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Quantitative evaluation of tackiness in polymer-oil solutions using modified probe tack method

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Tackifiers are high molecular weight polymers dissolved in oil that contribute tack to formulated lubricating oils. One problem that has emerged in the industry is the inability to measure the degree of tackiness in polymer-oil solutions. Several methods have been put forth to quantify tack including string length and the rotating disk method. The degree of tackiness is related to the amount of internal energy or cohesive energy of the fluid. A simple, inexpensive method was developed to quantify the tackiness of an oil solution by measuring the force required to pull a known mass from the solution. The force was correlated with other fluid properties including viscosity, contact angle, and capillary height. A linear relationship has been shown between string length and pull-off force and between viscosity and pull-off force.

KEYWORDS: Tackifier, Friction, Adhesion, Probe Tack

INTRODUCTION

Tackifiers are important in the lubrication of many processes. They may be used to provide adherence in way oils and chain lubricants, stringiness to greases, and anti-mist properties to metalworking fluids (1). Tackifiers are typically polymeric additives that impart tack or stringiness to a lubricant. Tack is considered a composite property; the ability of a material to function as a tackifier is determined by its cohesive and adhesive forces, viscosity and other factors such as the molecular weight and concentration of the polymeric additives used in the formulation of such additives. Tackifiers have high cohesive and adhesive forces. High cohesive forces allow the tackifier to remain together as a single mass while high adhesive forces cause the tackifier to remain on the surfaces to be lubricated (2).

Due to the many factors that influence tack, it has been difficult to quantitatively determine how tacky a particular solution is (3). Several methods have been developed which are able to measure some, but not all, of the relevant driving forces of tackiness.

Current Test Methods

Test methods for measuring tackiness are generally most suited to the adhesives market including pressure sensitive adhesive tapes and adhesive coatings. Several organizations provide test standards to the adhesives market including the American Society of Testing and Materials (ASTM), the Pressure Sensitive Tape Council (PSTC), the European Association of the Self-Adhesive Labelling Industry (FINAT), the British Standards Institution (BSI) and the Tag and Label Manufactures Institute (TLMI). The test methods currently used for the pressure sensitive tapes market include probe tack (ASTM D2979), loop tack (BS EN 1719, TLMI LIB 1/2), rolling ball tack (ASTM D3121, BS EN 1721) as well as tests for double-sided tapes (BS 7116) (4).

These methods use a technique where the adhesive is coated onto a solid support or applied on a tape and then placed in contact with a second surface. The force required to separate the surfaces is then measured as an indication of adhesiveness or tackiness. These tests are useful for comparing adhesives to one another but are not suitable for use in the lubricant tackifier industry. This is due to the fact that these tests measure pressure sensitive tackiness rather than adhesiveness as it relates to cling or adherence of an oil solution to a metal part. Cohesion is also an important property that is generally not assessed using test methods designed for the adhesives industry. Cohesion provides the string-forming ability of a tackifier solution due to the interaction of the individual polymer molecules of the solution.

Further test methods have been developed specifically for use in the lubricant tackifier industry. One such method is the Brookfield spindle method. This method determines the amount of oil left on the surface of a Brookfield spindle. The spindle is submerged in the tackifier in oil solution then spun for 10 minutes at a high rpm and then the weight of the spindle and adhered tackifier solution is recorded. The amount of tackifier left on the spindle is an indicator of its ability to adhere to a metal surface. Depending upon the concentration, base oil properties and the temperature the effectiveness of a tackifier can be assessed relative to each other (5). Another test is the open (or ductless) siphon test method. In this test, a capillary tube attached to a vacuum pump is used to withdraw a dilute tackifier solution from a graduated cylinder. The tackiness is quantified by the maximum length of the polymer string measured before the string breaks (1). Neither of these tests has been standardized by ASTM or any testing body.

In this study, the pressure sensitive tack of adhesives using an inverted probe machine (ASTM D2979) method used in the adhesives industry is modified to make this test more suitable for the lubricant industry. In the standard test the force required to remove the adhesive from a solid surface shortly after it has been in contact after a short period of time is measured using an inverted probe machine. The adhesive is removed from the solid surface at a constant rate and the maximum force required to break the adhesive bond is measured. A further modification of the test procedure is required because of differences in the rheological properties and the expected pull-off force (3). The standard ASTM test is also simplified in order to eliminate the need for expensive test equipment.

A test similar to the ASTM probe tack test has been used in greases to determine the pull-off force (6). The expected pull-off force in a grease is much higher than for a lubricant tackifier solution.

Adhesion and Cohesion

In many industrial applications the lubricating oil must not drip or form a mist when bearings or machine surfaces are in motion; the addition of a tackifier will decrease the tendency of a lubricant to do so. Oil mists have been associated with various health issues in plant workers so the impetus is to lower the misting of oils in the workplace (7). To alleviate oil mists, a tackifier can be added to the oil. Cohesion is determined by the attractive forces between the molecules of a substance that tends to hold the substance together. Materials with high cohesive energies are able to resist separation of the oil into separate small droplets thus the mist does not form (7). Adhesion is determined by the attractive forces between the molecules of a substance together.

Adding a tackifier to a lubricant package will tend to increase the cohesiveness and adhesiveness of the lubricant without substantially increasing its viscosity. The cohesive forces within a tackifier result in the string forming ability that is a key component of tackiness. Cohesion also drives the elastic nature of these materials. Adhesion is also increased when using a tackifier. Higher adhesiveness is required to make a lubricant stick to bearing surfaces at high speeds than at low speeds. At low speeds, greater

cohesiveness is required to keep the lubricant from being squeezed out from between the bearing surfaces (8).

Contact Angle

Cohesion and adhesion are important to the performance characteristics of tackifiers in the lubricant industry. One way to measure the relative strength of these two forces is by determining the contact angle.

Cohesive forces between molecules cause the surface of a liquid to contract to the smallest possible surface area. This general effect is called surface tension. Molecules on the surface are pulled inward by cohesive forces, reducing the surface area. Molecules inside the liquid are surrounded by other liquid molecules on all sides and therefore experience zero net force (9).

Interfacial tension is proportional to the strength of the cohesive force, which varies with the type of liquid and the surface that it is in contact with. Interfacial tension, γ , is defined to be the force, *F*, per unit length, *L*, exerted by a stretched liquid membrane, as shown in Equation 1.

$$\gamma = \frac{F}{L} \tag{1}$$

The contact angle, θ , of a droplet is defined as the angle within the droplet between a tangent line drawn on the droplet surface at the solid-liquid interface and the solid surface, as shown in Figure 1. A θ of less than 90° indicates wetting behavior while a θ of greater than 90° indicates non-wetting behavior.



Figure 1: Contact angle of a liquid droplet on a solid surface.

The relative strengths of the cohesive and adhesive forces of the droplet determine the shape of the droplet. A material that is more cohesive than adhesive will show more non-wetting behavior, i.e. the contact angle will be larger. The forces between the molecules of the drop are stronger than the forces between the molecule and the surface which results in droplet molecules that are more stable when interacting with other droplet molecules rather than the surface molecules (10).

Capillary Action and Surface Tension

The adhesiveness of a tackifier is related to the surface tension which can be determined from the contact angle and capillary height. Liquids in contact with confined spaces such as small pores will fill these spaces without an external force, even against the force of gravity. The cohesive forces between the molecules of the fluid and the adhesive forces between the fluid molecules and surface molecules create the driving pressure that will force the fluid into the capillary space (11).

The Lucas-Washburn equation describes the rate of fluid flow through a cylindrical capillary of radius *r* as a function of the driving pressure. Making the assumptions that flow is laminar viscous and incompressible and that the capillary is much longer than it is wide, Washburn applies Poiseuille's Law for the pressure drop in a fluid flowing through a cylinder to derive Equation 2

$$\frac{dl}{dt} = \frac{\sum P}{8\eta l} \left(r^2 + 4\epsilon r \right) \tag{2}$$

where η is viscosity and ΣP is the sum of atmospheric pressure (zero if the ends of the capillary are open), hydrostatic pressure, and capillary pressure. ϵ is the coefficient of slip, taken to be zero for a fully wettable surface (11). Capillary pressure is given by Equation 3

$$P_c = \frac{2\gamma\cos\theta}{r} \tag{3}$$

where γ is interfacial energy and θ is the solid-liquid contact angle.

If a capillary tube is placed vertically into a liquid capillary action will raise or suppress the liquid inside the tube depending on the materials at the interface. The effect depends on the relative strength of the cohesive and adhesive forces and, thus, the contact angle. If θ is less than 90°, then the fluid will be raised; if θ is greater than 90°, it will be suppressed.

In the cases of horizontal and vertical capillaries, where hydrostatic and atmospheric pressure are negligible, the surface tension σ for non-steady state conditions is given by Equation 4

$$\sigma = \frac{2h^2\mu t}{r\cos\theta} \tag{4}$$

where *h* is the height in the capillary, μ is the dynamic viscosity, *r* is the radius of the capillary tube, θ is the contact angle, and *t* is the time it takes the solution to rise in the capillary (12).

However, when evaluating polymer solutions some assumptions need to be made in regard to time. For long liquid rise times in a capillary tube the Lucas-Washburn equation is not the best method to determine the surface tension of a fluid as the equation predicts a continuous rise in height. In reality, the liquid height will eventually stop rising as an equilibrium is reached between the capillary force and the force of gravity (12).

Zhmud (13) derives an equation and solutions for different time intervals specifically over long time intervals. This equation was modified by the Lambert function to describe the behavior using an inverse exponential function. The modified equation results in an equilibrium height that a liquid will reach in a capillary tube under the force of gravity when solutions are considered at infinite time. The surface tension of the liquid can be calculated from steady state capillary height using Equation 5

$$\sigma = \frac{hr\rho g \sin \varphi}{2\cos \theta} \tag{5}$$

where ρ is the polymer solution density and ϕ is the inclination of the capillary tube from the horizontal plane.

EXPERIMENTAL METHODS

Tackifier solutions were prepared with a total polymer concentration of 3% (w/w). Solutions of an olefin copolymer (OCP), polybutadiene (PBR), natural rubber (NR) and polyisobutylenes (PIB) were used as shown in Table 1. Solutions with more than one component are listed with the major component first. The PIBs used have viscosity average molecular weights ranging from 1000 to 4000 kDa.

Solutions were prepared by dissolving polymer in the diluent at 95°C with low shear mixing to avoid shear degradation of the polymer.

	Polymer	Molecular Weight	Diluent Oil
А	OCP	Low	Group I Paraffinic
В	PBR	Med	Vegetable
С	PBR/NR	Med/High	Vegetable
D	PIB	Low	Group I Paraffinic
Е	PIB/PIB	Med/Low	Group I Paraffinic
F	PIB	Med	Group I Paraffinic
G	PIB	Med	Group III Paraffinic
Н	PIB	Med	Group I Paraffinic
Ι	PIB	High	Group I Paraffinic

Table 1: Properties of the 3% (w/w) polymer solutions prepared for use in this study.

Modified Probe Tack Test

A small dish having a radius of 7.3 cm was used to perform this test. The center of the dish had three raised ridges of about 1 mm height. A 50 gram hooked weight was placed on three small ledges at the bottom of the dish in order to minimize the capillary force generated when liquids are placed in confined spaces. The polymer test solution was added to the dish so that the weight was submerged to a depth of 3 mm. A hand-held spring scale was attached to the hook. A steady upward force was applied to the weight, normal to the surface of the liquid, over a 3 second period. The weight registering on the scale was recorded by a camera. The mass of the weight was subtracted from the weight registering on the scale. This yields the pull-off force required to remove the mass from the polymer solution. This operation was repeated 10 times for each polymer solution. The highest mass recorded on the scale is recorded just before the weight is lifted from the solution. From the maximum mass the pull-off force, *F*, can be calculated using Equation 8

$$F = \frac{m}{a} \tag{8}$$

where *m* is the maximum mass recorded on the spring scale and *a* is acceleration. In this case acceleration is taken to be only the acceleration due to gravity as the weight is stationary until enough force is applied to remove it from the tackifier solution.

Capillary Test

A borosilicate glass capillary tube having a radius of 0.35 mm was used for the measurement of capillary height of the polymer solutions. The tubes were lowered vertically into a polymer solution to a depth of one mm and the distance that the solution traveled up the tube was measured from the surface of the test solution. A time of 600 seconds was allowed to reach steady state.

Contact angle

Contact angles of three of the polymer solutions on borosilicate glass were measured using a contactangle goniometer.

RESULTS

Modified Probe Tack Test

Based on the results of this study, it can be shown that the pull-off force follows the same trend as the string lengths as measured by the ductless siphon method. Both tests provide a measure of the cohesive energy of the tackifier solution. Materials with high cohesive energies are able to resist separation of the material into separate droplets which would result in their removal from the surfaces to be lubricated.

In the modified probe tack test, the cohesive energy of the tackifier resists the separation of the layers of fluid between the bottom of the weight and the dish. The higher the cohesive force between the layers of fluid within the tackifier solution, the more force must be applied to separate them, resulting in a higher pull-off force. Another point of separation that could occur during pull-off would be the breaking of the adhesive forces between the tackifier solution and the weight or the dish. This is not observed to be the case; there is a film of tackifier that covers the bottom of the weight after it has been removed. Further, strings of tackifier solution form as the weight is lifted from the dish. As shown in previous studies, an increase in molecular weight of the polymer improves its performance as a tackifier. This has been confirmed in this study where an increase in molecular weight corresponds to a higher pull-off force. This also correlates to an increase in tackifier performance as measured by the ductless siphon test, as shown in Figure 2.

The string formed during the ductless siphon test is held together via the cohesive forces within the string. As a result of increased cohesive force a longer string can be formed as the material is able to hold itself together to an increased height.



Figure 2: Pull-off force from the modified probe tack test and string length from the ductless siphon test correlate. An increase in polymer molecular weight for PIB samples (E-I) also correlates to improved tackifier performance. Values for pull-off force were averaged and the standard deviation is shown.



Figure 3: Pull-off force from the modified probe tack test and viscosity show a correlation as both properties are dependent on the cohesive forces within the tackifier solution.

It has also been determined that the pull-off force follows the same trend as the viscosity, as shown in Figure 3. Viscosity is another parameter that determines how well a tackifier will perform. Viscosity is determined by several factors. In polymer solutions, the large polymer materials must untangle and move past on anther in order for the fluid to flow.

Another important factor is the cohesive force between the molecules themselves. For one molecular layer to flow past another, the cohesive force between those molecules must be overcome. As a result, the layer in motion will experience a drag force from the next layer which will resist flow. Increasing the cohesive forces will result in higher drag forces, i.e. more resistance to flow and higher viscosity.

Capillary Test

Based on the data obtained from the capillary test,

Table **2**, it can be shown that the calculated surface tension values show an inverse correlation to both the string length and the pull-off force of the polymer solutions. The capillary height is dependent on the adhesive strength of the material. As a material is better able to adhere to the surface of the capillary, the higher it will be able to rise in the tube against the force of gravity.

Tackifiers require some adhesive strength, as well as high cohesive strength, in order to stay in place during lubrication. The capillary test is a measure of adhesive strength rather than cohesive strength as the modified probe tack test and ductless siphon tests are. As the adhesive strength of the material increases, the surface tension increases, but the cohesive force decreases. There is a trade-off between increasing cohesive forces and decreasing adhesive forces as shown by the inverse correlation between the pull-off force and the surface tension calculated from the data obtained using the capillary test.

	Height (mm)	Density (22°C, kg/m³)	Contact Angle (°)	Dynamic Viscosity (100°C, cP)	Surface Tension* (N/m)
А	15	857	24.4	137.3	0.024
В	15	898		130.2	
С	16	922		145.4	
D	12	860		455.5	
Е	10	846		1411	
F	8	857	33.7	1971	0.014
G	8	830		857.8	
Н	7	864		2483	
Ι	6	845	41.0	3925	0.012

Table 2: Experimental data obtained from the capillary test including steady state capillary height and the calculated surface tension values.

*Values calculated using Equation 5.

The capillary test shows that as the surface tension increases, i.e. the adhesive forces also increase, the solutions are becoming less effective tackifiers. In order for a tackifier to be effective it must stay in place on the part surface and it must also have high cohesive energy in order for the tackifier to not be removed easily. A balance of adhesiveness and cohesiveness is required for the best performance of a tackifier.

CONCLUSIONS

A correlation exists between the pull-off force and string length as measured by the ductless siphon test of a tackifier solution. There is also a correlation between the pull-off force and the solution viscosity. Both the string length and viscosity of a tackifier solution are dependent on the cohesiveness of the material. Cohesiveness is partly responsible for the property of a lubricant known as tack. Another property that determines how well a tackifier performs is the adhesiveness of the solution. The capillary height of a tackifier solution is related to its adhesiveness. An inverse relationship between the adhesiveness as determined by the capillary test and the cohesiveness as determined by the probe tack test of a tackifier solution has been demonstrated.

Tack is a composite property and therefore must be measured indirectly. Multiple tests are necessary to understand how well a tackifier will perform as a lubricant additive. The pull-off test and the ductless siphon test quantify only a portion of tackifier behavior, the cohesiveness. The addition of the capillary test allows an understanding of another important property of a tackifier, the adhesiveness.

The pull-off and capillary test used in this study are relatively quick and simple to perform and require minimal equipment. Potential tackifiers can be quantitatively evaluated and judgments can be made about their performance. Based on the results of this study, a potential tackifier should have a high pull-off force and a low capillary height. Combined with previous tests such as the ductless siphon method and knowledge of the polymer molecular weight, a tackifier solution can be developed and evaluated more readily.

A similar method to determine pull off force in grease using expensive equipment was previously developed. Further work using the simplified probe tack method developed in this paper will be performed to determine its suitability for the characterization of tackiness in grease.

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A Perspective on Sustainability

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Abstract

Over the last several years, *sustainability* has become an industry buzz-word used to describe everything from bio-based products to renewable energy production, from recycling schemes to improving health and human welfare through building schools and hospitals. Coupled with this broad usage, comes an equally broad lack of clear understanding of sustainability; what it means and what is does not mean. The word itself is derived from the Latin 'sus-tinere', which translates as "to hold up or uphold", for example to hold up (sustain) future generations through today's activities. The currently accepted definition of sustainability was born of the Brundtland Commission in 1987: "...sustainability relates to any activity that meets the needs of the present, without compromising or impacting the ability of future generations to meet their own needs into the future¹". This definition was further clarified at the 2005 World Summit on Social Development where sustainability was shown to rest on three pillars: Economy, Society, and Environmental². Reconciling the impacts of all activities on these three pillars is necessary for an activity to be sustainable.

How do the concepts of sustainability relate to the lubricants and grease industry? Can a lubricant or grease, or the activities of a grease manufacturer or user, be considered sustainable? Is it possible to balance the three pillars of Economy, Society, and Environmental in the context of greases?

Sustainability – A definition

Dictionaries define sustainability in many different ways:

"The ability to be sustained, supported, upheld, or confirmed"	
	Dictionary.com
"Able to be used without being completely used up or destroyed	d"
	Merriam-Webster.com
"The property of being sustained, capable of being maintained"	
	Webster-Dictionary.com
"Exploiting natural resources without destroying the ecological	balance of an area"
	BING Distionary.com
"A process or state that can be maintained at a defined level fo	r as long as is wanted" <i>Wikipedia.org</i>

This lack of a common definition, coupled with varied company interpretations of what it means to be sustainable, fails to provide sufficient clarity and understanding of sustainability for both the producers of lubricants and greases, as well as the users.

Diving one level deeper, we find that in today's industrial ecosystem, sustainability has become a buzz-word used to describe the real or perceived benefits of a product, service, or activity, such as "*Product A*" has sustainability benefits. Used in this context, sustainability has been used to represent any number of benefits such as:

- ✓ Energy Efficiency
- ✓ Product Quality
- ✓ Waste Reduction / Recycling
- ✓ Regulatory Compliance
- ✓ Productivity
- ✓ Reliability

What does this mean?

How can this definition be used to represent the myriad of potential benefits, what can a customer expect from *Product A*, and what is a supplier expected to deliver, in the context of sustainability?

Sustainability has been depicted as the intersection of the three pillars of sustainability: Economy, Society, and Environmental. This is commonly visually illustrated as a Venn diagram as shown in *Figure 1 and Figure 2*. In this context, sustainability, and the act of being sustainable, is understood as the balance of Social, Environmental, and Economic, or alternatively Society, Environment, and Economy in a manner that allows the ever increasing needs of today to be met, without compromising the needs of future generations.



Only by balancing these needs, can a product, service, or activity be sustainable.

Balancing these needs is no easy accomplishment. According to *ExxonMobil Outlook for Energy: A View to* 2040^3 , by 2040 we should expect to see:

- 2 billion more people on the planet
- 130% larger global economy
- 35% increase in energy demand
- 90% growth in demand for electricity

All of these people will have needs similar to today: a need for food, a need for electricity, a need for housing, or a need for employment. These needs need to be met with an ever decreasing supply of raw materials. It is proposed that to be sustainable a product, service, or activity must balance these three pillars without preference. Only by balancing these needs, can a product, service, or activity be truly sustainable.

Sustainability in the Marketplace

Many firms no longer see a contradiction between 'doing good' and 'making a profit'; what is it that drives sustainability investments in the industrial marketplace?⁴ To some, it is the future. There is a natural alignment between sustainability goals and initiatives and global trends. Considering the referenced *ExxonMobil Outlook for Energy: A View to 2040*, population will grow by nearly 2 billion people, centered in the emerging economies of Asia Pacific. These people will require energy, for cooking, heating, home building, and employment to name a few. As the demand increases for energy, materials and energy will cost more, and become more difficult to find, procure, and deliver. Companies that can drive down costs by finding more efficient ways of using both materials and energy will likely have a competitive advantage. Balancing the evolving demand for materials and energy, today and tomorrow, with the needs of Social, Environment, and Economic is precisely what sustainability is about.

Companies around the world are making more investments in sustainability and sustainability messaging than ever before, even though it may be more difficult to gain recognition for doing so. *Figure 3* shows the year-on-year change in Sustainability Reality Score (+9.3 points) vs. Sustainability Perception Score (-2.7) over the period 2011 – 2012.

Year-over-year change in real and perceived corporate



Sustainability Perception Score (SPS) (Scale: 0 - 100)

Figure 3

These investments in sustainability are being realized in many ways.

- New industry reporting requirements and product labelling
- Increase in re-refining facilities
- Growth of bio-derived, bio-based product offer
- Customer expectations / requirements for measurable sustainability benefits becoming an integral part of RFCs and bid-process
- Increased focus on end-to-end energy efficiency, and resource management

Sustainability in Industrial Lubes and Greases

The question of sustainability as related to industrial lubricants is an interesting dichotomy. By the very nature of being based on crude oil as a raw material for both mineral based and synthetic based lubricants, lubricants appear to be the antithesis of sustainability. Crude oil is a finite resource that is fully consumed in the conversion process to a usable lubricant. The conversion process can be high energy intense, requiring additional energy beyond that needed to locate, produce, and transport crude. Conversely, without industrial lubricants, future economic growth would not be possible. Specific to greases, 76% of all greases produced in 2012⁵, nearly 725,000 metric tons, are based on castor oil / fatty acid derivatives and Lithium Hydroxide mono-hydrate, the former being a seed crop grown primarily in India, and the latter being a finite mineral found in primarily in Chile and China. Balancing Social, Environment, and Economic demands seems to be a challenge for the lubricants industry.

The resolution to this dichotomy comes in the form of energy and energy management. Industrial lubricants and greases play a key role in the effective management of energy. Lubrication by definition is the reduction of friction between two mating surfaces. Reducing friction in turn help to make better use of input energy, energy used to produce an outcome rather than overcome friction. From energy efficient lubricants to lubricants supporting renewable energy production, from long life or fill-for-life lubricants to lubricants offering excellent equipment protection, all help to more effectively manage energy, balancing the needs of Social, Environment, and Economic.

Energy and Energy Production

Renewable energy production is forecast to increase nearly 150% by 2040⁶, while electricity demand is forecast to increase 90% over the same period⁷. Industrial lubricants will play a central role in enabling this growth in a sustainable manner. Renewable power generation has a unique set of lubricant requirements given the harsh environmental conditions typical for these installations, development of lubricants addressing these needs can help provide sustainability benefits. Conventional fuel sources will continue to be the prime mover for over 65% of electrical power generation. Lubricants that enable the effective use of electrical power, through energy efficiency capabilities, can provide sustainability benefits.

Synthetic Lubricants

Synthetic lubricants offer unique performance benefits helping to extend equipment life, while lasting many times longer than conventional lubricants. Helping to maintain equipment in optimum operating condition can allow the equipment to perform as designed, in an un-rated capacity. The superb performance of synthetic lubricants at low and high temperatures helps to minimize energy usage and waste. Long operating life compared to conventional lubricants helps to reduce potential waste generation, and reduces the need to produce new lubricants as frequently.

Bio-Based & Bio-Derived Lubricants

Bio-lubes play an integral part in the overall scheme of sustainable lubrication. Sourced from plants or organisms that can replenish themselves, this class of lubricant seems poised to become the focus of sustainable lubrication. The benefit of being bio-derived must be balanced with the potential

negative impact of land usage, competition with food crops, high energy intensive conversion processes, and more narrow application range. Further development in this arena is needed to address the potential shortfalls.

Greases

It is unlikely that in the next 20-years a ready replacement for castor oil based fatty acids or Lithium Hydroxide can will be found, commercialized successfully, and accepted by the broad customer base. This does not preclude greases from having sustainability benefits. Continued research and development in the areas of energy efficiency, fill-for-life capability, improved structural stability, and broad operating ranges can help greases provide measurable sustainability benefits.

Summary

Sustainability is more than the word-of-the-day; it is a necessary part of meeting the needs of today, and the needs of tomorrow. Lubricants and greases play a necessary role in meeting these needs, enabling more efficient production of goods and services, more efficient use of available energy resources, and improved operation of equipment. Sustainability claims must be made based upon sound science, such as Life Cycle Analysis (LCA).

Balancing the competing priorities of Social, Environment, and Economic is a challenge, but one that can be achieved through continued research and development of new, better lubricants and greases, delivering ever higher levels of performance.

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⁴ The Conference Board. Conference KeyNotes, The 2013 Summit on Sustainability. June 2013.

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⁶ ExxonMobil. The Outlook for Energy: A View to 2040. www.exxonmobil.com/corporate/energy_outlook.aspx

⁷ ExxonMobil. The Outlook for Energy: A View to 2040. www.exxonmobil.com/corporate/energy_outlook.aspx

Lost your Bearings? Navigation Tools for High Temperature Bearing Grease Formulations

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Abstract

The tendency in all machines is to increase the power and thus the load going through a machine. This results in increased operating temperatures in bearings which impacts the efficiency and fatigue life of the bearing. In grease lubricated bearings, the nature of the torque increase and the effect of an increase in temperature on torque increases needs to be better understood in order to improve bearing efficiency and durability. The effect of temperature on torque increase has been measured in an Anton Paar rheometer modified to hold an FE9 bearing. Changes in torque with changes in temperature have been related to the stability of greases and their frictional properties.

Introduction

Lubricants and greases have to work in more severe conditions as machines are being built to transmit more power in an efficient manner. This increase in severity means that lubricants need to provide better protection against gear and bearing fatigue at higher temperatures. In the case of a oil lubrication, the stability of the base oil and the additives in the lubricants must be considered. When greases are used, additional factors, including the stability of the base grease, must be considered. By combining several existing techniques and the development of new techniques the integrity of greases at high temperatures can be determined. By improving the integrity of a grease formulation at high temperature, improvements in bearing fatigue life at these high temperatures has been achieved.

Experimental Details

A study was undertaken to investigate different aspects of a grease formulation and correlate them to the ability of that grease to protect bearings under operation at high temperature. The grease analysis was separated into three main categories. Each category represented a different aspect in understanding high temperature performance of grease.

Structural and Thermal Stability

Using rheology, differences in behaviour of greases under stress at different temperatures can be examined. Three greases were examined using this technique, first at 140 °C [Figure 1] then at 160 °C. The yield points were calculated and are shown in Table 1. As can be seen, the greases show significant differences in yield points depending on the temperature at which they are run. Grease 1 shows a minor drop in the amount of stress needed, while Grease 2 maintains its original structural stability even at the higher temperature. Grease 3, on the other hand, needs considerably less stress for the grease to lose its structural stability at the higher temperature.



Figure 1: Shear stress measured at 140 °C

Likewise, the % strain at the flow point (the point at which G' and G" are equal, or "crossover") [Figure 2] is a likely measure of how well the grease will maintain its ability to stay in the bearing under application conditions. The % strain at crossover was calculated for the same three greases for which yield points were calculated and these results are shown in Table 2.

	Yield Point (Pa)		
	140 °C	160 °C	
Grease 1	52.8	41.9	
Grease 2	18.3	18.6	
Grease 3	74.6	36.1	

Table 1



Figure 2: Measurement of flow point, or crossover

	%Strain @ Crossover (Gʻ = G")		
	140 °C	160 °C	
Grease 1	30.4% @ 525 Pa	24.9% @ 516 Pa	
Grease 2	27.2% @ 243 Pa	21.5% @ 270 Pa	
Grease 3	17.4% @ 896 Pa	20.1% @ 524 Pa	

Table 2

As can be seen from these results, there are wide differences in response, with Grease 1 and 2 showing little difference between measurements at 140 °C and 160 °C although the modulus values at crossover appear to be significantly different between the two greases. On the other hand, there is a relatively large change in modulus for Grease 3 when measured at 140 °C and 160 °C. This modulus measurement at the crossover point could be an indication of a grease's ability to "flow" into a contact area where metal-to-metal contact occurs. The modulus measurement is representative of the stiffness of the grease. Therefore, if the stiffness of the grease is high, there is less likelihood that the grease will move into the contact areas within a bearing to properly lubricate the metal surfaces.

Friction and wear

The second category used to study the high temperature performance of grease was studying the friction and wear reducing properties of grease in common tribological instruments.

Coefficients of friction were determined for a wide variety of greases using the MTM instrument. As an example, it can be seen from Figure 3, showing torque traces over time at 140 °C, that different greases can have widely different responses at the temperature of interest. A grease that has a high coefficient of friction in a bearing test or application will contribute to the failure of the bearing by increasing the amount of energy needed to turn the bearing. Many bearing tests used to determine the "life" of a grease formulation will use an increase in torque as a contributing factor in the determination that a bearing has failed.



Figure 3: MTM torque traces at 140 °C

The MTM-SLIM takes advantage of an additional "Space Layer Imaging Method" that uses interferometry to measure boundary film thickness. This allows for both visual and computer-generated observations of the tribolayer being generated by test greases as seen in Figure 4.



Figure 4: Tribolayer observations

The tribofilm composition can then be calculated and compared to examine the elemental composition of the layer put down by each grease

In an effort to judge the effect of wear, and therefore the potential role of antiwear additives, in bearing greases, the FAG FE-9 bearing test was used to evaluate a group of grease formulations. In these tests, individual bearings were stopped at approximately 24 hour intervals and the bearings and greases were examined [Figure 5].



Figure 5: Images of the inner race of bearings stopped at discrete intervals during FAG FE-9 test

Oxidative Stability

The third category for evaluating high temperature performance of grease was to study the oxidative stability of grease. A variation of the "Standard Test Method for Oxidation Characteristics of Extreme-Pressure Lubrication Oils" (ASTM D2893) was used to study the effect of high temperature on oils used in the grease formulations by heating them to a temperature of 160 °C for 96 hours. Then various analytical techniques

such as Fourier Transform Infrared (FTIR), Rotating Pressure Vessel Oxidation Test (RPVOT) and Pressure Differential Scanning Calorimeter (PDSC) were used to study the extent of oxidation of oil and grease formulations using various antioxidant combinations.

The role of oxidative stability of both the finished grease formulations and the base oil which makes up a majority of the grease formulation was examined in a number of different ways.

FTIR analysis was used to study levels of oxidation by examination of the carbonyl peak at 1750 cm⁻¹. This peak is typically used for this purpose since the oxidation process results in the formation of carbonyl groups. In one instance, greases were subjected to the IP 121 oil separation method using a temperature of 160 °C. The separated oil and grease thickener were examined by FTIR and compared to the spectra of the original grease and the grease thickener that had been further rinsed with pentane to remove any remaining oil. When the base grease is subjected to this treatment [Figure 6,7], the carbonyl peak is obvious in the aged oil sample, yet there is no sign of any oxidation in the grease thickener itself.



Figure 6: FTIR spectra of base grease & separated oil



Figure 7: Close up of Figure 6.

When a fully formulated grease is tested in the same manner [Figure 8, 9], the carbonyl peak is much reduced showing the effect of the antioxidants in the formulation in reducing oxidation of the base oil. The grease thickener again shows no sign of being effected by oxidation.

Alternatively, the effect of oxidation on a grease exposed to high temperature conditions in a bearing can also be studied by using FTIR in a similar manner. Grease samples were taken from bearings after an FAG FE-9 bearing rig test was completed at 160 °C and the height of the carbonyl peak was examined for these end-of-test (EOT) samples [Figure 10]. Clear signs of oxidation can be seen in these greases with the expected growth in the carbonyl peak due to the exposure of the grease to oxidative conditions at high temperature in the bearing test.



Figure 8: FTIR spectra of Grease A & base oil



Figure 9: Close up of Figure 8



Figure 10: FTIR spectra of EOT FE-9 grease samples

Given that the oxidative effect of high temperature exposure of these greases appears to be primarily taking place in the base oil and not the thickener, a further study of antioxidant effectiveness was completed on the base oil alone. ISO 220 PAO blends were made with a variety of antioxidant combinations using a design of experiment matrix. These oils were then evaluated using a modification of the S-200 gear oil test with the oils being exposed to 160 °C for 96 hours. The used oils were tested for oxidative stability using the previously described FTIR technique as well as PDSC and RPVOT. Additionally, the oils were evaluated for changes in viscosity and physical appearance [Figure 11] due to the likely importance of viscosity increase and sludge formation in increasing the torque of a bearing running at high temperature. The results from this study were used to guide the antioxidant combinations used in high temperature grease formulations.



Figure 11: Tubes of used oils from S-200 test

Finally, the effect of oxidation of various grease formulations was examined using a technique which arguably more closely mimics the conditions experienced by a grease in a high temperature bearing application. The use of the bearing attachment on a high temperature rheometer allowed differentiation of greases that were aged in the bearing at test temperature by comparing the torque of the fresh grease with aged [Figure 12, 13]. The results show a wide variety of responses of grease formulations to this aging process and can be very helpful in differentiating the potential performance of a grease in a high temperature bearing application.

Using the tools and techniques discussed above, various formulations were evaluated for potential effectiveness in a high temperature bearing application.





Figure 13: Aged grease torque in FE-9 bearings

Interactions between various performance components were evaluated and antioxidant combinations were screened for effectiveness in the presence of EP/AW and corrosion inhibitors. Then, formulations were evaluated as to their potential performance in a bearing application at 160 °C. Some of these were tested using the FAG FE-9 high temperature bearing rig [Table 3]. The results show the benefits gained from the evaluation of the potential effects of additives on high temperature performance and pre-screening of greases for effectiveness under high temperature operating conditions.

Bearing	Base Grease (hrs)	Poor Grease (hrs)	Good Grease (hrs)
1	24	24	111
2	38	52	107
3	21	57	91
4	30	36	97
5	26	61	84
F ₁₀	19	22	80
F ₅₀	26	46	99

Table 3: FAG FE-9 results of base grease and finished formulations

Conclusions

The importance of rheology in understanding various facets of grease performance is becoming clearer. Several techniques shown here allow the formulator to gain a better understanding of the behaviour of both the solid and the fluid aspects under conditions that more closely approximate real world conditions.

In addition, it is apparent that the adaptation and/or modification of more well-known analytical and bench tests can also offer clear insight into determination of critical performance factors in grease formulations. The ability to look at structural and thermal stability of grease, the effect of wear and friction on high temperature torque, or the oxidative stability of the oil used in the finished grease can all be invaluable tools to the grease formulator.

Clearly, the understanding gained from the study and use of the various high temperature screening tools discussed here can be quite an effective aid in the formulation of high temperature bearing greases. By breaking down the various aspects of the grease's performance in a given type of application, a better understanding can be gained regarding which performance parameters are most critical, thus clearing the way to optimizing a formulation in a more timely and cost-effective manner.

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