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A STUDY OF DITHIOCARBAMATE AND DITHIOPHOSPHATE COMPOUNDS AS GREASE ADDITIVES

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ABSTRACT

Grease is a complex mixture of science and engineering, requires an interdisciplinary approach, and is applied to most bearings worldwide. The grease can be more than a lubricant; it is often expected to perform like a seal, corrosion inhibitor, shock absorber, and noise suppressant. It has a coarse structure of filament within the matrix. Therefore, it is a viscoelastic plastic solid, a liquid or a solid, depending upon the applied physical conditions of stress and temperature, with a yield value, σo. The suitability of flow properties of grease for an appropriate application is determined using a controlled stress rheometer for frequency response of parameters - such as yield (σo), complex shear modulus (G), phase angle (δ) and the complex viscosity(η). The grease is synthesized from base oil, typically 85%, a thickener system at ~10% plus other possible ingredients imparting unique properties. Base oils are often paraffinic mineral oils, with some synthetic base oils used. Thickeners are based either on metal soaps, such as calcium and lithium, with complex soaps giving an outstanding performance at elevated temperatures. Inorganic thickeners widely used are clay, silica gel, and molybdenum disulfide. Polymeric thickeners include polyolefins, PTFE, and polyureas. Future demand divides into a commodity, low cost, essential grease at one end of the market, and increasing demands for higher performance, longer-lasting specialty products at the other.

KEYWORDS: Dithiocarbamate, Dithiophosphate Compounds, Grease Additives, Polymeric thickeners, molybdenum disulphide.

INTRODUCTION

The earliest greases were synthesized by reacting lime with vegetable oils, or animal fats, in the presence of water, to obtain a calcium soap of the fatty acid. This was adequate for simple lubrication tasks such as cart wheels and water wheel shafts and bearings. These calcium greases were found to be inadequate when the development of the steam engine led to higher operational temperatures. The melting point of the calcium grease is around 100^0C and higher running temperatures proved to be too challenging at that time. Such calcium greases are still in use today for less demanding applications and their manufacture is not changed much in last 100 years. Calcium soap is manufactured with a small residual water content which acts as a stabilizer for the soap matrix and thus provides the necessary structure to the thickener.

In certain operating conditions, when the temperature is consistently above 50^0C, water evaporation could result in the complete breakdown of consistency of the grease and it will convert back to a fluid state. Aluminum Stearate were further invented which provided higher operating temperature and good water tolerance. Both the properties required for Steam engine lubrication. However, aluminium thickened greases are not ery shear stable and loses the structure under shear stress losing the ability to lubricate further (99).

Clarence Earle in 1942–1943 patented the process for synthesizing Lithium based grease which found application in aircrafts. All advanced and recent lithium greases are based on the castor oil derivative, 12-hydroxy stearic acid. The lithium grease have excellent mechanical stability, good water resistance and reasonably good high-temperature performance, up to 120^0C. Due to this lithium greases replaced the earlier greases in the great majority of applications by the second half of the 20th century,. The only real disadvantage with lithium-12-hydroxy stearate grease is its pumpability at low temperatures, which can present a difficulty in centralized lubrication systems at temperatures below $–10^0$C. Lithium soaps are very elastic and due to this property the mobility is affected in long supply pipes (95).

THICKENERS IN GREASES

By definition, a soap is a metal salt of a fatty acid. The National Lubricating Grease Institute (NLGI) defines grease as a solid to semi-solid product of dispersed thickening agent in a liquid lubricant. Additives imparting special properties may be included. Grease making is a relatively simple one-pot batch reaction method. For a soap greases, fatty acids are added. And for non-soap, the other constituents are put into base oil. Commonly used acids include

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the high-molecular-weight fatty acids, stearic acid and 12-hydroxystearic acid and short-chain complexing acids such as tallow, sebacic acid, and azelaic acid. Once the acid gets up to the melting temperature the metal base is added. The process is known as saponification or soap making (see Figure 1). All the water is removed to keep the water content as much as low possible in greases. Then the material is cooled and gelled. This is where the mixture becomes a grease. The mixture is then adjusted for consistency by adding base oil (additives might be added, as well). It may have to be re-heated, re-cooled and tested several times to get the consistency or the penetration range that is required for the product . In most comercial greases, soap concentration is typically 10%-20% and major portion is of oil that is more than 70%.

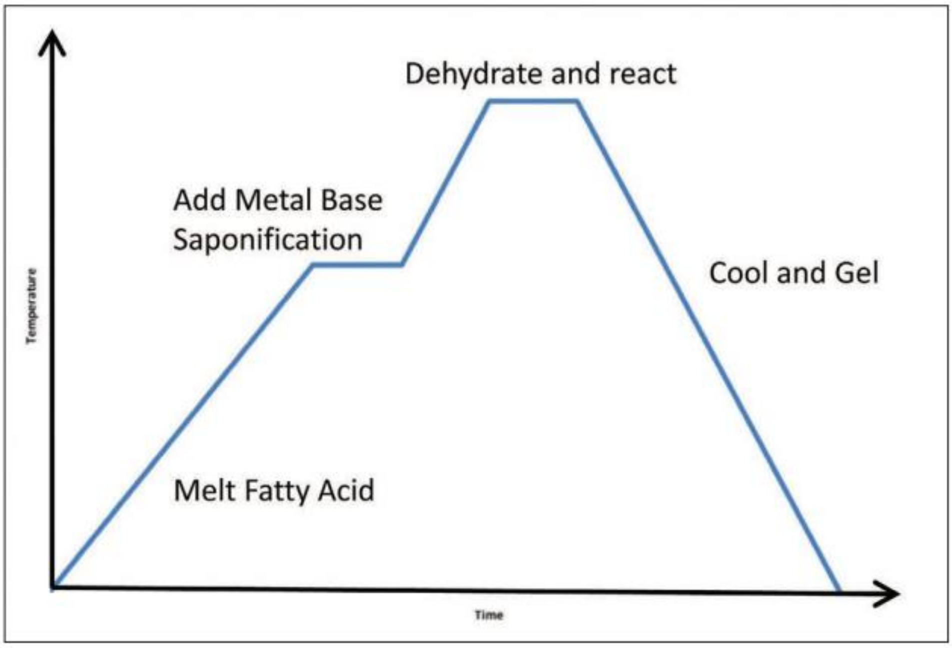

Figure 1 | **Greasing-making process: basically acid + base = soap + water.**

- Simple soaps - The main thickeners used in grease is a metallic soap. These metals include lithium, aluminum, calcium and sodium.
- Complex soap - Greases with complex soap thickeners are gaining more popularity because of higher operating temperature and superior load-carrying abilities they posses. Complex greases are manufactured by combining the metallic soap with a complexing agent. The most widely used complex soap grease is lithium based made

with a conventional lithium soap complexed with low-molecular-weight organic acid such as Sebacic or Azelic acid.

- Non-soap - Non-soap thickeners make sense in special applications such as bentonite clay for high temperatures where it does not melt.

The thickener soaps could be of below types:

1. Lithium - Because lithium soaps are very efficient thickeners, lithium 12-hydroxystearate greases are widely used. Lithium grease provides good lubricity and have great shear stability, thermal resistance and relatively low oil separation.

2. Calcium - These greases have better water resistance than lithium greases. They also have good shear stability. However, they have low dropping points and do not have good operating temperature range and can only be used in operating conditions up to 110 C (230 F).

3. Sodium - These greases offer high operating temperatures, up to 175^0 C but are confined to operating conditions no higher than 120^0 C because of poor oxidative stability and high oil bleeding. They also are not very water resistant. However, they do provide good lubricity and shear-stability.

4. Aluminum - These have excellent oxidative resistance and good water resistance. But they have a low dropping points of only 110^0-115^0 C. Their usage is hence limited to operating conditions less than 80^0 C. When the grease is overheated in bearings, they cause sharp torque increases.

The Non-Soaps type grease will be of below chemistry:

1. Urea - A polyurea thickener is a reaction product of a di-isocyanate with mono-amines and/ or diamines. This includes diurea, tetraurea, urea-urethane, and others. The ratios of ingredients determine the characteristics of the thickener. Polyurea thickeners are ashless as they do not contain metallic elements. Therefore are more oxidatively stable. They are used in Food grade greases.

2. Organophilic clay - These thickeners include minerals bentonite and hectorite. The minerals are purified to remove non-clay material—ground to the desired particle size—and chemically treated to make the particles more compatible with organic chemicals. Clay thickeners have no defined melting points, so they can be used in high-temperature conditions.

3. Others - Other non-soap greases include teflon, mica and silica gel.

The complex Soaps type grease will be of below chemistry:

1. Calcium sulfonate complex – These are not strictly a soap but are metal salt of a sulfonic acid detergent. These greases have high operating temperature and good water resistance. They are complexed with Phosphoric and/or Broic acid to improve its antiwear and extreme pressure properties.

2. Lithium Complex – These sopas are synthesized in a similar manner as Lithium soap with addition of complexinf acids such as azelic, sebacic or boric. More than one complexing acid could also be used to achieve the specific performances. Lithium Complex grease give high dropping points compare to simple lithium soap hence are preferred soap for high temperature applications.

3. Aluminum complex – Aluminum complex greases are synthesized by addition of complexing acid such as benzoic acid with the stearic acid (fatty acid). Complexing leads to high dropping point hence can be used at high temperature applications.

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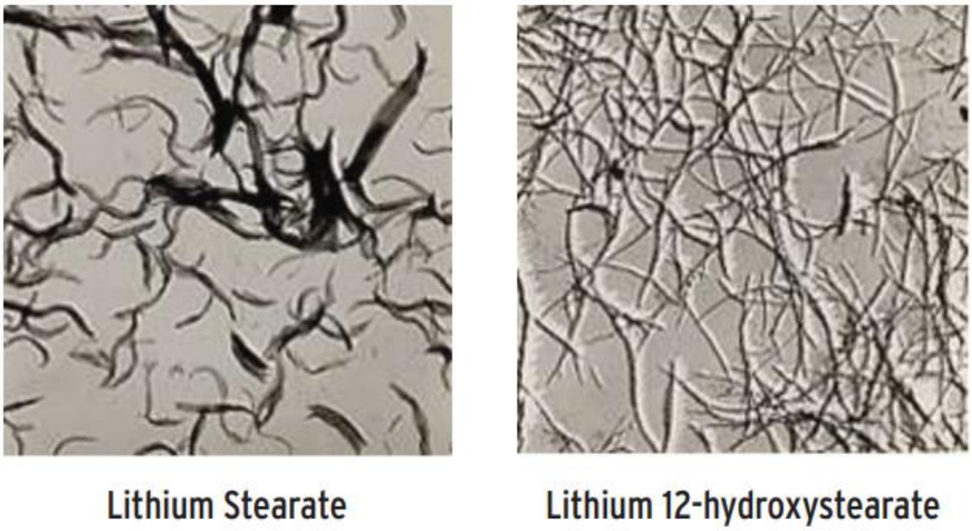

Figure 2 | Thickener fiber/micelle structure of two grease compounds.

MICELLE

Thickeners all self-assembled into threadlike molecular structures, called micelles. They allow a compound that is normally insoluble to dissolve. Micelles are formed when soaps and detergents are added to the water. The individual molecule of soap has a strongly polar head but a non-polar hydrocarbon chain tail. The non-polar tail aggregate into the center to form a ball like structure (micelle), when added to water. This aggregation is because of Van der Waals Forces between the molecules. The polar head of the molecule faces outward for interaction with the water molecules on the outside of the micelle because they are hydrophobic, while the tail faces inward (see Fig3). Lubricants are non-polar environments, hence these micelles are reverse or inverse micelles. The non-polar tails face outwards while the ionic head faces inward. Therefore, it is the micelle structures in thickeners that enable the thickeners to hold the liquid lubricant (100).

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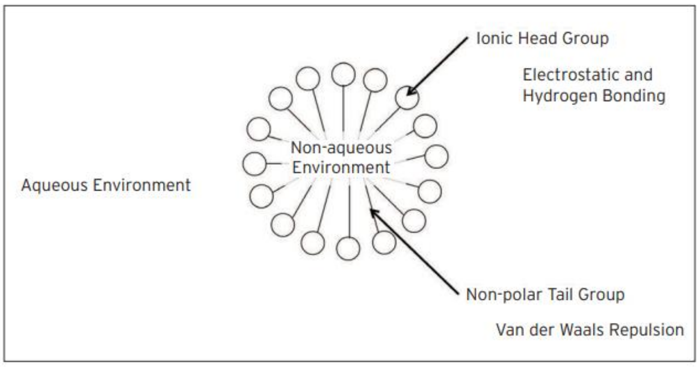

Figure 3 | **Micelle concept showing ionic head/non-polar tail formation. Non-polar tails aggregate into the center to form the ball-like micelle structure.**

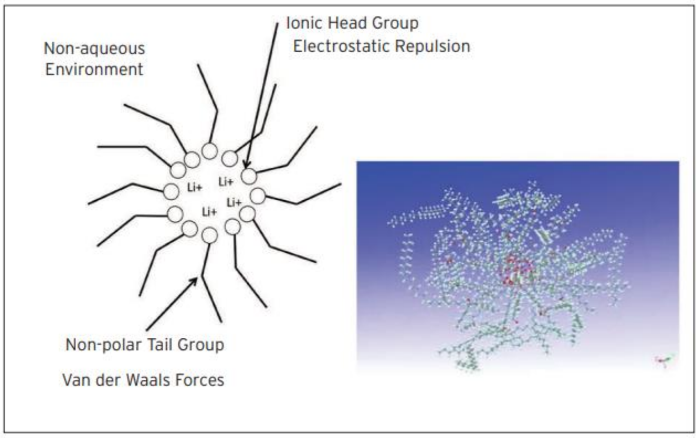

Figure 4 | **Reverse micelle concept. Since lubricants are non-polar environments, these micelles are reverse or inverse micelles. The non-polar tails face outward and the ionic head**

BASE OILS FOR GREASES

Most commonly used base oils in Greases are Mineral base oils, because of there high solvency and good Aniline point. Mineral oils are also economical option compare to other synthetic base oil. The demand for grease with synthetic base oils such as Poly alpha olefin, Esters, Alkylated Napthalene and Silicone oil is increasing rapidly due to their excellent thermal and oxidative stability, High Viscosity Index and Better lubricity.

In one of the study conducted by author, greases were made using lithium 12-hydroxystearate, lithium complex, and aluminum complex thickeners. Several base oils performance was compared such as Mineral oil, PAO, Ester and blend of these base oils with Alkylated Napthalene. PDSC results shows that higher oxidative and thermal stability can be achieved by using Synthetic base oils which can be further improvised by synergistic combination of synthetic base oils.

Additives for Greases

Addition of additives in greases is not as straight forward as adding additives in liquid lubricants. Grease being semi-solid, homogeinized mixing of additives is essential criteria. It is also important that the structure of the grease is not being altered by additives. Certain additives being very polar in nature could have impact on grease structure resulting in poor mechanical stability confirmed by ASTM D 217 (worked penetration after 10k and 100k strokes) & ASTM D 1831 (Roll stability). It is also important that polar additives are not used beyond certain concentration to maintain the mechanical stability of the base grease.

Work and Unwork Penetration (ASTM D-217)

To measure the penetration of greases, the test grease is filled in a worker cup and temperature of the grease is brought to 25°C. The cone assembly is placed over the surface of the de-areated grease. The cone is released and allowed to drop into the grease for 5 sec. The penetration of the cone (depth) into the grease is measured in tenths of a millimetre.

The reported result is generally an average of three determination of cone penetration. There are four test variations consisting of measuring unworked and worked grease samples under mechanical worker. The test variations are as follows:

1. Unworked Penetration
2. Worked Penetration - 60 double strokes in the grease worker
3. Prolonged worked Penetration - 10000+ double strokes in the grease worker

Roll Stability (ASTM D 1831)

The roll stability apparatus consists of a sealed cylindrical chamber in which a grease sample is inserted with a weighted roller. This assembly is rotated in an oven for a set time and temperature, after which the grease is removed and its penetration is measured.

Larger penetration change numbers show greater grease thinning and, therefore, less stability. The results in figure 2 show data using four different test conditions developed by two different laboratories. Data are presented for rolling times of 24 hours and 50 hours at test temperatures of 60^0C and 80°C.

Four Ball Wear Test (ASTM D 2266)

In this test, Three ½ inch diameter steel balls are clamped together and covered with the test grease. The grease is heated to 75°C, and then a forth identical ball (referred to as the top ball) is pressed downward with a force of 40 kgf into the cavity formed by the three clamped, stationary balls. This arrangement forms a three-point contact. The top ball is then rotated at 1200 rpm for 60 minutes.

CONCLUSION

The conclusion can be drawn, therefore, that replacing ZDDP in Greases with ashless chemistry is possible by combining synergictic combination of two or more chemistries together. The Antiwear performance can be improved in greases not necessarily by increasing the treat rate of one additive chemistry. Combination of two or more chemistries may help in reducing the overall treat rate of additives used in the greases, providing reduced negative impact on environment.

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