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In	This Issue	Page No.
1.	President's Desk	3
2.	Technical Paper	
	Overbased Calcium Sulfonate Greases for Extreme Environment	5
3.	Technical Paper	
	Viscosity Modifiers for Biodegradable Ester Based Lubricants	13
4.	Technical Paper	
	Understanding the Intricacies of Cam Gear-Split Gear Lubrication in Diesel-Electric Locomotives	23
5.	Technical Paper	
	Real Life Performance Study of Different Metal Shop Thickened Greases in DRI Kiln Seal Application	26

Application for Membership

On Our Cover

Glimpses of 14th Lubricating Grease Conference held at Hotel Clarks Amer, Jaipur from February 2-4, 2012.

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OVERBASED CALCIUM SULFONATE GREASES FOR EXTREME ENVIRONMENT

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Abstract

There are number of grease thickeners available for making lubricating greases. However, each one of them possesses its own strengths and weaknesses. Calcium sulfonate complex greases, not new to the industry, are known for over six decades and have been improved over times by various people to make suitable grease for different applications. This class of greases is known for having excellent high temperature, extreme pressure and rust protection characteristics. The down side of its performance is poor pumpability, poor low temperature properties and higher cost compared to lithium greases.

In general, the art in preparing this class of greases involves converting liquid overbased calcium sulfonate to grease containing calcite particles. The degree of conversion to calcite form can greatly influence the properties of the finished grease and therefore the art lies how best one controls the process parameters and incorporate the other performance enhancing ingredients during processing stage.

The worldwide volume for calcium sulfonate greases is increased from 1.2 % in 2005 to 1.4 % in 2010. In North America, its volume increased significantly from 3.8 % in 2005 to 5.4 % in 2010, where in India it's merely about 0.8 %. In North America by virtue of its characteristics these greases are gaining more popularity over others and are gradually becoming true multi-purpose greases.

Besides having robust multi-purpose calcium sulfonate greases, the authors have recently developed some innovative specialty sulfonate greases as a result of perfecting unique process parameters and optimized compositions. One of the products developed is a super heavy duty grease for extreme pressure conditions that exhibit 800 kg weld load and 70 lbs Timken load. Other grease covered in this paper is grease for marine applications having excellent rust protection and passing 1000 hrs salt fog test and the third one is arctic grease for extreme low temperature characteristics having mobility of 18 gm / minutes at - 40°C. The details of those performance characteristics will be covered in this paper.

Key Words: Lubricating grease, Calcium sulfonate, Weld load, Penetration

Introduction

Over based calcium sulfonate greases, also popularly known as sulfonate greases, are not new to the industry as it appears and were patented as early as in 1940's. One of the reasons for development of this class of greases appears to be the efforts to improve the high temperature capabilities of calcium greases. Calcium base greases are known to possess excellent water resistance and low temperature properties but poor in high temperature capabilities. Zimmer et al, patented sulfonate base grease having good water resistance and having melting point over 400 °F (204 °C) (1,2) . Sproule and Pattenden (3) reported that grease prepared using combination of high and low molecular weight sulfonates as thickening agent provide grease with higher drop point. McMillen in 1960's patented calcium sulfonate greases having dropping point over 500 °F (260 °C). Since then, the basic principle of making gelled overbased calcium sulfonate greases using liquid over based calcium sulfonate with total base number (TBN) ranging from 300 to 500 remains practically unchanged . In a general process, highly overbased sulfonate is mixed with base oil and treated with acid, lime and suitable promoters where amorphous

calcium carbonate is converted into desired crystalline calcite form followed by removal of promoters and water from the mixture (5). During the process, amorphous calcium carbonate can readily be converted either to calcite (desired form) or vaterite, an undesired form of calcium carbonate. The process is highly sensitive to the processing parameters and ingredients used and therefore, end use properties greatly depend upon how the grease is processed. Muir et al, reported high performance calcium borate modified calcium sulfonate complex grease exhibited dropppoint point over 570 °F (299 °C) and excellent other performance characteristics (6).

Conventional overbased calcium sulfonate greases reported, in general, are known to possess high dropping point, good water resistance and rust protection properties, and superior inherent extreme pressure properties. The down side of these greases is found to be inferior low temperature and limited pumpability due to high thickener content used to make these greases. Due to their superior characteristics over other greases especially over most popular lithium greases, its volumes worldwide are on gradual increase. NLGI 2010 worldwide market survey indicates that volumes of calcium sulfonate greases has increased from 1.2 % in 2005 to 1.4 % in 2010 (7). These greases are gaining more popularity in North America with its volume increase from 3.8 % in 2005 to 5.4 % in 2010. By virtue of greater awareness and unique characteristics, this class of greases has started to gain importance in Indian industry as well, though the volumes are just merely 0.8 % in 2010.

A wide variety of overbased calcium greases are reported in literature and are commercially available with different claims. However, the properties of this grease are greatly dependent upon the process parameters, reacting components and the type of additives used to enhance the properties. The conventional additives used in other greases like lithiums do not necessarily provide the similar effect in calcium sulfonate greases. Royal Mfg Co LP has been making overbased calcium sulfonate greases for decades and the formulae and compositions have been customized and perfected many times so as to meet most severe application requirements of the industry. We have recently developed 3 new products, one having super heavy duty grease having 800 kg weld load, second one for marine applications passing over 1000 hrs in salt fog test and the third one with extreme low temperature properties exhibiting mobility of 18 gm/minutes at - 40 °C as per US steel mobility test. The performance characteristics of these greases have been covered in this paper.

Experimental

The base oils used in preparing greases are commercially available mineral and/or synthetic oils of different viscosities. The mineral oils used are either neat or blend of paraffinic and / or naphthenic oils. The overbased calcium sulfonate thickeners were prepared using 400 TBN sulfonate. The greases reported in this paper are commercially manufactured grease in oil heated counter rotating kettles having capacity of about 5 Tons per batch and were either milled through Charlotte mill or APV Gaulin homogenizer. The greases were tested as per standard ASTM / IP test methods. The grease mobility has been tested as per US Steel mobility test. The salt spray test was tested as per ASTM B 117 test method.

Results and Discussion

Development of Heavy Duty Calcium Sulfonate Grease

There are different kinds of greases being regularly used in automotive and industrial applications. In general, extreme pressure (EP) greases used automotive in wheel bearing, chassis, disc brake, universal joints, fifth wheel etc are either lithium/ lithium complex, aluminum complex, and calcium sulfonate greases meeting NLGI GC-LB specifications. Similar kind of greases can also be used in industrial applications with minor modifications for moderate operating conditions. Typical properties of commercially marketed grease for medium to high speed bearings are tabulated in Table -1. Such greases are normally made with group I or naphthenic base oils and fall in viscosity grade ranging

VG 150-220. Typically these greases possess weld load of the range 250-400 kg and Timken OK load to the tune of 40-50 lbs where calcium sulfonate greases possesses little higher Timken load of about 50 lbs or more. The water washout for these greases typically is less than 15 % wt 79 °C. However, there are some more severe applications like off high-way applications, construction and mining equipments which require much better extreme pressure and heavy load carrying characteristics and other properties compared to typical NLGI GC-LB or multipurpose grease. The EP greases used in such severe industrial applications like in metal processing industry, mining, construction, drilling, paper mill etc are typically lithium/lithium complex, aluminum complex, clay base and calcium sulfonate greases and general characteristics of those greases are tabulated in Table-2. The industrial applications where the loads are much heavier and bearings size sometime are larger, VG 320-460 oil based greases are recommended and are doped with higher amount

of EP additives to meet stringent requirement of the industry. On the other hand calcium sulfonate greases do not require much additives to meet these requirements. Interestingly, it is difficult to further boost the EP characteristics of the calcium sulfonate grease.

As there are a number of manufactures and suppliers of these classes of greases, there is increasing emphasis from the market to develop some niche products having heavy duty grease capable of handling not only extreme heavy duty and shock load conditions but also stand out providing competitive advantage. In view of this, we have recently developed a heavy duty greases specially designed for heavy duty industrial operations like in mining, steel and construction industries. The comparative test data of this grease are tabulated in Table-3. Table -3 indicate that the new heavy duty grease exhibit superior performance characteristics compared to conventional sulfonate greases available in the

S.No.	Property	Test Method	Lithium Grease	Li-complex Grease	Al-complex Grease	Ca-sulfonate Grease
1.	Thickener type	-	Lithium 12 Hydroxy	Li-complex	Al-complex	Calcium sulfonate
2.	Appearance	Visual	Smooth	Smooth	Smooth	Smooth
3.	NLGI grade	-	2	2	2	2
4.	Penetration, 60 x strokes	ASTM D217	265-295	265-295	265-295	265-295
5.	Penetration after 100,000 strokes		+ 30	+ 30	+ 30	+ 25
6.	Drop point, °C	ASTM D 2265	180 Min	260 min	260 min	260 min
7.	Viscosity grade	ASTM D 445	VG 220	VG 220	VG 220	VG 220
8.	Copper Corrosion	IP 112 / ASTM 4048	1a	1a	1a/1b	1a
9.	Rust preventive properties	ASTM D 1743	Pass	Pass	Pass	Pass
10.	Weld load, Kg	ASTM D 2596	> 250	315	315	400
11.	Wear scar dia., mm	ASTM D 2266	0.60	0.60	0.60	0.50
12.	Timken OK load, lbs	ASTM D 2509	40-45	45-50	40-45	50-55
13.	Water washout, 79 ºC, % wt	ASTM D 1264	10-15 max	10-15 max.	10 max.	10 max.

Table-1

Typical Properties of Conventionally Used Greases in Heavy Duty / Critical Applications										
S.No.	Property	Test Method	Li-complex	Al-complex	Ca-sulfonate					
1.	Thickener type	-	Li-complex	Al-complex	Ca-sulfonate					
2.	Appearance	Visual	Smooth	Smooth	Smooth					
3.	NLGI Grade	-	2	2	2					
4.	Penetration, 60 x strokes	ASTM D 217	265-295	265-295	265-295					
5.	Penetration after, 100,000 strokes		+ 30	+ 30	+ 30					
6.	Drop Point, °C	ASTM D 2265	260 Min	260 min	277 min					
7.	Copper Corrosion	IP 112	1a	1a/ 1b	1a					
8.	Rust preventive properties	ASTM D 1743	Pass	Pass	Pass					
9.	Viscosity Grade	ASTM D 445	VG 220 - 460	VG 220- 460	VG 220-460					
10.	Weld load, Kg	ASTM D 25	3	3	400					
11.	Wear Scar Dia, mm	ASTM D 2266	0.60	0.60	0.50					
12.	Timken OK load, lbs	ASTM D 2509	45-50	40-45	50-55					
13.	Water Washout,79 °C, % wt	ASTM D 1264	10 max	10 max.	10 max.					
14.	Water Spray off, % wt	ASTM D 4049	50	40	30					

Table-2

Table-3

Comparative Test Data of Regular Calcium Sulfonate and New Heavy Duty Calcium Sulfonate Grease

S.No.	Property	Test Method	Regular Ca- sulfonate Grease	New Heavy Duty Ca-sulfonate Grease
1.	Thickener type	-	Ca-sulfonate	Ca-sulfonate
2.	Appearance	Visual	Smooth	Smooth
3.	NLGI Grade	ASTM D 217	2	2
4.	Penetration, 60 x strokes	ASTM D-217	265-295	265-295
5.	Penetration after 100,000 strokes		+ 20	+ 20
6.	Drop Point,ºC	ASTM D 2265	277 min	277 min
7.	Viscosity Grade	ASTM D 445	220	460
8.	Copper Corrosion	IP 112	1a	1a
9.	Rust preventive properties	ASTM D 1743	Pass	Pass
10.	Weld load, Kg	ASTM D 259	400-50	800
11.	Wear Scar Dia, mm	ASTM D 2266	0.50	0.45
12.	Timken OK load , lbs	ASTM D 2509	50-60	70
13.	Water Washout ,79 °C, % wt	ASTM D 1264	5 max.	1.3 max.
14.	Water Spray off, % wt	ASTM D 4049	< 40	20 max
15.	USS Mobility Test	USS DM 43		
	@ 0 °F, gm/min		13.6	13.2
	@ - 20 °F , gm/min		4.0	3.2

market. The conventional calcium sulfonate greases available in the market exhibit weld of about 400 to 500 kg range where as new developed grease has indicated maximum possible weld i.e., 800 kg tested as per ASTM D 2596 Method without adding molybdenum disulphide or graphite. Similarly the Timken OK load for conventional greases ranges from 45-55 lbs where as the new grease has exhibited much superior Timken OK load of 70 lbs.

This much superior performance could possibly be attributed due to the combination of factors. One of them is optimizing the process parameter in such a way where total conversion amorphous calcium carbonate to crystalline calcite takes place minimizing the formation of undesirable vaterite form. Greases having dominant calcite form of calcium carbonate are reported to possess better EP properties as compared to the one having predominant vaterite form of calcium carbonate. Calcite fish like platelet structure is reported to helps in better film formation and thus provide superior EP properties whereas carbonate particles in vaterite are oriented perpendicularly (8). On the other hand, conventional EP additives like sulphur-phosphorous and/or antimony-zinc type additives typically used in lithium greases do not perform well in sulfonate greases and therefore it is rather difficult to further boost EP properties of calcium sulfonate grease. Additionally, we have identified a synergistic combination of additives that help to achieve highest weld load of 800 kg and very high Timken of 70 lbs. Figure-1





comparatively indicate that new heavy duty calcium sulfonate grease exhibit much superior EP properties in terms of weld load with respect to its other counterpart. Besides this, this new greases exhibited very good pumpability characteristics at normal and below normal temperatures. As per US Steel mobility test (USS DM 43), this grease indicated mobility of 13.2 gm/minutes at – 18 °C (0 °F) and 3.2 gm/minutes at - 30 °C (-20 °F) which is considered good and comparable to our conventional grease having base oil viscosity of VG 220. This makes this grease better suitable for applications where greases are pumped through centralized lubrication systems especially in steel mills and mining.

Superior Calcium Sulfonate Grease for Marine Applications

In applications like marine and off shore drilling, grease exposed to either directly or indirectly to salt water and therefore rusting of equipments is pretty common. For such applications having sultry environment, lubrication of bearings, gears and wire ropes requires grease having resistance to water washout, water spray off and resistance to corrosion in salt water environment. In such applications, calcium sulfonate greases are an obvious choice, having inherent properties of rust inhibitions. The water washout characteristics are tested by ASTM D 1264 method and water spray off by ASTM D 4049 test method. For testing anti-rusting properties for marine applications, salt fog spray test (as per ASTM B117) has emerged to be better than other rust tests. Some of the customers are demanding greases meeting salt fog spray test data as high as 1000 hrs. This stringent test requirement is not met through lithium or even a majority aluminum complex greases. If calcium sulfonate grease is not formulated carefully, it may not meet this stringent requirement. We have developed grease specifically for marine application meeting this requirement and test data are tabulated in Table-4. This grease exhibited excellent mechanical stability; very good extreme pressure properties in terms of 620 kg weld load and 65 lbs Timken OK load and excellent rust protection properties as tested by ASTM D 1743 test and salt spray test ASTM B 117. This grease passes rust test (ASTM D 1743). In salt



Fig. 2 : Test panel after 1000 hrs

spray test this grease exhibited excellent performance in terms of passing over 1000 hrs salt spray test where other greases failed early. This grease might have run more hrs but test was discontinued after completing target 1000 hrs. Other grease which is also calcium sulfonate base grease in same viscosity range failed after 360 hrs (Figure-2) thus providing the superior performance . The reasons for this superior performance are not completely understood however, it could possibly be attributed due to interaction of polar heads of overbased calcium sulfonate with the other ingredients / additives.

Table-4

Comparative Test Data of Calcium Sulfonate Grease for Marine Applications

S.No.	Property	Test Method	Regular Ca-sulfonate Grease	New Ca-sulfonate Grease for Marine
1.	Thickener type	_	Ca-sulfonate	Ca-sulfonate
2.	Appearance	Visual	Smooth	Smooth
3.	NLGI Grade	ASTM D 217	2	2
4.	Penetration, 60x strokes	ASTM D-217	265-295	265-295
5.	Drop Point ,0 C	ASTM D 2265	277 min	277 min
6.	Viscosity Grade	ASTM D 445	220	220
7.	Weld load, kg	ASTM D 2596	620	620
8.	Wear Scar Dia, mm	ASTM D 2266	0.45	0.45
9.	Timken OK load , lbs	ASTM D 2509	65	65
10.	Water Washout, 79 °C, % wt	ASTM D 1264	2.3max.	1.3max.
11.	Water Spray off, % wt	ASTM D 4049	20	10
12.	Copper Corrosion	ASTM D 4048	1a	1a
13.	Rust Preventive Properties	ASTM D 1743	Pass	Pass
14.	Salt Spray Test , hrs	ASTM B 117	360 hrs	> 1000 hrs

Arctic Calcium Sulfonate Grease for Cold Climate Applications

Calcium sulfonate greases are known to be inferior in pumpability due to higher thickener used to make NLGI 2 grease compared to other greases like lithium complex and aluminum complex greases. Calcium sulfonate complex greases, on the other hand, have proved to advantageous over lithium complex and aluminum complex greases in certain applications like mining and steel due to better extreme pressure and natural rust protection properties. Aluminum complex greases are also known for better water resistant properties and thus the candidate for mining and drilling operation. However, the more popular greases in these applications are either lithium or lithium complex greases so far and for transition, the choice lies between either aluminum complex or calcium sulfonate complex grease. Calcium sulfonate complex earns more points due to better compatibility with lithium and lithium complex greases over aluminum complex greases.

There are some applications in mining and drilling operations like up in Canada, China and some European countries where the temperatures can be very low specially in winter and the greases are required to pump as low as $-40 \,^{\circ}\text{C/}^{\circ}\text{F}$. Therefore the challenge lies to make a grease having good pumapability at such low temperatures and many of the calcium sulfonate available in the market do not meet this requirement. The greases used in these applications are generally synthetic oil based lithium, calcium and or aluminum complex greases. In some cases there are two grades of greases used like summer grade in NLGI 2 consistency and winter grade in NLGI 1 grade. Synthetic greases do fill this void to an extent but their high cost is the limiting factor.

We have recently developed arctic calcium sulfonate grease in semi-synthetic base oil, meeting cold climate requirements. The test data are tabulated in Table-5. Table -5 indicates that the grease in NLGI 2 consistency exhibited excellent mechanical stability only 11 units change in 100,000 double strokes

S.No.	Property	Test Method	Arctic Ca-sulfonate Grease
1.	Thickener type	-	Calcium sulfonate
2.	Appearance	Visual	Smooth
3.	NLGI Grade	-	2
4.	Penetration, 60x strokes	ASTM D-217	285
	Penetration after 100,000 strokes		296
5.	Drop Point ,0 C	ASTM D 2265	277 min
6.	Viscosity, 40 0C	ASTM D 445	62
7.	Weld load, K	ASTM D 259	620
8.	Wear Scar Dia, mm	ASTM D 2266	0.45
9.	Timken OK load , lbs	ASTM D 2509	60
10.	Rust Preventive Properties	ASTM D 1743	Pass
11.	USS Mobility test ,	USS DM 43	
	- 18 0C/ 0 0F, gm/min		140
	- 40 0C/0F, gm/min		18

Table-5 Typical Properties of Arctic Calcium Sulfonate Grease

penetration and a high drop point of + 277 °C. Weld load of 620 kg and Timken OK load of 60 lbs indicates that this grease encompasses excellent extreme pressure properties as well. This grease also possesses good rust preventive properties as indicated by ASTM D 1743 test. US steel mobility test data conducted at -18°C and -40 °C/°F indicate its mobility 140 gm/min at -18°C and 18 gm / min at -40 °C/°F. In general, the customer requirement for such applications is minimum 4 gm/min mobility at -40 °C/°F and therefore this arctic grease has exhibited much superior data. This may primarily be attributed due to the fact that we have carefully optimized and perfected our manufacturing process and control in such a way that uses reduces amount of thickener to make NLGI 2 grease and also the viscometrics are adjusted in such a way that help us to meet this stringent low temperature requirement simultaneously while retaining the other properties.

Conclusions

Overbased calcium sulfonate greases constitute significant volume of worldwide grease market and its volume is considerably increasing in North America. Calcium sulfonate greases are known to possess superior high temperature, extreme pressure and rust protection properties as compared to other greases. The drawback associated with this class of greases is limited pumapability especially at low temperatures. These greases in different base oil viscosities and grades are being regularly marketed by different manufacturers / marketers across the globe. In order to further enhance the scope of this important class of greases in critical applications areas, we have successfully developed three greases. The first grease developed exhibited very high extreme pressure properties as indicated by 800 kg weld load and 70 lbs Timken. The second grease has been intended for humid environment specially in marine and off shore drilling operations. This grease has exhibited excellent test results in salt fog test and successfully passed over 1000 test hrs. The third grease was developed for very cold climate and tested as per US Steel mobility test at -18 °C and -40 °C and test result indicate its mobility of 140 gm/minute and 18 gm/minutes respectively which is considered pretty good for calcium sulfonate greases.

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VISCOSITY MODIFIERS FOR BIODEGRADABLE ESTER BASED LUBRICANTS

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Abstract

Environmental mishaps that have occurred worldwide have resulted in an ever increasing interest in ecofriendly, readily biodegradable and non-toxic fluids as alternatives to petroleum-based products in the lubricant industry. Biodegradable lubricant products can reduce the negative environmental impact caused by leaks and spills and have gained increasing importance in marine lubricants, gear oils, hydraulic fluids, and for down-hole oil and gas extraction. The ester structure gives synthetic esters and natural ester oils biodegradable properties.v However, the ester structure introduces significant molecular polarity into the ester base oil, compared to petroleumbased mineral oils. Some polymeric viscosity modifiers used in the mineral oil formulation are not compatible with ester oils. In this work, the compatibility between several polymers and ester oils including synthetic ester and vegetable oils were studied. The relationship between the structure of the polymer and the ester and their solubility characteristics in the ester oil was investigated. The ester oils studied in this work includes typical synthetic esters such as mono ester, adipate ester, phthalate ester, trimellitate ester, polyol ester, and trimethylopropane ester and natural esters such as soybean oil, canola oil, and castor oil.

Mutual compatibility requires similarities in structure of the polymer and the base oil such as the presence of double bonds and/or the presence of ester functionality. Polymers that contain ester functionality such as alkyl-diester (AD) copolymers and polymers that contain double bonds such as polybutadiene (PB) have been found to be the most soluble in a variety of synthetic ester and vegetable base oils.

Introduction

In lubricant formulations, viscosity modifiers are polymers which can help improve the viscosity of lubricants over a wide temperature range so that the lubricant maintains its effectiveness. Viscosity is a measure of the resistance of the fluid to flow at a given temperature. A general property of fluids is that the viscosity decreases as temperature increases and conversely, the viscosity increases as the temperature is decreased. Too thin of a fluid at high temperature and too thick of a fluid at low temperature is a concern in formulating lubricants. Generally, the least viscous lubricant which still forces the two moving surfaces apart is desired. If the lubricant is too viscous, it will require a large amount of energy to move; if it is too thin, the surfaces will rub and friction will increase. This can cause wear of the surface leading to part failure.

Viscosity index (VI) is a measure of the viscositytemperature dependence of fluids; it is an arbitrary measure for the change of viscosity with temperature. It is used to characterize lubricating oils in the automotive industry. With a higher VI, the fluid viscosity will be less sensitive to temperature change. Many lubricant applications require the lubricant to perform across a wide range of conditions; for example, in an engine. Automotive lubricants must reduce friction between engine components when it is started from cold as well as when it is running (up to 200°C/392°F). The oils with the highest VI will not vary much in viscosity over such a temperature range and therefore will perform the best.

The mechanism of the mode of thickening of viscosity modifiers is associated with the hydrodynamic volume that the polymer chain occupies in the oil. Polymers typically consist of a long molecular chain and a high molecular weight compared to th base oil. The base oil is the solvent for the polymer. The polymer chain forms a coil in the solvent. The polymer coil size depends on the solubility of the polymer in the solvent. Solubility is governed by many factors including Van der Waals forces, i.e., Fluctuations in the polarizations of nearby molecules, chemical affinity for other polar atoms present in the polymer and the base oil.^{viii} Also, steric affects, temperature and pressure affect the solubility of polymers. Polymer molecular chains can

be nearly fully extended in a good solvent and form a large coil or not extended and form a small coil as in a poor solvent. The large coil not only occupies more hydrodynamic volume but also has the tendency to entangled with each other and generate more friction between molecules during the flow, as a result, it gives a fluid with a high viscosity. For most polymers, the solubility between polymer and base oil is increased at higher temperatures as illustrated in Figure 1. Higher temperatures favor a more fully extended polymer hence a larger hydrodynamic volume.

Another aspect of polymer solubility is association of like structures. In particular for PB and vegetable oil one can describe the orientation of groups around the double bonds. The Latin prefixes *Cis* and *Trans* describe the orientation of the hydrogen atoms with respect to the double bond. *Cis* means "on the same side" and *Trans* means "across" or "on the other side". Naturally occurring fatty acids generally have the *Cis* configuration. For example, the natural form of 9-octadecenoic acid (oleic acid) found in olive oil has a "V" shape due to the *Cis* configuration at position 9. The *Trans* configuration (elaidic acid) looks more like a straight line.vii PB has a minimum of 40% *Cis* and vegetable oil is around 97% *Cis*. Similarity of conformations allows for more efficient packing and



Cis Configuration Trans Configuration





alignment of like structures in molecules thus better solubility.

Several different types of polymers have in the past been studied and are useful as viscosity modifiers, including elastomers such as ethylene-propylene (OCP), styrenehydrogenated butadiene (SBR), styrene-hydrogenated isoprene (SI), radial hydrogenated polyisoprene (Star), and acid functionalized polymers (FP), and other less elastomeric types such as polyisobutylene (PIB), polymethacrylate (PMA), and styrene ester copolymers (SE).

The major lubricant base stocks include mineral oils, polyalpha olefins, synthetic esters, vegetable oils, polyalkyl glycols, and silicone fluids. For the last decade, there has been an ever increasing interest on eco-friendly, readily biodegradable and non-toxic fluids as alternatives to petroleum-based products in lubricant industry. Every year there are several millions gallons of petroleum oil released into the ocean. These are nonrenewable resources and break down in the environment much more slowly than natural bio-based oils. Table 1 shows the biodegradability for several common base stocks. Among them, many synthetic esters and all natural esters (vegetable oils) are readily biodegradable, as a result of their unique ester structure.ⁱⁱ The biodegradable properties allow them

Lubricant type by basestock	Range of biodegradability as evaluated by CEC-L-33-A-93 (% loss at 21 days)
Mineral oil	25-45
Hydrocracked Mineral oils	25-80
Bright stock	5-15
Polyalpha Olefins	20-80
Diesters	50-100
Aromatic esters	0-95
Polyols	5-100
Vegetable oils	75-100
Polyethylene glycols	10-30
Polypropylene glycols	10-70

Table 1 : The biodegradability of several common base stocksiii



Fig. 2 : The chemical structures of several typical synthetic esters

to break down in the environment and reduce the negative impact. They are renewable and reduce the dependence on nonrenewable petroleum resources.^{i,ii} Vegetable oils contain a high fraction of unsaturated fatty chains, which make them even easier to biodegrade then fully saturated chains.

Synthetic esters are synthesized by the esterification reaction between an acid and an alcohol or by transesterification between a vegetable oil and an alcohol. There are many different synthetic esters that can be obtained because of the ready availability of low-cost acids, alcohols or vegetable oils. The ester oils can be tailor made to provide certain lubricity and biodegradability characteristics that cannot be obtained from a vegetable oil. Further discussion on the synthesis of esters will not be discussed here as it is beyond the scope of this paper. Synthetic esters are becoming one of the most common biodegradable base oils in the lubricant market.

The commonly referenced ester types are monoesters, adipate diesters, phthalate esters,

trimellitate triesters, polyol esters, and trimethylopropane (TMP) esters as illustrated in Figure 2. The number of carbons in the chains can vary tremendously for each ester type and gives rise to slightly differing properties but the synthetic esters used for this study are in Figure 2.

The polymers used for mineral oil-based lubricants may not be compatible or have poor solubility in vegetable oil-based lubricants due to differences in there chemical structure. It requires similar structures and similar polar functional groups between polymer and the base fluid to achieve compatibility. The basic structure of a vegetable oil is called a triglyceride, which is an ester derived from glycerol and a mixture of different saturated and unsaturated fatty acids as illustrated in Figure 3. For example, the major unsaturated fatty acids in soybean oil are linolenic acid, linoleic acid and oleic acid. The saturated fatty acids are stearic acid, palmitic acid, etc.^{iv,v} Table 2 lists the fatty acid components in different vegetables oils. The ester group in ester oils increases the polarity, compared with mineral oil which is composed



Fig. 3 : Chemical structures of (a) triglyceride (R1, R2 and R3 represent different unsaturated and saturated hydrocarbon chains) and (b) an example of triglyceride: an unsaturated fat triglyceride from esterification of glycerol with linoleic acid, oleic acid and linolenic acid.

of hydrocarbon and has no polarity. Ester oils may also contains saturated hydrocarbon chains in the molecular structure. Therefore, some polymers compatible with mineral oils can still be compatible with ester oils composed of long saturated hydrocarbon chains, but incompatible with the ester oil with short hydrocarbon chains. The ester structure and unsaturation (double bonds) are sites were chemical cleavage and attack by microbes can occur. These are the primary functional groups responsible for why vegetable oil is readily biodegradable. In general, for a polymer to be soluble in a vegetable oil at least one of these functional groups is necessary in the polymer. However, this may not always be true as will be discussed later.

Fatty Acids		Almond	Apricot Kernel	Avocado	Canola	Coconut	Corn	Cottonseed	Flaxseed	Grapeseed	Hazelnut
Common Name	Saturated										
Caproic acid	6:0					0.6					
Caprylic acid	8:0					7.5					
Capric acid	10:0					6.0					
Lauric acid	12:0					44.6					
Myristic acid	14:0					16.8	0.24	0.8		0.1	0.1
Palmitic acid	16:0	6.5	5.8	10.9	4.0	8.2	10.58	22.7	5.3	6.7	5.2
Margaric acid	17:0						0.07				
Stearic acid	18:0	1.7	0.5	0.66	1.8	2.8	1.85	2.3	4.1	2.7	2.0
Arachidic acid	20:0				0.7		0.43				
Behenic acid	22:0				0.4						
Lignoceric acid	24:0				0.2						
Total		8.2	6.3	11.56	7.1	86.5	13.17	25.8	9.4	9.5	7.3
	Monounsaturated										
Palmitoleic acid	16:1	0.6	1.5	2.67	0.2		0.14	0.8		0.3	0.2
	17:1										
Oleic acid	18:1	69.4	58.5	67.89	56.1	5.8	27.33	17.0	20.2	15.8	77.8
Gadoleic acid	20:1				1.7						
Erucic acid	22:1				0.6						
Total		70	60	70.56	58.6	5.8	27.47	17.8	20.2	16.1	78
	Polyunsaturated										
	Omega 6										
Linoleic acid	18:2n6	17.4	29.3	12.53	20.3	1.80	53.52	51.5	12.7	69.6	10.1
Arachidonic acid	20:4n6							0.1			
	Total n6	17.4	29.3	12.53	20.3	1.80	53.52	51.6	12.7	69.6	10.1
	Omega 3										
Alpha linolenic acid (ALA)	18:3n3	0	0	0.96	9.3	0	1.16	0.20	53.3	0.1	0
	Total n3	0	0	0.96	9.3	0	1.16	0.20	53.3	0.1	0
Total Poly		17.4	29.3	13.49	29.6	1.80	54.68	51.8	66	69.7	10.1
	Ratio n6/n3	no n3	13.1	2.2	no n3	no n3	46.1	258.0	0.24	696.0	no n3

Table 2. Fatty acid components in different vegetables oils vi

January 1 - March 31, 2012

Fatty Acids		Mustard	Oat	Olive	Palm	Peanut	Rice bran	Safflower	Sesame	Soybean	Sunflower	Walnut	Wheat gram
Common Name	Saturated												
Caproic acid	6:0												
Caprylic acid	8:0												
Capric acid	10:0												
Lauric acid	12:0		0.39		0.1								
Myristic acid	14:0	1.39	0.24		1.0	0.1	0.7			0.1			0.1
Palmitic acid	16:0	3.75	16.67	10.93	4.3.5	9.5	16.9	4.29	8.9	10.3	5.9	7.0	16.6
Margaric acid	17:0						0.07						
Stearic acid	18:0	1.12	1.05	1.98	4.3	2.2	1.6	1.92	4.8	3.8	4.5	2.0	0.5
Arachidic acid	20:0			0.42		1.4							
Behenic acid	22:0			0.13		2.8							
Lignoceric acid	24:0					0.9							
Total		6.26	18.35	13.46	48.9	16.9	19.2	6.21	13.7	14.2	10.4	9	17.2
	Monounsaturated												
Palmitoleic acid	16:1	0.22	0.2	1.16	0.3	0.1	0.2		0.2	0.2		0.1	0.5
	17:1			0.14									
Oleic acid	18:1	11.61	34.9	72.29	36.6	44.8	39.1	14.36	39.3	22.8	19.5	22.2	14.6
Gadoleic acid	20:1	6.19		0.31	0.1	1.3			0.2	0.2		0.4	
Erucic acid	22:1	41.18											
Total		59.2	35.1	73.9	37	46.2	39.3	14.36	39.7	23.2	19.5	22.7	15.1
	Polyunsaturated												
	Omega 6												
Linoleic acid	18:2n6	15.33	39.08	9.21	9.1	32	33.4	74.6	41.3	51.0	65.7	52.9	54.8
Arachidonic acid	20:4n6												
	Total n6	15.33	39.08	9.21	9.1	32	33.4	74.6	41.3	51	65.7	52.9	54.8
	Omega 3												
Alpha linolenic acid (ALA)	18:3n3	5.90	1.79	0.79	0.2	0	1.6	0	0.3	6.8	0	10.4	6.9
	Total n3	5.9	1.79	0.79	0.2	0	1.6	0	0.3	6.8	0	10.4	6.9
Total Poly		21.23	40.87	10	9.3	32	35	74.6	41.6	57.8	65.7	63.3	61.7
, ,	Ratio n6/n3	2.6	21.8	11.7	45.5	no n3	20.9	no n3	137.7	7.5	no n3	5.1	7.9

Table 2 (Contd.) : Fatty acid components in different vegetables oils vi

Experimental

In this study, the compatibility between several polymers including ethylenepropylene copolymer (OCP), polybutadiene (PB), polystyrene-butadiene copolymer (SBR) and alkyl-diester (AD) copolymers with typical types of synthetic ester oils and vegetable oils is presented. The solubility and thickening efficiency of these polymers in ester oils, as well as the kinematic viscosity of the solution were studied. Polymer was added into base oil and then the solution was heated to around 100°C and stirred for 2 days to ensure the polymer has sufficient time to dissolve. Solutions with 1% and 5% concentrations were prepared. The kinematic viscosity of the polymer solution was measured by capillary rheometer submerged in a temperature controlled bath according to ASTM D-2270. The viscosity at 40°C and 100°C were measured and their VI's calculated.

The polymers used in this study including EPDM, polybutadiene, polystyrene butadiene copolymer and alkyl-diester (AD) copolymers. The synthetic esters include 2-ethylhexyl stearate, Di-tridecyl adipate, Di-isodecyl phthalate, Tri-isodecyl trimellitate, C6-C8

polyol ester, trimethylopropane tricaprylate. The vegetable oils include soybean oil, canola oil and castor oil. The chemical structures of the polymers are listed in Table 3 and the properties of the base oil used in this study are listed in Table 4.

Polymers	Chemical structure
Ethylene/propylene copolymer (EMP) (saturated hydrocarbon)	$- \underbrace{\left[\left(CH_2 - CH_2 - \frac{1}{x} \left(CH_2 - \frac{CH_2}{y} \right)_{x} \right]_{CH_3} \right]_{Y} - n}_{CH_3}$
Polybutadiene (PB) (unsaturated hydrocarbon)	$\begin{array}{c} - \begin{bmatrix} -CH_2 & CH_2 \end{bmatrix}_{n} \\ - \begin{bmatrix} -CH_2 & CH_2 \end{bmatrix}_{n} \\ - \begin{bmatrix} -CH_2 & -CH_2 \\ - CH_2 & -CH_2 \end{bmatrix}_{n} \\ - \begin{bmatrix} -CH_2 & -CH_2 \\ - CH_2 & -CH_2 \end{bmatrix}_{n} \\ - CH_2 & -CH_2 \\ - CH_2 &$
Polystyrene butadiene copolymer (SBR) (unsaturated hydrocarbon with pendant phenyl group)	$- \underbrace{\left(CH_2 - CH = CH - CH_2 \right) \left(CH_2 - CH_2 \right)}_{x}$
alkyl-diester (AD) copolymer	Proprietary

Table 3 : Chemical structures of polymers used in this study

Table 4 : Properties of synthetic esters and vegetable oils

				Kinemati	c viscosity		
Oil		Chemical name	Synthetic ester type	@40°C	@100°C	VI	Pour point °C
# A		2-ethyl hexyl stearate	Monoester	10	3	170	5
# B		Di-octyl adipate	Adipate diester	8.2	2.3	88	-67
# C		Di-tridecyl adipate	Adipate diester	27	5.4	136	-57
# D		C6 to C8 Polyol ester	Polyol ester	25	5	130	-60
# E	Synthetic esters	Trimethylol propane tricaprylate	Trimethylol propane ester (TMP)	20	4	140	-51
# F		Tri-isodecyl trimellitate	Trimellitate ester	124	11.9	81	-36
# G	Tri-octyl trimellitate		Trimellitate ester	86.5	9.5	84	-35
#H		Di-isodecyl phthalate	Phthalate ester	38	5.4	62	-42
# I	Vegetable	Soybean oil	triglycerides	32.1	7.6	218	-9
# J	Oils	Canola oil	triglycerides	35.1	8.2	216	-21
# K		Castor oil	triglycerides	315	18.5	51	-24

Results and Discussion

The compatibility between polymers and esters

From Table 5 our assertions made about polymer structure and ester type are generally true. An ethylene-propylene polymer not having ester functionality or unsaturation is not soluble in a synthetic ester as shown in table 5 or a vegetable oil as in Table 6. The exceptions are 2-ethyl hexyl stearate and tri-isodecyl trimellitate. One can see from the structures above that the ester structure is at the core of the molecule and is somewhat shielded from the long hydrocarbon chains that extend outward. These long hydrocarbon chains are more like the long hydrocarbon chains of the EPM polymer. These esters therefore act as better solvents for the EPM polymers and hence become partially compatible with the polymer. Because of this partial compatibility the EPM polymer was not studied further.

The other polymers in the table, PB, and SBR, each having unsaturated structures and alkyl-diester (AD)

copolymer having ester functionality are all soluble in various esters as expected except for one ester. A peculiar ester is the C₆, C₇, C₈ polyol ester. From the structure shown in Figure 2 the shape of the molecule is a star with the ester functionality tightly packed around the core. The ester is partially shielded by the C₆ to C₈ hydrocarbon chains. The C₆ to C₈ hydrocarbon chains are not long enough to solubilize the hydrocarbon portions of the EPM, SBR, or PB polymers. Only the AD polymer which is most like the polyol ester is soluble.

The compatibility study shown in Table 6 also included various vegetable oils such as soybean, canola and castor oil. Castor oil is unique from the other vegetable oils in that it possesses a third functional group, the hydroxyl group, -OH. This group renders the molecule to have more polar characteristics then regular vegetable oil. Therefore we find that typical PB and SBR polymers that are soluble in vegetable oil are not soluble in castor oil.

		EPM	PB	SBR	AD
#A	2-ethyl hexyl stearate	yes	yes	yes	yes
#B	Di-octyl adipate	no	yes	yes	yes
#C	Di-tridecyl adipate	no	yes	yes	yes
#D	C6, C7, C8 polyol ester	no	no	no	yes
#E	trimethylolpropane tricaprylate	no	yes	yes	yes
#F	Tri-isodecyl trimellitate	yes	yes	yes	yes
#G	TriOctyl trimellitate	no	yes; no at high conc.	yes; no at high conc.	yes
#H	Di-isodecyl phthalate	no	yes	yes	yes

Table 5 : General compatibility between polymers and synthetic ester

Table 6 : General compatibility between EPM, PB, SBR, and AD polymers

		EPM	РВ	SBR	AD
#	Soybean oil	yes	yes	yes	yes
#J	Canola oil	no	yes; no at	yes; no at	yes
#K	Castor oil	no	yes	yes	yes

The thickening efficiency of different polymers in different esters

In Tables 7, 8, and 9 a set of eight synthetic esters were used in a solubility study evaluating PB, SBR, and AD polymers at 1 and 5% concentration. The esters are in order of decreasing VI. As the VI decreases, the changeover from aliphatic ester to aromatic ester is seen. Much lower VI's are observed with polymers dissolved in aromatic esters. For all of the polymers the general trend is that as the concentration of polymer increases the VI increases and the higher the starting VI of the base ester the higher the VI with added polymer. Concentration affects the VI because of the fact that there are more molecules occupying a constant volume therefore a greater amount of chain entanglement, i.e., slower molecular motion occurs. The change in viscosity from 40°C to 100°C is minimized because polymer flow is impeded. The ester, trimethylopropane tricaprylate and the esters containing aromatic rings, the trimellitates and the phthalates have lower VI's then the non-aromatic esters.

Oil	Chemical name		0% PB		1% PB			5% PB		
		40°C	100°C	VI	40°C	100°C	VI	40°C	100°C	VI
#A	2-ethyl hexyl stearate	10.0	3.0	171	19.3	5.7	271	491.0	122.5	337
#B	Di-octyl adipate	7.0	2.3	157	15.3	4.5	235	41.6	11.0	270
#C	Di-tridecyl adipate	27.0	5.4	139	42.3	8.8	194	221.4	39.4	231
#D	C6, C7, C8 polyol ester	25.0	5.0	129	N/S	N/S		N/S	N/S	
#E	trimethylopropane tricaprylate	20.	4.0	92	38.2	8.5	209	142.2	28.5	240
#F	Tri-isodecyl trimellitate	124.0	11.9	81	222.5	20.3	106	3796.	315.6	234
#G	TriOctyl trimellitate	88.3	9.4	78	123.0	14.1	114	N/S	N/S	
#H	Di-isodecyl phthalate	38.0	5.4	62	64.0	9.2	121	501.0	62.5	198

Table 7 : Viscosity data of synthetic esters with 1% and 5% PB

Table 8 : Viscosity data of synthetic esters with 1% and 5% SBR

Oil	Chemical name		0% SBR 1% SBR			5% SBR				
		40°C	100°C	VI	40°C	100°C	VI	40°C	100°C	VI
#A	2-ethyl hexyl stearate	10.0	3.0	171	19.8	5.7	261	651.2	125.6	294
#B	Di-octyl adipate	6.7	2.3	157	12.5	3.6	189	55.3	13.9	263
#C	Di-tridecyl adipate	27.0	5.4	139	32.7	6.4	152	61.4	10.9	171
#D	C6, C7, C8 polyol ester	25.0	5.0	129	N/S	N/S		N/S	N/S	
#E	trimethylopropane tricaprylate	20.	4.0	92	24.2	6.5	245	147.3	26.2	215
#F	Tri-isodecyl trimellitate	124.	11.9	81	177.7	17.4	106	921.2	75.4	157
#G	TriOctyl trimellitate	88.3	9.4	78	121.9	13.3	104	N/S	N/S	
#H	Di-isodecyl phthalate	38.0	5.4	62	70.2	9.4	111	581.0	54.0	155

Oil	Chemical name		0% AD		1% AD			5% AD		
		40°C	100°C	VI	40°C	100°C	VI	40°C	100°C	VI
#A	2-ethyl hexyl stearate	10.0	3.0	171	14.2	4.6	283	66.5	19.6	316
#B	Di-octyl adipate	7.0	2.3	157	14.5	4.1	204	103.0	21.6	238
#C	Di-tridecyl adipate	27	5.4	139	46.6	8.2	151	286.7	39.0	189
#D	C6, C7, C8 polyol ester	2.5	5.0	129	44.3	7.8	147	304.5	58.0	259
#E	trimethylopropane tricaprylate	20	4	92	33.7	7.4	195	268.2	48.4	242
#F	Tri-isodecyl trimellitate	124	11.9	81	241.2	19.8	94	1488.	97.2	147
#G	TriOctyl trimellitate	88.3	9.4	78	149.3	15.9	111	1147.	82.8	149
#H	Di-isodecyl phthalate	38	5.4	62	81.7	9.5	92	543.5	48.4	146

Table 9 : Viscosity data of synthetic esters with 1% and 5% AD

		PB			SBR			AD		
		40°C	100°C	VI	40°C	100°C	VI	40°C	100°C	VI
#	Soybean oil	827.7	150.6	294	N/S	N/S		115.5	21.7	216
#J	Canola oil	2069.	341.4	326	508	88.7	262	327	49.2	214
#K	Castor oil	N/S	N/S		N/S	N/S		410.7	29.9	102

Note: The EPM polymer (not included) was not soluble in any vegetable oil

In Table 10 natural esters were used in a solubility study with the polymers PB, SBR, and AD at 5% concentration. As was discussed previously, castor oils highly polar structure precludes polymers that are much less polar to dissolve. AD copolymer dissolves but does not give a high VI solution. From Table 1, castor oil itself has a low VI of 51.

Conclusions

Natural vegetable oils are predominantly of *cis* configuration around the double bond. In three dimensions this means that a plane cutting through the double bond would show the attached groups to be on the same side of the plane. The thermodynamically favored configuration as in synthetically manufactured ester is trans where the groups would be on opposite sides of the plane. Most normal synthetic esters that are manufactured are of mostly trans configuration. Polybutadiene where the

double bonds are a minimum of 40% in the cis conformation is compatible with vegetable oils.

The ester structure and unsaturation (double bonds) are the functional groups that make vegetable oil readily biodegradable. These functional groups also account for why PB and AD polymers are soluble in vegetable oils and EPM polymers are not.

Of the synthetic ester base fluids studied, 2-ethylhexyl stearate and di-octyl adipate give polymer solutions having the highest VI for a given polymer.

Of the vegetable ester base fluids studied soybean oil and canola oil are effective at solubilizing PB and AD polymers and giving high VI blends. SBR was found to be only minimally soluble therefore the viscosity could not be determined. Castor oil is not effective at solubilizing polymers except AD and then only providing a nominal VI.

EPM polymers are not soluble in vegetable oils and only partially soluble in a few synthetic esters such as 2-ethylhexyl stearate and tri-isodecyl trimellitate as shown in Table 5.

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UNDERSTANDING THE INTRICACIES OF CAM GEAR-SPLIT GEAR LUBRICATION IN DIESEL-ELECTRIC LOCOMOTIVES

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Abstract

In diesel-electric locomotive, the camshaft is driven from the crankshaft by the gears and the engines oil is additionally required to lubricate these cam gear/ split gear. This paper attempts to understand the intricacies of the cam gear lubrication and the relationship of engine oil property indices to match such lubrication requirements. Effects of the design attributes emanating out of the constant up-gradation of locomotives designs and the stringent requirements of the operational dynamics has been attempted to be studied through a detailed analyses of cam gear/split gear failure case study. This paper brings forth the attributes of the railroad engine oil to address such complexities of engine and gear lubrication requirement of diesel-electric locomotives.

Introduction

The main and critical part of diesel locomotive lubrication are piston ring / cylinder lubrication on account of high pressure, high contact area, ever changing angularity, inertia, reciprocating action, changes in directions coupled with extremely high temperature and varying speeds. This necessitates oil to have sufficient viscosity and load carrying property even under such extreme conditions. This is apart from expectation from the oil to protect against chemical wear, to keep the engine clean, to keep contaminants in finely suspended form so that they do not interfere in lubrication, excellent oxidation property and thermal stability for effective control on viscosity. The effect of railroad oils in piston ring / cylinder lubrication has, earlier, been reported by us^[1]. Same engine oil is also required to lubricate various other part such as connecting rods, small / large end bearings, main bearings, cam shaft bearings, rocker arms bearings, value guides, timing gears and cam gears etc. Cam gears operate under lower temperatures but may be at varying pressures. This paper brings forth the attributes of the railroad engine oil to address the complexities of engine and gear lubrication requirement of diesel-electric locomotives and elaborates the oil property indices in obviating failure causes.

Prognosis

The study was initiated due to reported rise in failure of mainly split gears and cams in a section of the total population of 3100 hp locomotives of a given make at given locations. Stepwise analyses, were, therefore undertaken to examine the dimensions of operational matrix viz., the lubricant, the engine design changes and the operational stress. In this process the complexities of the lubrications and steps to obviate the cam gear failure have been formulated.

Railroad Oils : Issues

Although the total population of the 3100 hp locomotives were not affected, yet it was pragmatic to examine the multi-grade lubricating fluid as the first dimension of study. In the diesel-electric locomotives, the engine oils are additionally required to lubricate the cam gear/split gear. The camshaft is driven by the crankshaft through split gear and cam gear arrangement. Hence the design of the railroad oils both with respect to the detergent inhibitors and the viscosity modifiers is extremely important^[2-3].

Hence a Generation V Railroad Oil RREO-T of SAE 20W-40 viscosity grade, utilizing a combination of high performance DI as performance enabler and a 24 SSI VM as robust micro-structure provider, has been compared to a mono-grade reference oil RREO-R. The viscosity of the mono- and multi-grade railroad oils RREO-R and RREO-T do not show any significant difference at the reported temperatures of 80°C. The multi-grade oil, additionally, meets the



Fig.1 Comparative Viscosity Traces for Railroad Oils under Mechanical Shearing Stress

stringent requirements of 10.8 cP min of GE sheer stability test, thereby ensuring its capability to maintain its structural integrity even under stressed shear conditions. RREO-T has been found to remain in stayin grade even after 90 pass shear stabilty test by a margin of 18 percent. Comparative traces of viscosity determined at different temperatures for RREO-T for both fresh oil and sheared oil did not show any significant difference with respective to RREO-R fresh oil samples. Viscosity traces at different temperatures for RREO-R diluted by 5% with HSD and that of the heared multigrade RREO-T, also subjected to same level of fuel dilution compared well. This would mean that the multi-grade railroad engine oil would offer similar viscosity attributes as of the mono-grade engine oils for the temperature range of cam gear working.

Identical wear scar diameter and weld load at nearseizure load for both the test and reference oils indicate similar antiwear and EP properties for the product [table 1], and indicate the equivalent efficacy of RREO-T in countering any aspect of scuffing failure which is an instantaneous failure where the gear flanks are welded together under pressure and temperature of tooth contact without any protecting layer to prevent metal-to-metal contact. Higher FZG rating of





RREO-T is also indicative of better AW-EP associated with the multigrade oil. Infact, these values are in line with API GL-4 requirements of the gear oils for spur gear application. This confirms identical tribological features for the two categories of the railroad lubricant.

Table 1 : Comparative Analyses of Antiwear-EP Parameters

S.No.	Parameter	Monograde	Multigrade
1.	Lube Oil	RREO-REF	RREO-TEST
2.	Wear Scar Dia,mm 40 kg 60 kg	0.40 0.80	0.40 0.80
3.	Weld Load, kg	280	280
4.	FZG Stage	9	10

Engine Designs : Issues

It appears that pitting might have started due to increased load on the gears due to increased power generation with the same engine [3100 hp] keeping the bore and stoke length similar to the earlier designs [2600 hp]. Increase the plunger diameter from 15 mm, 17 mm for increased fuel intake for higher power might have increased the load on the cam lobe and cam/ split gear combination. An additional retainer spring was provided on the FIP for effective retraction and this might have added load on the gears. An increase in overlap in inlet and exhaust opening from 123° to 140° to allow more air intake to match the higher fuel input to higher hp could also have added onto the load on the gears. Inadequate hardness of the gears and/or lack of case carburizing could have added onto the load on the gears.

Operational Dynamics

Since the fatigue life expressed as millions of stress cycles before failure is inversely proportional to the cube of the stress, loading due to above reasons will have an impact on the life of the components which may reduce the gear life considerably. The extended POH will inadvertently allow the gear, which otherwise would have been replaced after due inspection in the original POH, to continue in operation at an added stress and thereby causing its failure. Added to this, improper lubrication supply system at the cam/split gear contact lead to starvation at this contact point.

Discussions

Mono-grade railroad engine oils were formulated with MVI base oils with VI 70-75 during the earlier phase of dieselization. Monograde railroad engine oils shifted from MVI to HVI base oils due to availability constraints. This resulted in a shift of Viscosity Index from 70-75 to 90-95. Higher VI of HVI base oils would result in comparatively lower viscosity at low temperature. Similar trend followed in India also. In view of nonreporting of any component failures like cam gears/ split gears, cam lobes, cam bushes etc. it could be assumed that the design features of 2600 HP locos could accommodate the shift to lower viscosity at lower temperatures. Multigrade railroad engine oils used VMs as additional lube oil component resulting in increase in VI in excess of 100. This would result in still lowering of the viscosity at low temperatures. However the inclusion of viscosity measurements addressing the shearing features and design of the lubricant for similar viscosity profile under all perceivable operational variations ensure adaptibility of RREO-T, the test oil to the engine designs.

Inferences

 Stable viscosity of the Generation V Multigrade Railroad Oil RREO-TEST, while maintaining structural integrity over the entire range of the operation under varying operating conditions, indicate effective lubrication of not only the engine components but also the cam gear and split gear components as well.

- Revisiting our earlier work^[3] of heuristic selection of an appropriate viscosity modifier has also resulted in differentiating the candidate railroad lubricant RREO-TEST for its structural integrity.
- The domain of wear control has been addressed adequately. While the adhesive wear control is ensured through stabilized viscosity over the entire operation range, the gear lubrication is ensured by bench marking for AW-EP properties.
- While an optimum design approach entail looking at the possibility of increasing the width of the gear teeth for decreasing the contact stresses on the gears and/or case carburizing with increased hardness, a localized modification for ensuring supply oil at the point of the teeth meshing in a the direction of the oil squeeze to avoid starvation of the oil at the contact zone can provide a pragmatic solution for effective lubrication of cam gear–split gear in high horsepower diesel electric locomotives.

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REAL LIFE PERFORMANCE STUDY OF DIFFERENT METAL SOAP THICKENED GREASES IN DRI KILN SEAL APPLICATION

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Abstract

The first Coal based unit was since built in for manufacture of Direct Reduced Iron (DRI) in India; the industry has grown rapidly to a developed sector over a period of last 10 years. Lubricants are put to reduce friction and / or often carry out alien particles too. In DRI manufacturing, lubricant has to face the bumpy conditions of soaring temperatures and dusty environment and unlike other consumables of a machine, lubricant have no physical dimensions to describe it on paper that eases the job of evaluation on prima facie. It is best assessed through real life performance of lubricants. This paper is aimed at bringing about the mechanism how different metal soap thickened greases face effectively the challenges of leakage of thermal energy through kiln slip seals and plays contributory role in cost saving through demonstrating its functional role of providing for slip seal segment application in DRI kiln.

Introduction

India is 5th largest iron ore reserve base & 4th largest coal reserve base in the world that worked as the catalyst to steel growth and today, India has also emerged as the 5th largest producer of crude steel in the world. Limited reserves of coking coal, difficult availability of scrap & their unpredictable prices have been the main driver for growth of manufacture of DRI or Sponge Iron as the developed sector in steel industry. Today India continues to be the largest producer of Sponge Iron and accounts for over 16% of world total DRI production.

Abundance of non-coking coal & good grade iron ore in India and limited natural gas resource has predominantly made Coal based technology edges over gas based technology. DRI coal based technology or often called "Kiln Process", reduction is conducted in a refractory lined rotary kiln which is suitably supported in two-four support stations. Amongst, steel manufacturing is the highest consumer of lubricants and still recent past, lack of awareness of role of lubricants, price continues to be the preferred criterion for procurement of lubricants.

The kiln operates in two high temperature zones – pre-heat zone (800-900 °C) and metallization zone (1000-1050 °C). The kiln waste gases so generated at about 850 – 900 °C, is then passed through a waste heat recovery boiler (WHRB) where sensible heat of flue gases is extracted and high pressure steam is generated. The high pressure steam thus run turbine to produce electricity. It is estimated that waste heat recovery from a 100 tpd kiln is sufficient to run a generating unit of a 2.2 MW power plant. Present field investigation is aimed at selection of a suitable high temperature grease to minimize the leakage loss of thermal energy through slip seal in DRI kiln.

Rotary Kiln & Slip Seal

Rotary kiln, generally inclined is held with support stations and rotated around its longitudinal central axis by torque transmission through girth gear – pinion assembly. Inlet & outlet cone of the kiln shell are provided with slip seals to minimize / eliminate leakage of hot flue gases & dust due to continual blow of CB air from opposite end centrally to inlet direction. The skin temperature of the kiln shell around inlet & outlet & near the slip seals ranges from 170 0C to 270 0C. The seal mating faces are not only subjected to hot flue gas environment, they also face a highly coal & ore dust environment. The paper is aimed at understanding mechanism of sealing by organic soap thickened grease vis-à-vis metal & non soap thickened grease through real life performance studies and addressing the pressing need to meet challenges of high temperature sealing of hot gas discharge to the environment by use of organic soap thickened grease.

Approach

Beginning last decade, construction of 50 tpd and 100 tpd module DRI plants picked up momentum and over the year they have grown to a sizable numbers. Detail survey was carried out in early 2000 for uses of different types of lubricants as per OE recommendation and consumptions in 50 tpd / 100 tpd & 300 tpd modules in **Barbil, Chhatisgarh and Jharkhand**. Also, the tribological challenges that the slip seal undergoes were carefully studied.

Li-Complex soap thickened grease are being predominantly used in modules 50 tpd & 100 tpd and in modules 300 tpd & above, clay based grease is being commonly used. Each of the above modules was closely monitored & performance of lubricants was inspected during every campaign.

Parameter Investigation

Unlike other tribological components, friction mechanism matrix is observed to be different in slip seal and is subjected to preferably sliding force. Temperature gradient along the length of the kiln shell causes floating up & down of the kiln shell along the axis to nearly 30 -40 mm swing. This movement creates the opening between the seal mating surfaces and also intermittently transmit load to the seal face. Often un-burnt grease drips off through the opening so created, allowing the hot flue gases to come out. Furthermore, deleterious effects of oil bleed & evaporation occurs at this temperature and results in residue of abrasive cake being deposited on the mating surfaces that attributes to wear / pitting. At times, grease nozzles are heavily choked with solid build ups / cake formations and require replacement during maintenance / campaign.

Conceptualization & Recommendation

The performance details of metal soap thickened grease and clay base grease were recorded along with average consumptions. Key areas of concerns were carefully analyzed and identified the causes and remedies. The ash & soap content of *Licomplex* soap thickened & *clay base* grease of field samples were estimated.

Thickener / Filler	wt % Soap Content	Estd. Wt% Ash Content
Li-complex	12-16 %	1-1.5 %
Clay	9-11 %	8 - 11 %

Failure of any soap thickened grease at high temperature involves a complex of melting and bleed and most mineral oil base complex will perform to about 160 – 170 °C. The soap particles in such cases are bonded together by some chemical bonding and also by some physical force like Van der Waals forces. They form a fibrous network and a very little, **combines with base oil**. When used for extended period of time at elevated temperature, such grease bleeds base oil to evaporate and the soap gets melted out & over a shorter period of time, forms solid abrasive cake.

Thickener in clay base grease matrix is different from that of soap thickened grease. Clay forms a gel like structural network that differs from fibrous structure of soap thickened greases. Base fluid is more tightly held in gel structure due to more polar nature of clay like thickener and forms some *degree of layer lattice*. Under intermittent impact load & prolong exposure to elevated temperature, oil bleed starts to lubricate the component and over a period of time, oil evaporate out leaving non-melting thickener in the application point forms a hard cake causing a filling in the grease nipple near the seal & shortens the seal life with abrasive wear.

With above finding on structural characteristics and performance mechanism, it is evident that none of the thickeners is capable of effectively addressing the dire application requirement.

Based on the above investigation and findings, it transpires that the critical / stringent nature of the seal lubrication calls for a noble thickener which would take care of the short coming of above thickeners. The target thickeners as conceptualized should exhibit underlined characteristics.

- 1. Very High Dropping Point (320 C plus)
- 2. Superior Adherence to the Seal Surface

- 3. Good Pumpability
- 4. Sufficient Load Carrying & Anti-wear properties in sliding applications
- 5. Superior Corrosion Protection
- 6. Reversible Characteristics with Temperature and
- 7. Thickener with Inherent Lubrication Characteristics

The above sequence of findings delved into selection of a organic base soap thickened grease that would meet all the above requirements. Over based Calcium Sulphonate soap micelle are of water like platelet structure and unlike soap base or clay base thickener, soap micelle layers are bonded with electro static forces of attraction that enables the soap fibre to perform boundary lubrication even in absence of base oil. Then it works more like a solid lubricant having lattice structure. This unique characteristic of the sulphonate thickener also ensures continual lubrication and sealing against leakage of hot flue gas through the openings even after the base oil being evaporated over a period of long exposure to high temperature. The performance of the formulated grease is compared with the commonly used slip seal grease in different module having average campaign period indicated in Table: A, is summarized as under.

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Modulel	Avg. Campaign Period
50 tpd	70 days
100 tpd	90 days
300 tpd & above	180 days

Table-1 Module : 50 tpd

Average Cnsumptions per month, in kgs								
KilnKiln out /CoolerTotalInletCoolerOutlet(kgs)								
Li-complex	155	295	100	550				
Clay Base	130	195	75	400				
Organic Base	Organic Base 70 110 35 215							

Table-2 Module : 100 tpd

Average Cnsumptions per month, in kgs						
	Kiln Inlet	Kiln out / Cooler	Cooler Outlet	Total (kgs)		
Li-complex	165	495	145	805		
Clay Base	130	385	95	610		
Organic Base	90	210	60	360		

Table-3 Module : 300 / 350 tpd

Average Cnsumptions per month, in kgs						
	Kiln Inlet	Kiln out / Cooler	Cooler Outlet	Total (kgs)		
Li-complex	205	840	170	1215		
Clay Base	165	720	130	1015		
Organic Base	130	560	85	775		

Conclusion

The effective performance in lubrication of slip seal with Organic base Soap (Over based Calcium Sulphonate) thickened Grease out performs other conventional soap / clay thickened grease available in the name of High Temperature greases. Lubrication mechanism of Ca-Sulphonate grease is provided by actually forming lubricating solids on evaporation of base oil & contributes to true boundary layer lubrication without base oil. It demonstrate exceptional high temperature resistant and because of its high water Spray off characteristics & fibrous texture, it stays in even gap between the seal faces are created due to floating of kiln shell and thereby addresses the pressing need to meet the challenges to seal out thermal leakage & hot gas to the environment.

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