid		202	0.45
5.	Citric acid		192	0.70
6.	12HSA		306	0.15

Table -2: Abbreviations of Greases and 3% of different carboxylic acids used as processing aids.

Greases and Different Carboxylic acids used	Abbreviations
Calcium Sulphonate Grease	CSG
Acetic acid	AA
Itaconic acid	IA
Succinic acid	SUA
Sebacic acid	SEA
Citric acid	CA
12- Hydroxy Stearic acid	HSA

Instruments: Dropping Point Apparatus, Mechanical Grease Worker, Roll Stability Tester, and Extreme Pressure Property by the Four-Ball EP tester and Penetrometer.

Dropping Point determination of Lubricating greases: The standard procedure adopted for grease sample as per ASTM D 2265 was used using semi-automatic dropping point apparatus. The dropping point of grease is a very important parameter which defines the temperature up to which grease can retain the semisolid structure beyond which the soap melts leading to fluid state.

Table -3: Variation of dropping points of calcium sulphonate grease with different carboxylic acids and their carboxylic contents.

CSG with varied carboxylic acid content	Dropping Point Deg C	COOH eq per mole
CSG	330	0
CSG+3 % AA	345	0.75
CSG+3 % IA	337	0.7
CSG+3 % CA	340	0.70
CSG+3 % SUA	342	0.76
CSG+3 % SEA	247	0.45
CSG+3 % HSA	316	0.15

The over basified CSG gets neutralized on treatment with carboxylic acids resulting in additional micelle formations and the added base oil gets effectively entrapped in the micelle. In the case of CSG treated with Acetic acid (AA), Succinic acid (SUA) and Citric acid (CA), there are effective enhancement in Dropping point and it has increased to 15^{0}C, 12^{0}C and 10^{0}C respectively. The carboxylic equivalent per mole in cases of Acetic acid (AA), Succinic acid (SUA) and Citric acid

(CA) are much higher, in the range of 0.76-0.7 and there is a fall in drop points for Sebacic acid (SEA) from 330 to 247^{0}C due to its long chain unit and the COOH eq / mole is low to the value of 0.45. But in the case of CSG with 3% HSA, there is not such a fall in drop point as compared to CSG with succinic acid. Although, the COOH eq/ mole in HSA is 0.15, the presence of hydroxyl group may result in complexation with more hydrogen bonding. The variations in dropping points with 3% addition of various carboxylic acids and their COOH Eq / mole are shown in Fig.2 and neutralization of calcite phase with carboxylic acids resulting in additional micelle formation is shown in Fig.3 below.

Fig.2

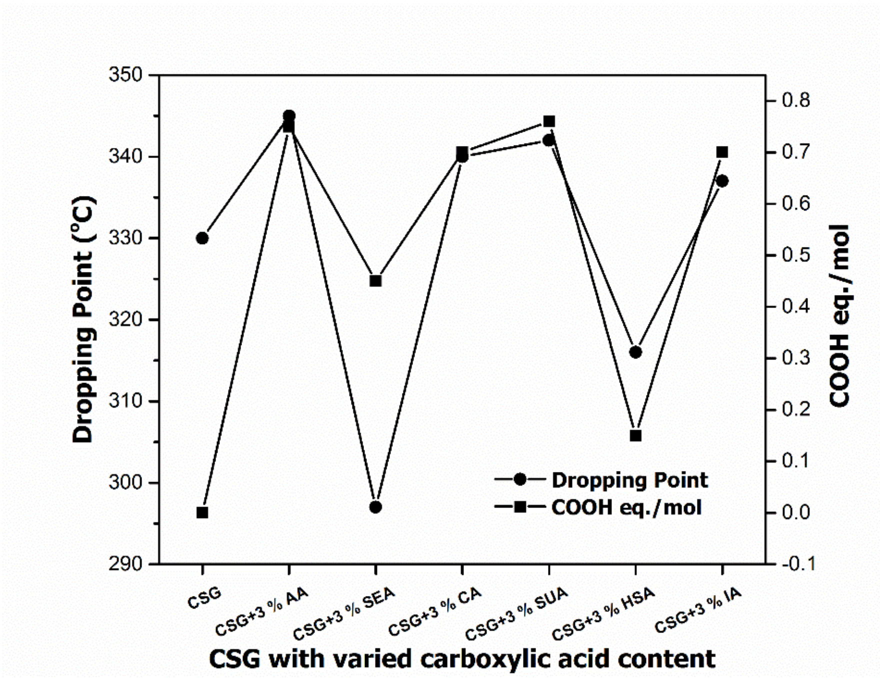
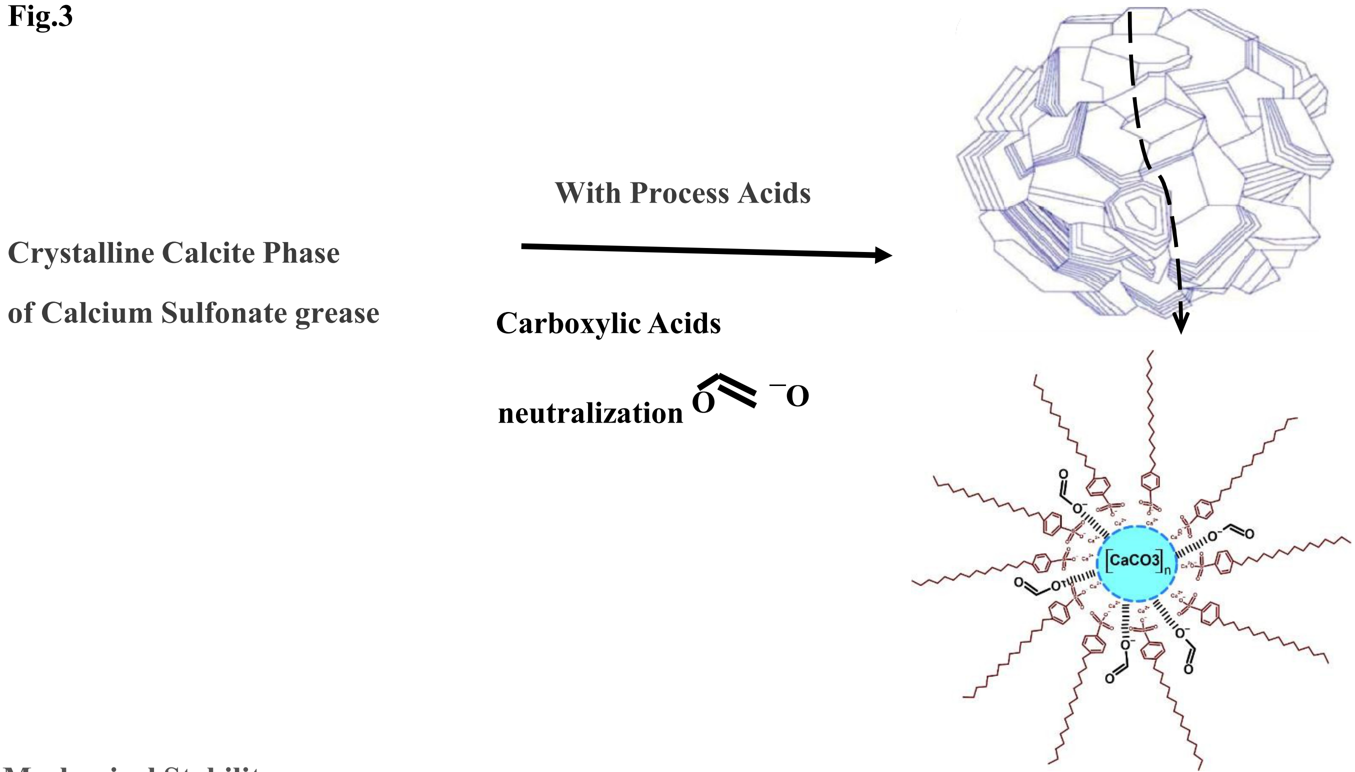


Fig.3



Mechanical Stability:

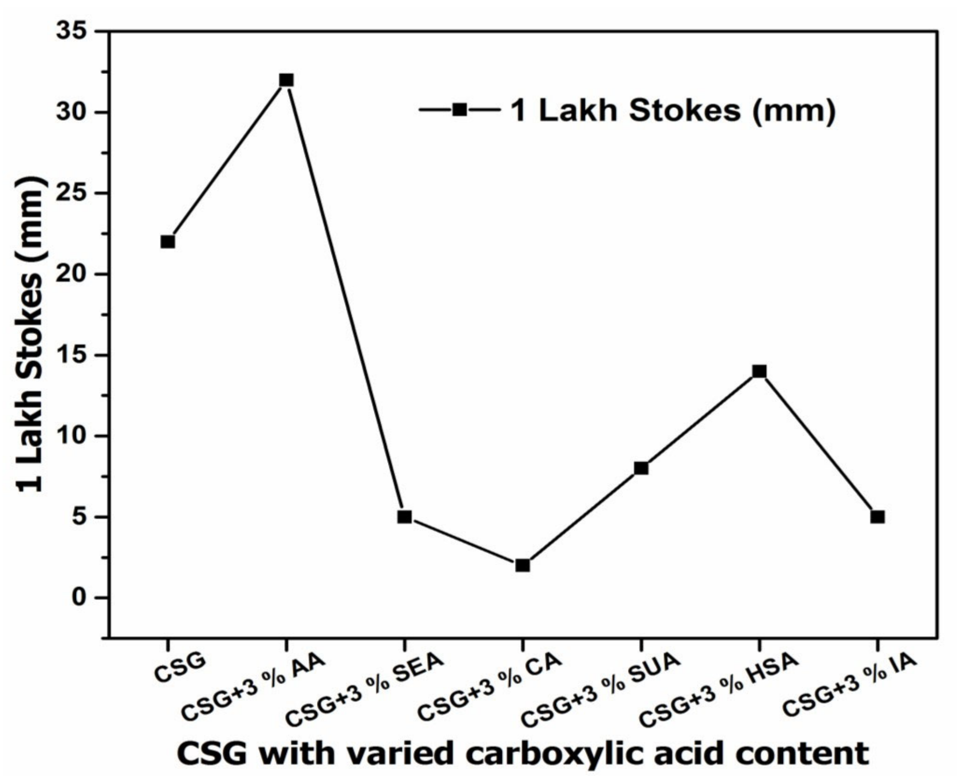
Mechanical degradation by shear is one of the mechanisms that limits the life of lubricating greasein a bearing. It results in a change of the micro-structure of the thickener–oil system, leading to a change in bleed and consistency. The resistance to degradation can be quantified using a grease worker generally refers to the ability of a grease to resist changes in consistency from continued mechanical shearing after 1 Lakh stokes in lab methods like worked cone (ASTM D217)

Table -4 and Fig.4: Variation of mechanical properties of calcium sulphonate grease with different carboxylic acids and their carboxylic contents.

CSG with varied carboxylic acid content	Mechanical properties after 1L stokes, Penetration (mm)
CSG	22
CSG+3 % AA	32
CSG+3 % CA	2
CSG+3% IA	5
CSG+3 % SUA	8
CSG+3 % SEA	5
CSG+3 % HSA	14

There is a huge improvement in mechanical properties with addition of 3% citric acid in calcium sulphonated grease with variation in penetration to just limiting to 2mm. Similar trends are observed with incorporation of Succinic acid and Sebacic acid. The reasoning could be the formation of branched micelle with Citric acid, Succinic and long chain Sebacic acids. The mechanical shear load is equally taken by the formation of branched and rearranged micelles as shown in **Fig.4** below. The addition of acetic acid results in more crystalline formation calcium acetate phase and the mechanical load is not dissipated as in case multifunctional carboxylic acids.

Fig. 4



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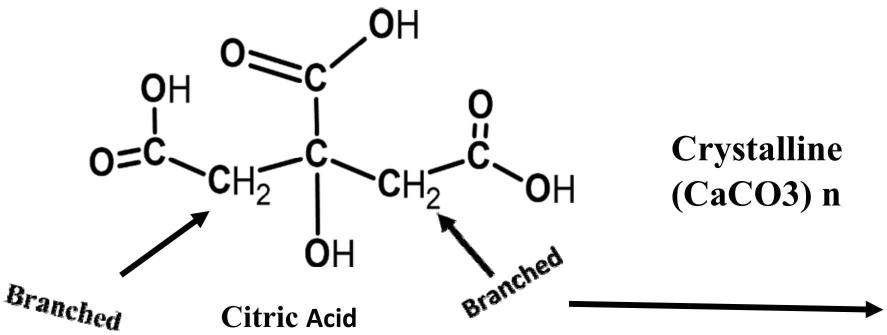
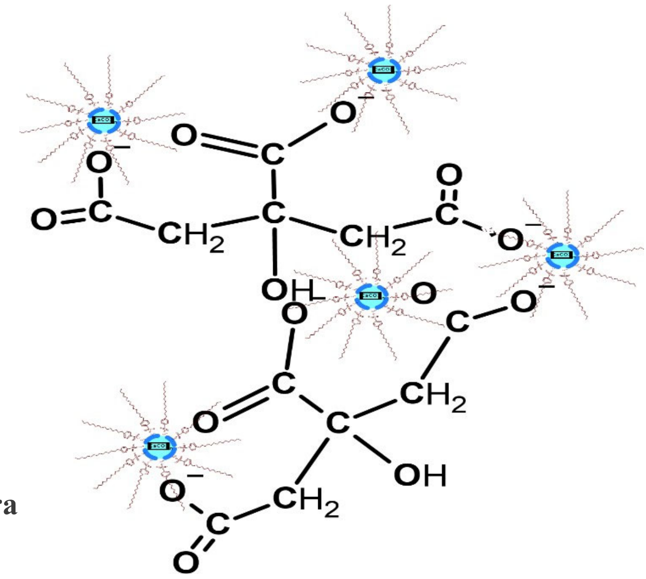




Formation of network like branched structureon rearra

Roll Stability Property:

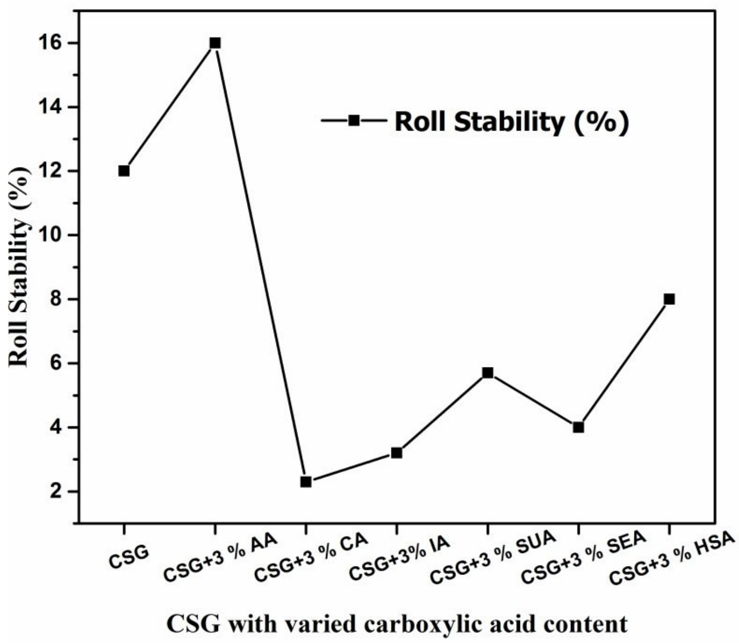
Micelle is rearranged.

The roll stability apparatus consists of a sealed cylindrical chamber into which a grease sample isinserted with a weighted roll. This assembly is rotated in an oven for a certain time, after which the grease is removedand its penetration is measured. Larger penetration change numbers indicate greater grease thinning and therefore less stability. Condition used was 16 hours at room temperature test was performed on each grease sample as per ASTM D 1831 method. The effect of change in penetration before and after the test is measured and % change in Roll Stability of each of these greases are evaluated.

Table -5

CSG with varied carboxylic acid content	Rolling Stability %
CSG	16
CSG+3 % AA	12
CSG+3 % CA	2.3
CSG+3% IA	3.2
CSG+3 % SUA	5.7
CSG+3 % SEA	4
CSG+3 % HSA	8

Fig.6 shows the variation of % Roll stability with CSG added with 3% of different carboxylic acids.

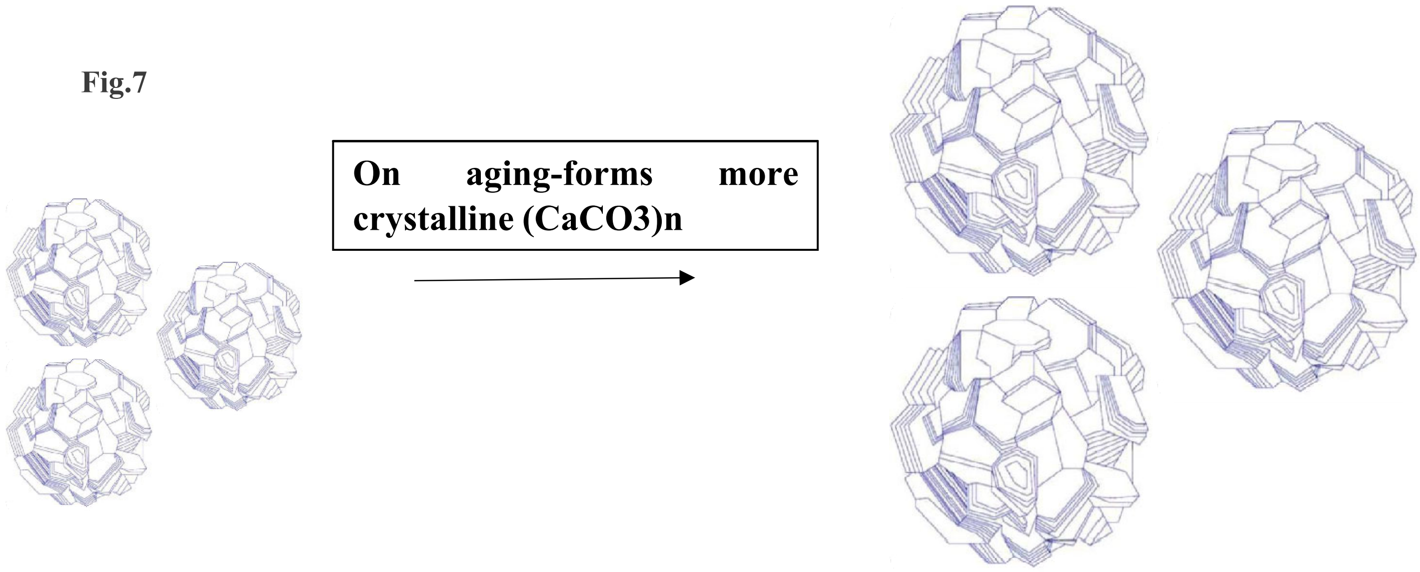


A similar trend like that of mechanical stability is observed with CSA loaded with 3% citric acid is performing much better in terms of shear measured from roll stability.

Surface Hardening of Sulphonated Grease

Hardening of sulphonate grease happens on ageing resulting in pumpability issues. Some of the reasons could be the carbonation when carbon dioxide in the air diffuses into pores and reacts with water, it creates carbonic acid, which reacts with excess base to form the calcium carbonate. The excess calcium carbonate formed results in more crystalline calcite formation leading to hardening in grease as shown below in **Fig. 7.**

Fig.7



Before interaction with air/aging

Size – 1.5-15nm

Interaction with Air with increase in Size: 15-500 nm

This can be prevented by adding a surfactant that neutralizes the excess base or a processing aids like various carboxylic acids. The hardening of CSA with and without of different carboxylic acids were observed for a month and reading on a scale 1-5 are given the **Table-6.**

Table -6: Surface Hardening of Sulphonated after a month on a scale of 1-5
5 – highest hardening and 1- lowest hardening

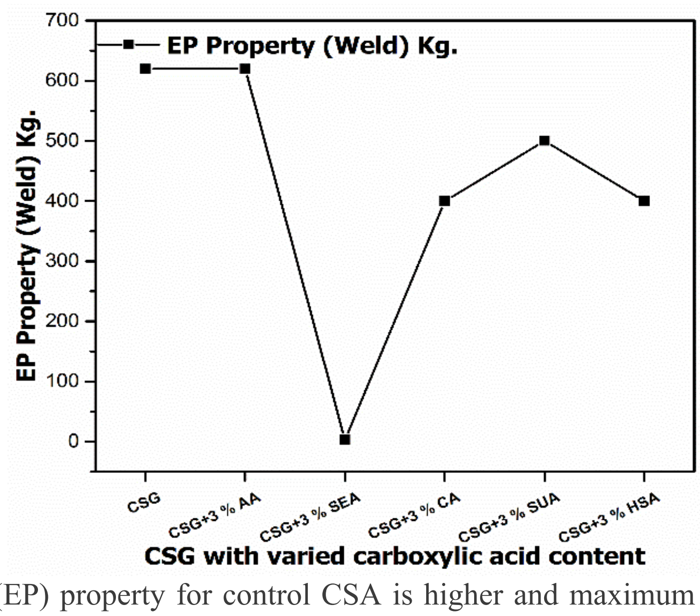
CSG with varied carboxylic acid content	Visual Observation and marking on a scale 1-5
CSG	4
CSG+3 % AA	5
CSG+3 % CA	1
CSG+3 % IA	2
CSG+3 % SUA	3
CSG+3 % SEA	3
CSG+3 % HSA	2

It is observed that quite a significant difference in surface hardening for CSA mixed with 3% Citric acid due to the presence of three carboxyl groups which can neutralize the excess base and rearranges to form a branched micelle as shown in **Fig.7**. The branched micelle in turn avoids the excess carbonation and similarly it is observed with dicarboxylic acids of Succinic and Sebacic acids. In case of 12 –HSA, it acts as a surfactant and prevents additional calcite formation on ageing. This is an interesting observation where in the hardening of sulphonated greases can be prevented by adding correct quantities of suitable carboxylic acids.

Extreme Pressure property by Four Ball Weld Load Test:

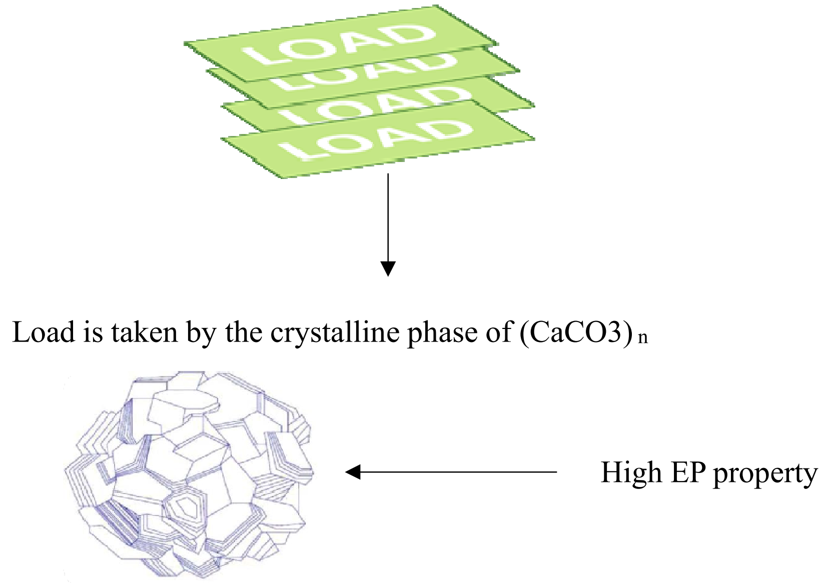
One of the most widely used and accepted tests to characterize the extreme pressure or load carrying capacity of high-performance industrial greases is to evaluate the four-ball weld load as per IP 239 method. In the present study we have used this test to evaluate the four-ball weld load of all the greases. In this test one stainless steel ball kept in a spindle attached to a motor is rotatedagainst three stationary balls kept immersed in the lubricating grease in a ball pot assembly. Loadis applied on the three balls from below. Test is conducted as per IP 239 method. (Speed = 1470 rpm; Time = 10s). As the applied load is increased, at a particular load the four balls weld togetherwhen the lubricating grease loses its load carrying capacity. This load is declared as the weld load for the particular lubricating grease. The values obtained for all the greases are used to differentiate the extreme pressure property of the greases taken for the study.

Fig.8



Extreme Pressure (EP) property for control CSA is higher and maximum at 620 Kg for weld and drops down on addition of all carboxylic acids. It is well understood the crystalline phase of calcite which forms the lubricating surface is responsible for withstanding the load. On addition of carboxylic acids, the calcium carbonate is neutralized and resulting rearranging of the micelle (Fig.9). On addition of 0.5 to 1% of SIB as a EP additive to the CSA with processing aids, the EP property got enhanced to the control values.

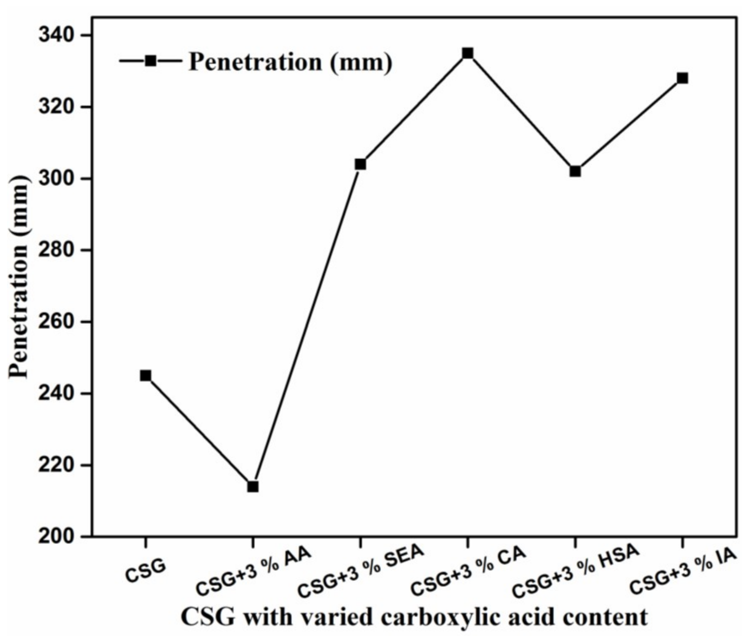
Fig.9



Comparative study for Consistency (ASTM D 217).

Further study has done to check the effect of carboxylic acids and the other EP additives on the consistency of the treated grease. This study also clearly shows that there is an increase in penetration (mm) for the treated greases with carboxylic acids which could be an indication of softer rearranged micelles due to the breaking of crystalline calcite phase. **Fig.10** shows variation of consistency parameter (Penetration) with addition of different carboxylic acid in Calcium Sulphonate Grease (CSG)

Fig.10



Conclusions:

The effects on various parameters on post addition of various carboxylic acids (different carboxylic contents per mole) to Calcium Sulphonate Grease (CSG) have been studied.

1. There is a distinct variation in dropping point observed with addition of different carboxylic acid into Calcium Sulphonate Grease (CSG). Some of Carboxylic acid (AA, SUA & CA has shown increase in dropping point and others (IA, HSA & SEA) has shown drop in dropping point . SEA has shown highest fall. The possible reason for variation of droppingpoint was explained by COOH eq per mole for each carboxylic acid.
2. Shear Stability Parameters (both mechanical and roll stability parameters) of Calcium Sulphonate Grease (CSG) Greases have shown distinct variations after addition of differentco aids- carboxylic acid. Both the mechanical & roll stability properties are very much enhanced for CSG with Citric Acid up to 90% improvement as compared to others. Polyhydroxy acids such as citric acid can improve mechanical & Rolling Stability of Calcium Sulphonate Grease (CSG).
3. It is also observed that there is a drastic reduction up to 70% in surface hardening whichis a characteristic feature of CSA with addition of citric acid among carboxylic acids used for study .
4. The study on extreme pressure property by each of grease sample with different carboxylic acid by Four Ball Weld Load Test, it was observed that there is a significant drop in EP property on addition of all carboxylic acids to CSG . This can be compensated by additionof EP additives.
5. The consistency of grease is shifted from NLGI-3 to NLGI-2 and this can be controlled by reducing the addition of amount of base oil used to meet NLGI 3 and by controlling milling pressure.
6. The information obtained through this study, will be useful in selecting the right type of co-aid agents to produce better thickening / yield of sulphonate complex grease and above study will be useful in process understanding by complexation process for better thinning/ thickening with help of different co-aids required for manufacturing different variety of these greases other than Calcium Sulphonate Grease
7. Further work is in progress regarding hardening study and similar study on lithium / complex greases.

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