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Effect of Additives on the Properties of Different Types of Greases

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Abstract

The aim of this research is to study the influence of additives on the properties of soap greases, such as lithium, calcium, sodium, lithium-calcium grease, by adding varies additives, such as graphite, molybdenum disulfide, carbon black, corrosion inhibitor, and extreme pressure.

These additives have been added to grease to obtain the best percentages that improve the properties of grease such as load carrying, wear resistance, corrosion resistance, drop point, and penetration.

The results showed the best weight percentages to all types of grease which give good properties are 1.5% extreme pressure additive, 3% graphite, 1% molybdenum disulfide, 2.5% carbon black.

The other hand, the best weight percentage for corrosion inhibitor is 1% to lithium-calcium grease, 2% to lithium grease, and 3% to sodium grease. It was concluded that there is no need to add corrosion inhibitor to calcium grease.

Key Words: Greases, Lubrication, Lubricating oil

Introduction

Grease is a complex multi-phase material whose way of functioning needs to be clarified because of its growing use in modern machines [1].

True grease consists of oil and or other fluid lubricant that is mixed with another thickener substance such as a soap to form a solid.

Greases generally cannot satisfy the requirements of high performance lubricants without using the benefits of modern additive technology. Additives are natural or synthetic chemical substances that can improve lots of different parameters of lubricants [2].

Anti-wear and extreme pressure (EP) additives improve, in general the load carrying ability in most rolling contact bearings and greases. Fillers are sometimes used as fine solids in grease formulations to improve grease performance. Typical fillers are graphite, molybdenum disulfide, carbon black and others [3].

The important properties which affect the characteristics of grease are amount and type of thickener, oil viscosity, additives and low or high temperature performance.

Additives enhance performance and protect the grease [4].

The grease is a mixture of a fluid lubricant, a thickener, and additives. Common thickeners are the fatty acid soaps of lithium, calcium, sodium, aluminum, and barium or in organic non soap thickeners [5].

Lederer in 1933 introduced first greases which are aluminum soap –

based, used the aluminum soap represented by aluminum stearate [20].

Calhoun in 1962, reported that the tendency of molybdenum disulfide to decrease the wear of grease. However, the extreme pressure properties of greases were increased by the addition of this agent [21].

Tarunendr Singh in 2000, showed that the blends of bis (1,5-diaryl-2,4-dithiomalonamido) dioxomolybdenum complexes in lithium base grease are evaluated for their extreme pressure activity. The greases fortified with additives, prevent rusting and corrosion of bearings, and also have better oxidation protection as compared to the grease have no additive [22].

Edward in 2003 showed that greases composed of mineral oil blended with a soap thickener, additives enhance performance and protect the grease and lubricant surfaces [4].

Theo et.al in 2007 stated that the greases cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive, such as corrosion inhibitor, antiwear, and extreme pressure additives [2].

The aim of this work is to study the influence of some additives on properties of (lithium, calcium, sodium, and lithium – calcium) soap greases by adding; additives which include graphite, molybdenum disulfide, carbon black, corrosion inhibitor, and extreme pressure

Additives

Additives can play several roles in lubricating grease. These primarily include enhancing the existing desirable properties, suppressing the existing undesirable properties, and imparting new properties [8]. The most common additives are oxidation inhibitors, corrosion inhibitors, extreme pressure, antiwear, viscosity index improver and friction modifiers such molybdenum disulfide or graphite.

1. Antioxidants

Greases are apparently oxidized in different ways statically as in storing and dynamically as in service because of the different temperature involved [6].

Oxidation inhibitor is natural anti-oxidants among the most important additives used in greases. The steps involving in the oxidation are initiation, propagation and termination.

Oxidation inhibitors function by preferentially combining with peroxides or radical species, there by terminating the free radical chain reaction. Chemical compounds typically used to inhibit oxidation include hindered phenols, aromatic amines, heterocyclic nitrogen compounds, and zinc di-alkyl di-thiophosphate and di-thiocarbonates [7].

2. Corrosion and Rust Inhibitor

Corrosion and rust inhibitor completely coat the metal, in order to protect these surfaces from rusting, since rusting is an electrochemical process and proceeds in the presence of air-providing oxygen and water.

Two types of corrosion inhibitors are used commercially: oil soluble material, such as lead soaps, molybdenum disulfide, and water soluble compounds protect by strong adsorption on the metal. Sodium nitrite is corporate as dispersion of very small crystals to avoid roughness in bearing [8].

3. Extreme Pressure (Anti Wear Agents)

The addition of this additive to lubricate grease increases mechanical efficiency and diminishes wear and destructive heating reducing friction and avoiding surface damage of sliding surfaces whilst increasing the load carrying capacity [9].

Molybdenum disulfide has the advantage of durability under severe operating conditions such as temperature up to 400 °C [10].

4. Viscosity Modifiers

Viscosity modifiers are generally oil soluble organic polymers. Many types of viscosity modifiers are available, such as polyisobutylene, volatilized paraffin wax, unsaturated polymerized esters of fatty acids and monohydric alcohols, and condensation products of olefin and diolefin hydrocarbons [11].

These modifiers consist of aliphatic carbon to carbon backbones. The major structural differences are in the side groups, which differ chemically and in size. These variations in chemical structure are responsible for various properties of viscosity modifiers such as, oil-thickening ability, viscosity temperature dependency, and oxidation stability [8].

Types of Greases

1. Calcium Soap Grease

It is one of the earliest known greases and is water resistant and mechanically stable. Calcium soap grease usually has a low dropping point; typically 95 °C.

High temperatures cause a loss of water and a consequent weaking of soap structure, and therefore the use of this grease is limited to a maximum temperature of about 60 °C [12].

2. Sodium Soap Grease

It is fibrous in structure and is resistant to moderately high temperature but not to water. Sodium soap grease has a high dropping point (175 °C) than calcium grease [12].

3. Aluminum Soap Grease

It is smooth, transparent grease with poor shear stability but excellent oxidation and water resistance, but tends to have poor mechanical stability and so is not suitable for rolling bearings [12].

4. Lithium Soap Grease

It is normally smooth in appearance but may exhibit a grain structure. Lithium soap grease offers both the water resistance of calcium soap grease and high-temperature properties of sodium soap grease [12].

5. Mixed Soap Grease

It is generally manufactured by saponifying the fatty material with mixed alkalis derived from metals. One of the soaps usually predominates and determines the general character of the greases while the other modifies the structure in some way. This results, for example, in changes in texture and improved mechanical stability [13].

6. Complex Soap Grease

It is formed when two dissimilar acids are attached to the same metal molecules, thus restricting complexes to only polyvalent metals [14]. There are several types of complex grease, such as, calcium complex grease, aluminum complex grease, and lithium complex grease.

7. Non Soap Grease

Two non-soap greases are present. One is organic, the other inorganic.

A. Polyurea

It is the most important organic non soap thickener. It is a low-molecular weight organic polymer produced by reacting amines with isocyanates, which results in an oil soluble chemical thickener.

B. Organo – Clay

It is the most commonly used inorganic thickener. Its thickener is modified clay, insoluble in oil in its normal form, but through complex chemical processes, converts to platelets that attract and hold oil. Organo – Clay thickener structures are amorphous and gel-like rather than the fibrous, crystalline structures of soap thickeners. This grease has excellent heat resistance since clay does not melt.

Experimental Wok

The greases used in the experimental work are produced in Al-Daura refinery, which are; lithium soap grease, calcium soap grease, and sodium soap grease. Table (1) shows the main characteristics of these greases used in the experimental work according to ASTM methods.

Additives which were used in the experimental work, extreme pressure additive, graphite, molybdenum disulfide MoS2, carbon black, and corrosion inhibitor. All these additives were from Al-Daura refinery have the properties shown in tables (2), (3), and (4).

Oil-base stocks have been selected on the basis that they are widely used in commercial production of lubricating oil and greases.

Experimental Procedure

A. Four Ball Welding Test

This test aimed, to find the force required to cause metal surfaces to weld after subjected to friction under high pressure, using lubricating grease to be tested.

ASTM D-2596 method was used, with the apparatus four-ball extreme pressure lubricant tester. The ball pot was filled completely with the grease to be tested. The three steel test balls were embedded in the grease. The lock ring was carefully placed over the three balls. The weight tray and weights were placed on the horizontal arm in the correct notch for a base test load of 80 Kg_f.

B. Four-Ball Wear Test

The aim of this test is to find the ability of metal surfaces to wear after rubbing one another, using lubricating grease in certain temperature and specific load. ASTM D-2266 method was used, with the apparatus four-ball wear tester. A small amount of the grease was placed in the ball cup sufficient to the fill the void between the three balls tobe inserted in the ball cup and the balls were locked in position into the ball cup. The diameter of the affected areas caused by friction was measured using the provided microscope

C. Copper Corrosion Test

The aim of this test was to cover the detection of the corrosiveness to copper of lubricating grease. ASTM D-4048 method was used, with instrument for copper strip corrosion measurement. The surface of the sample was pressed into contact with copper strip and leveled with the spatula. The corrosiveness was reported in accordance with one of the special classifications.

D. Dropping Point Test

This test covers the determination of the dropping point of lubricating grease; this point is being the temperature at which the first drop of material falls from the cup. So the dropping point is the temperature, at which the grease passes from a semi solid to a liquid state, under the conditions of the test. ASTM D-2265 method was used. Dropping point assembly manufactured by KOEHLER instrument used as a tester.

E. Work Penetration Test

This test measured the consistency of lubricating grease by penetration of the standard cone. ASTM D-217 method was used, with the apparatus of penetration tester manufactured by the

NomalAnalis Company, France. A penetrometer shall be capable of indicating depth in tenths of a millimeter, since cone shaft rapidly released, and allowed to drop for 5.0 ± 0.1 sec. The penetration was read and recorded from the indicator

Results and Discussion

The effect of concentration of additives on the bearing pressure, wear resistance, drop point, and worked penetration were discussed.

1- Effect of Extreme Pressure (EP) Additive:

Extreme Pressure additive was added to achieve good properties of load carrying to the lubricating grease. Fig.(1) shows the effect of wt.% of extreme pressure additive on four-ball welding test at different types of grease. It is clear from this figure, that the addition of 1 % of EP, the lithium-calcium has 800 Kg_f extreme pressures which are higher than the other and equal to the extreme pressure of lithium grease, since less frictional heat is generated and the potential for severe welding is reduced. The addition of 1.5% wt. of extreme pressure additive shows a remarkable change in characteristics, after this percentage of addition, the load remained almost constant.

Fig. (2) Shows the effect of extreme pressure additive on wear test for different types of grease. The addition of 1% of EP to each type of grease shows that the wear reduction using lithium grease is better than using the other greases. Also, the calcium, sodium grease were less effected by EP. Extreme pressure additive react with the surface to form protective films which prevent metal to metal contact and the consequent scoring or welding of the surfaces.

Fig. (3) Shows that the drop point temperature remained constant despite the increase in additive in lithium grease. This is a good indicator that the other characteristics remained unchanged in this type and the other types of grease, except for calcium grease where drop point decreased slightly because of soap fiber length that holds the structure of the grease [11].

Fig.(4) shows that the addition of EP has a slight increase in worked penetration for all types of greases means that the basic texture of greases do not change significantly, shear stability is maintained.

2- Effect of Graphite Additive:

Graphite is physical additive. It is one of the most widely used fillers and that found applications in numerous types of lubricating greases [11].

Figure (5) clarifies that the addition of graphite will increase the bearing load for all types of greases. Since the load increased from 400 kg_f to 800 Kg_f in lithium grease, from 160 kg_f to 400 kg_f in calcium grease, from 250 kg_f to 800 kg_f in sodium grease and from 620 kg_f to 800 kg_f in lithium- calcium grease. The best additive percentage ranges was between 3.0 – 5.0 %.

The addition of graphite will decrease the wear in all kinds of greases as shown in fig. (6), the response of lithium grease to wear resistance additive is higher than that in calcium grease and lithium-calcium, thus there is no need to mix these greases for wear resistance purposes. The best percentage of added graphite was 5 % for lithium grease, 15 % for calcium, sodium, and lithium – calcium grease

The lithium grease has a higher drop point from other types of other greases as shown in fig. (7), and till the percentage of added graphite reached 15 %, and so did the other greases, which means that adding graphite does not change the structure of grease.

The work penetration has shown in fig. (8), a little change when graphite is added, since the filler has a little influence upon the consistency of the product. As the amount of filler is increased, the effect becomes evident [11].

3- Effect of Molybdenum Disulfide Additive:

It is noted from fig. (9) that when adding different percentages of molybdenum disulfide (1 – 15 %) to lithium, calcium, sodium, and lithium-calcium grease to become suitable to prevent seizures under conditions of high temperatures, heavy loading or extended periods of operation, Four-ball welding reading will increase. The load carrying using molybdenum disulfide is higher due to their structure, since this additive has a "layer lattice" structure in which the atoms in each layer or "basal plane" are located at the corners of regular hexagons

The addition of MoS_2 will decrease the wear in all types of greases used as shown in fig. (10), this makes the molybdenum disulfide more economical than graphite, since it is more efficient in wear test, as shown in fig. (11).

There is no change in drop point for all types of grease with the addition of molybdenum disulfide as shown in fig. (12), while the work penetration was increased which clarified clearly in fig. (13).

4- Carbon Black Additive:

Carbon black can be classified as a physical type of additive which is selected as alternative for molybdenum disulfide and graphite on the basis of availability and low cost as factors contributing in the extensive use of this additive.

The best addition percentage ranges of carbon black is between (2.5 – 10 %) as shown in figures (14), (15), (16), and (17) for four-ball welding, wear, drop point, and worked penetration test.

It was noted from this additive in the selected range the followings:-

1- Maximizing the heavy load carrying, i.e. welding.
2- Minimizing the wear effect.
3- Increasing the dropping point.
4- A little effect upon consistency, thus it is safe to be used.

5- Effect of Corrosion Inhibitor Additive:

One of the most important additives is the corrosion inhibitor. It can be classified as a chemical additive type. Its effect is measured by observing a cupper strip using a methodology set by ASTM. There are three cases to recognize the corrosion on this strip according to the blackening of the strip. This additive is added to prevent corrosion in a grease medium.

The effect of this additive is clearly shown in figure (18). The effect of addition of this additive starts after adding 1 % to lithium-calcium grease where the strip becomes bright, while calcium grease is basically, without additive, shows a bright strip since calcium base lubricating grease is water repellant it has been supposed that they do started after adding 2 %. In the case of sodium grease, the effect appears at 3 %.

To insure that this additive does not have any negative effect on grease, the drop point and worked penetration is measured for each addition as shown in figures (19), and (20). Lithium, sodium, and lithium-calcium greases proved that the drop point does not change at any percent of addition, while calcium showed a slight transition because its fiber length is short [11].

Table 1, Characteristics of used Lubricating greases

Specifications	Lithium soap	Calcium soap	Sodium soap
Worked penetration (mm^{-1})	270	273.8	334.2
Drop point (°C)	202	100	150
Copper corrosion test (24 h at 100°C)	2a	1a	2a
Four-ball weld load (kg_f)	400	160	250
Four-ball wear test (wear scar diameter mm)	0.31	0.65	0.566
Texture	Soft	Soft	Fibrous
color	Brown	Yellow	Green

Table 2, Properties of HiTEC 343 extreme pressure additive [19]

Property	Specification
Appearance	Bright Clear and Amber Liquid
Viscosity @ 100 °C. mm^2/s	9.0
Density @ 15.6°. g/ml	1.082
Phosphorus. %wt	1.17
Sulfur. %wt	36.1

Table 3, Properties of graphite additive [18]

Property	Specification
Formula	C
Color	Black
Crystalline form	Hexagonal
Melting point (°C)	4200

Table 4, Properties of molybdenum disulfide additive [18]

Property	Specification
Formula	MoS_2
Color	Black
Crystalline form	Hexagonal
Melting point (°C)	1185

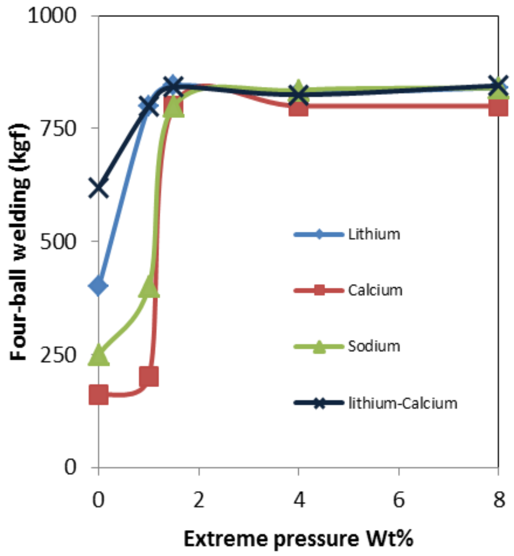

Fig. 1, effect of EP additive on four ball welding test at various types of greases

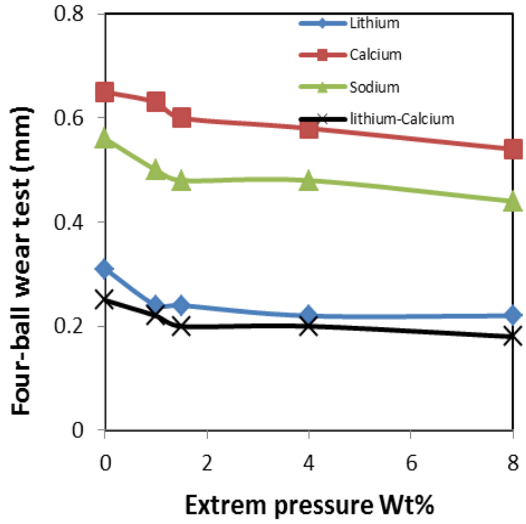

Fig. 2, effect of EP additive on four ball wear test for various types of greases

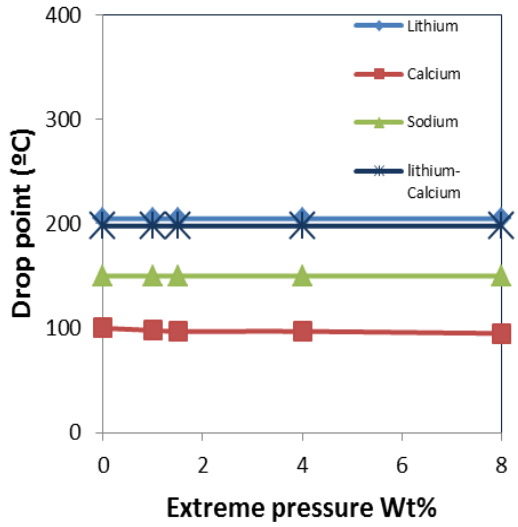

Fig. 3, effect of EP additive on drop point test at various types of greases

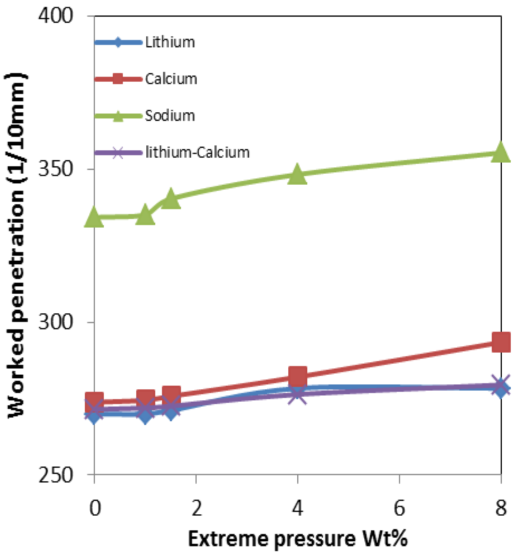

Fig. 4 effect of EP additive on work penetration test at various types of greases

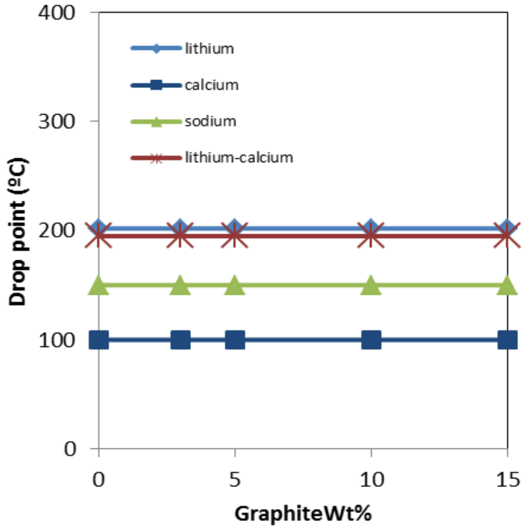

Fig. 7, effect of graphite percent of additive on drop point test

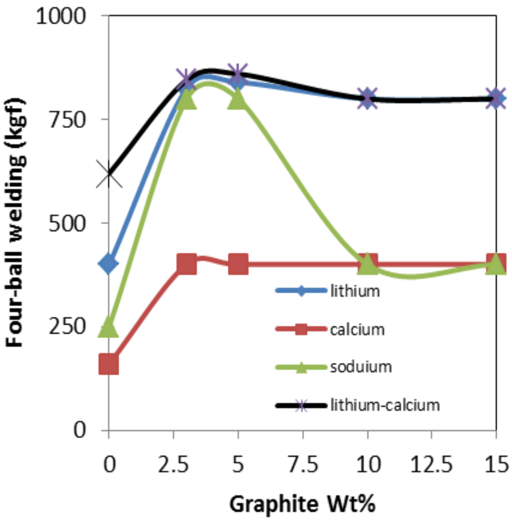

Fig. 5, effect of graphite on four ball welding test

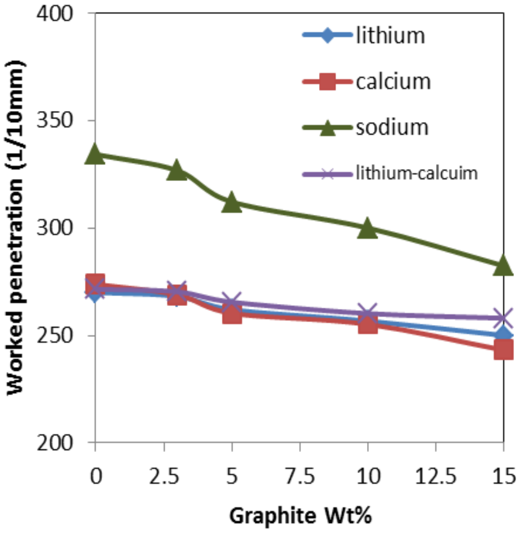

Fig. 8, effect of graphite additive on work penetration test

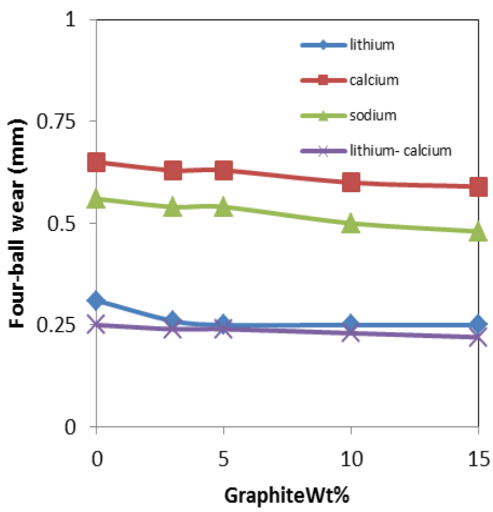

Fig. 6, effect of graphite additive on four ball wear test

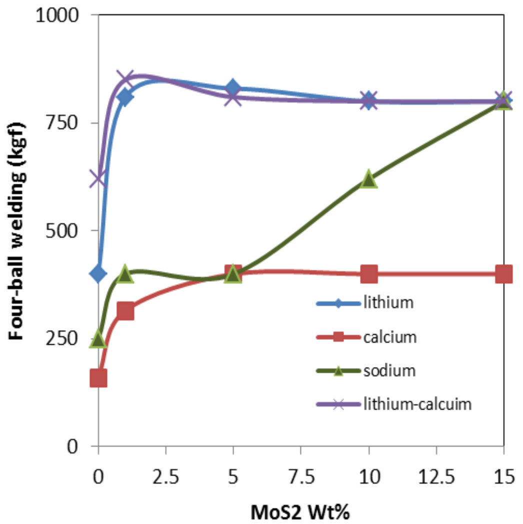

Fig. 9, effect of molybdenum disulfide percent additive on four ball welding test

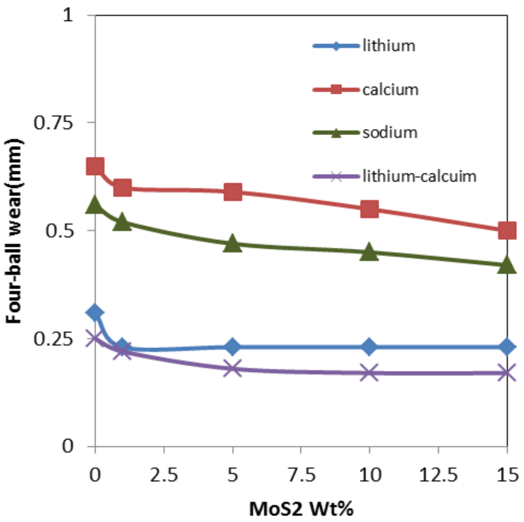

Fig. 10, effect of molybdenum disulfide percent additive on wear test

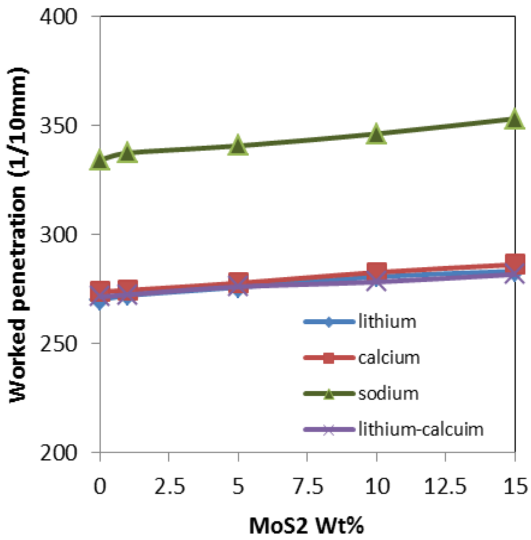

Fig. 13, effect of molybdenum disulfide on work penetration test

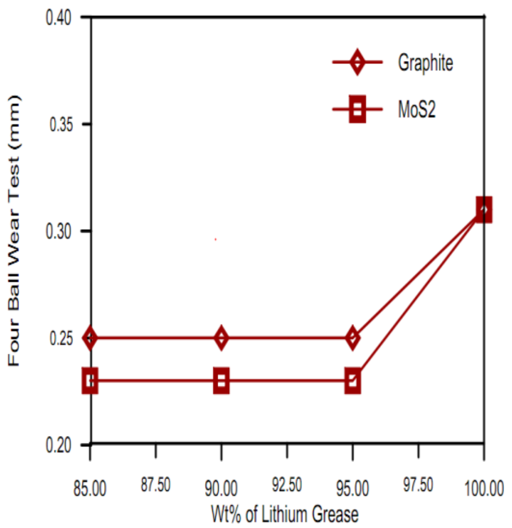

Fig. 11, effect of graphite and molybdenum disulfide percent additive on wear test in lithium grease

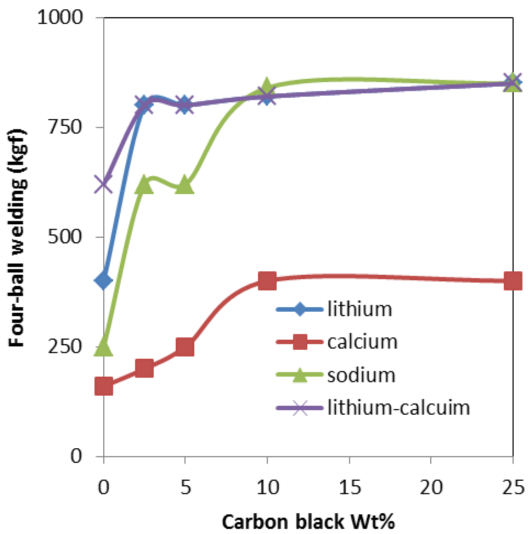

Fig. 14, effect carbon black additive on four ball welding test

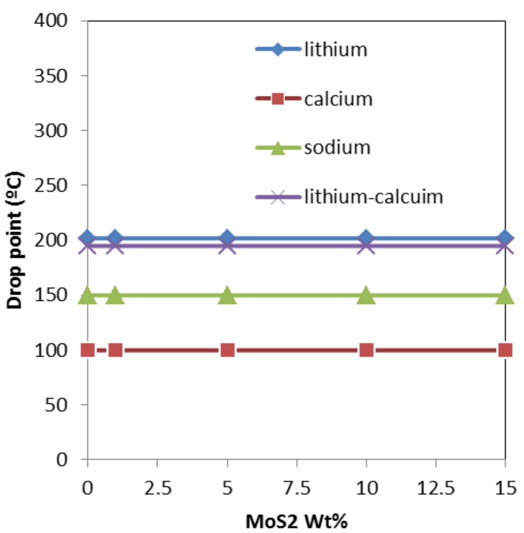

Fig. 12, effect of molybdenum disulfide on drop point test

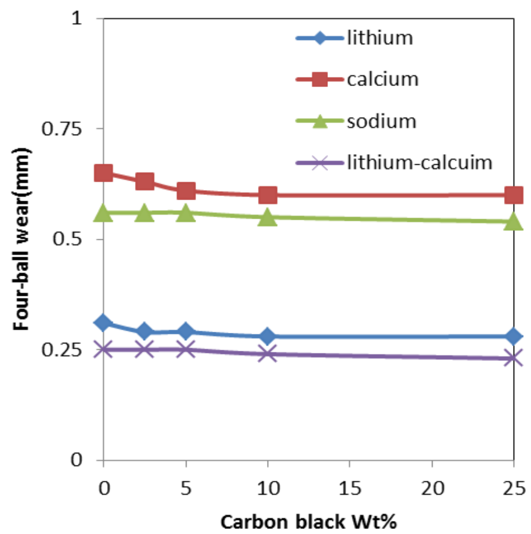

Fig. 15, effect carbon black additive on four ball wear test

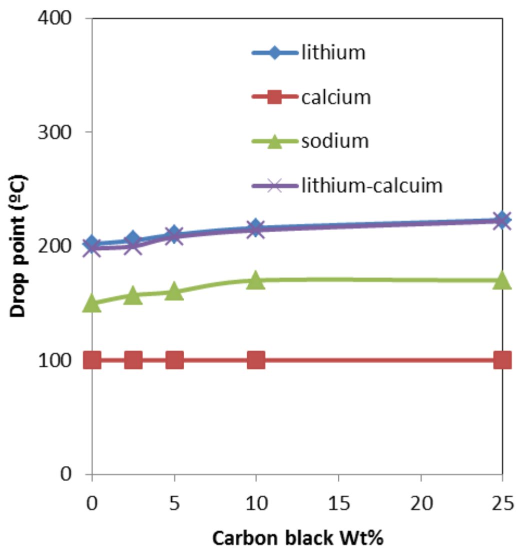

Fig. 16, effect carbon black additive on drop point test

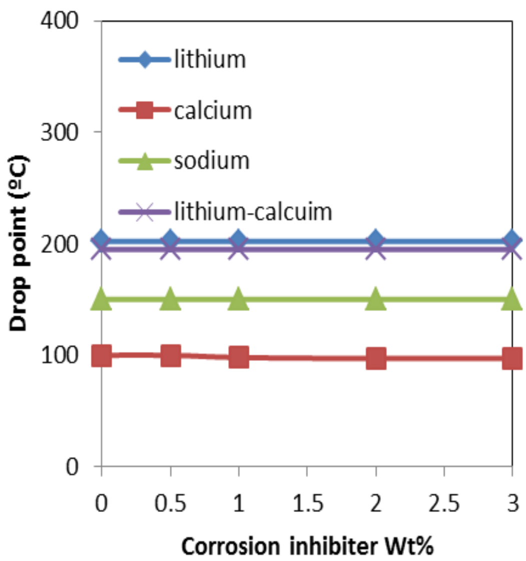

Fig. 19, effect of corrosion inhibiter additive on drop point test

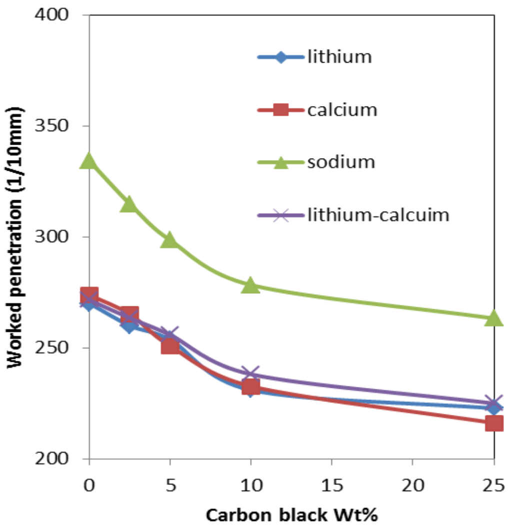

Fig. 17, effect carbon black additive on work penetration test

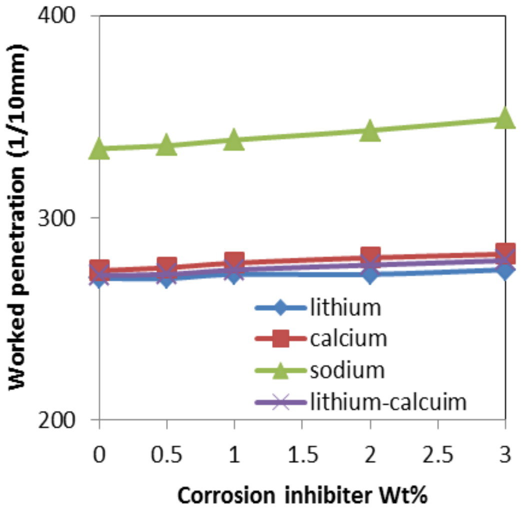

Fig. 20 effect of corrosion inhibiter additive on work penetration test

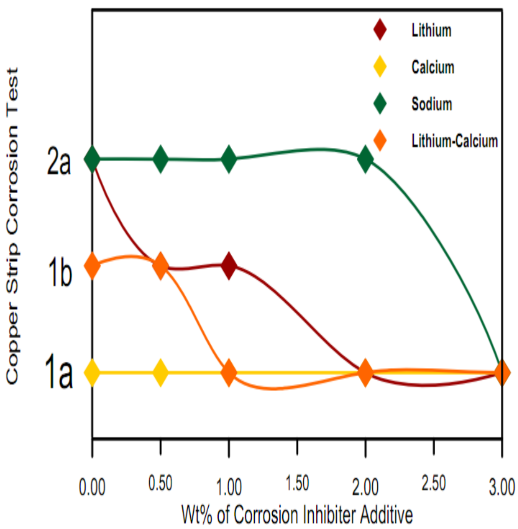

Figure (18) effect of corrosion inhibiter additive on copper strip corrosion test

Conclusions

The following conclusions are drawn from this research:-

1- Improvement of grease to withstand high pressure and having less wear is much affected by the type and percentage of additive used. The addition of extreme pressure, graphite, molybdenum disulfide, and carbon black additive are 1.5, 3, 1, and 2.5 % respectively in all types of greases used in this study.

2- When adding corrosion inhibitor to calcium grease, the test strip did not show any sign of corrosion. This is an indicator that calcium grease is water repellant and does not need the addition of corrosion inhibitor. The effect of adding corrosion inhibitor to lithium-calcium grease started to be noticed at 1 %, 2 % at lithium grease and 3 % at sodium grease.

3- Lithium grease has many good properties such as load carrying, high temperature performance and shear stability, thus it is considered valuable grease and very commonly used in most parts of the world.

4- When mixing lithium grease with calcium grease and comparing it with lithium grease, it is found that it has slightly better properties than lithium grease. This does not justify leaving the use of lithium grease. That is true for economic reasons due to the need for mixing equipment and electrical power and consequently a higher cost is incurred.

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