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Advanced greases with outstanding extreme pressure and anti- wear properties based on IF-WS_2 nanoparticles

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Introduction:

Conventional metal dichalcogenide materials of the form MX_2 (M = Mo, W; X = S, Se) are well known for their application in solid lubricantion as well as an additive in lubricating oil to reduce wear and friction between contacting surfaces (1).It was found that the performance of the solid additive in lubrication oil is significantlyvary with the size of the particle (2). Nanoparticle show unique properties due to remarkable increase in surface to volume ratio compared to their bulk counterpart. Hence, there is great interest in research and development of nanoparticle and nanotechnology base products in industries as well as academia during past decades.

Tungsten disulfide is an important solid lubricant material which has shown good potential for tribological applicationsowing to its unique layered structure. It was prof. Reshef Tenne of Weizmann Institute of Science who first reported closed-caged nanostructures of tungsten disulfide in 1992 (3). He observed that layered nanomaterials of WS_2 in platelet form is unstable due to dangling bonds on both sulfur and tungsten atom. Consequently, they re-structure themself to form closed-caged nanostructure of quasi-spherical closely resembled carbon fullerenes or carbon nanotubes (fig. 1) (3, 4). Due to their fullerene-like structure, they are called closed-caged inorganic fullerene (*IF*) nanostructure of metal dichalcogenide. They are multi-layered hollow core nanoparticle of quasi-spherical, elastic in nature, chemically and thermal stable, and highlyappropriate for the tribological applications. The enhanced properties of the IF particle is primarily due to change in morphology from their predecessor counterpart, as well as increase in surface to volume ratio area due to nanosize.

From the time of its invention, *IF*-WS_2nanoparticle is been extensivelystudied as a solid lubricant and also as an additive in lubricating oil (3). Various scientific papers and patents are available reporting superior lubrication properties of the *IF*-WS_2 nanoparticles (5-7).The reported characteristics of this novel materials suggested extremely promising and innovative commercialization in field of tribological applications.

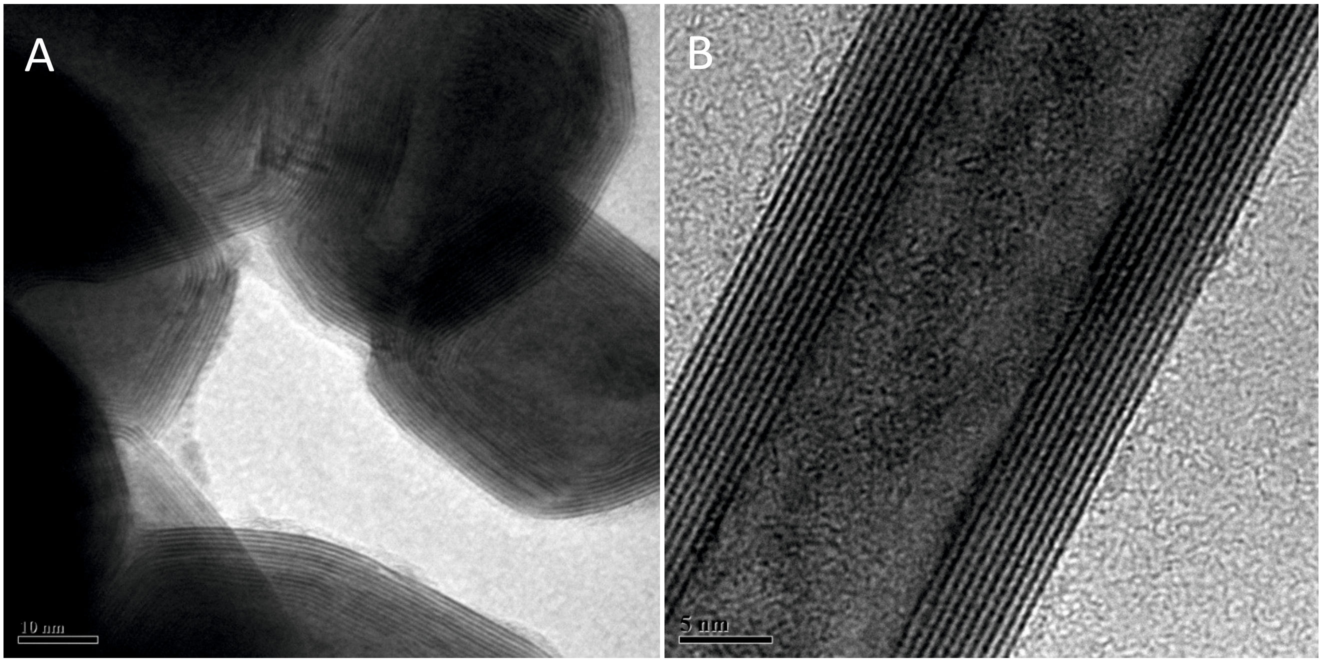

Fig.1. TEM images of (A) several closed-caged onion-like *IF*-WS_2 nanoparticles (B) a multi-wall WS_2nanotube

In addition, extended studies on the *IF*-WS_2nanoparticles resulted in suggesting several new applications including electronic, photoconductors, catalysis and energy storage, and shock-wave resistance applications (8-12).

With numerous possibility of commercial applications, this novel nanostructure materials was commercialized by a company called NanoMaterials in 2002.

De-agglomeration, Dispersion and Formulation

The nanoparticle powder obtained by the chemical method have average size of100nm with size distribution ranging from 30 to 170 nm. It was observed that particles tend to stack together to form large aggregates and agglomerate (fig.2). Enormous increase in surface energy of the individual nanoparticle could be the primary reason for such agglomeration. Several techniques to de-agglomerate the particles were investigated such as ultrasonication, high shear mixing, surface treatment with various surfactants etc. A 1st generation dispersion of *IF*-WS_2 nanoparticle wasdeveloped by de-agglomeration of the *IF*-WS_2 nanoparticles in powder form as well as monodispersed dispersion of nanoparticle in oil for the laboratory and industrial applications.

However, variation of some tribological results conducted at different laboratories suggested requirement for further improvement of the stability of the dispersion. A tendency of slow sedimentation of the particles over the time was reason behind variation of the results. The settling of the particles reduced the concentration of dispersed particles and thereby reducing the performance of the materials. Hence, it was the new challenge for the researchers to find the way to transform powder into almost fluid-type of materials with improved stability and greater performance. After an extensive fundamental research to understand the nature and surface chemistry of the nanoparticle and vigorous testing, scientist and engineer developed a 2nd generation dispersion of *IF*-WS_2 nanoparticles with cutting-edge manufacturing technique resulting in high level of long term stability and superior performance of lubricating materials.

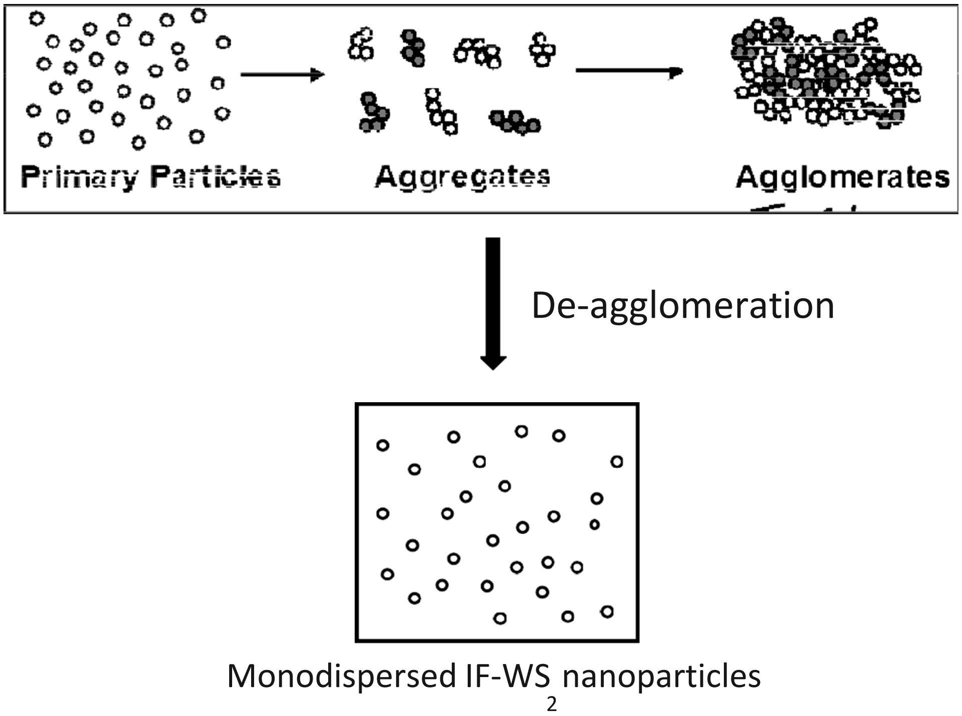

Fig. 2. Schematic of de-agglomeration of the primary agglomerated particles using advanced de-agglomeration technique

The availability of the stable monodispersed dispersion of the *IF*-WS_2 closed-caged nanoparticles (fig.3) have further boosted the research and development of nanotechnology base solid lubricant products. A decade of research and testing have lead to development of series of stable and high performance *IF*-WS_2 base formulations in oil to be used as an additive in lubricant industries and nanocomposite materials for other industries.

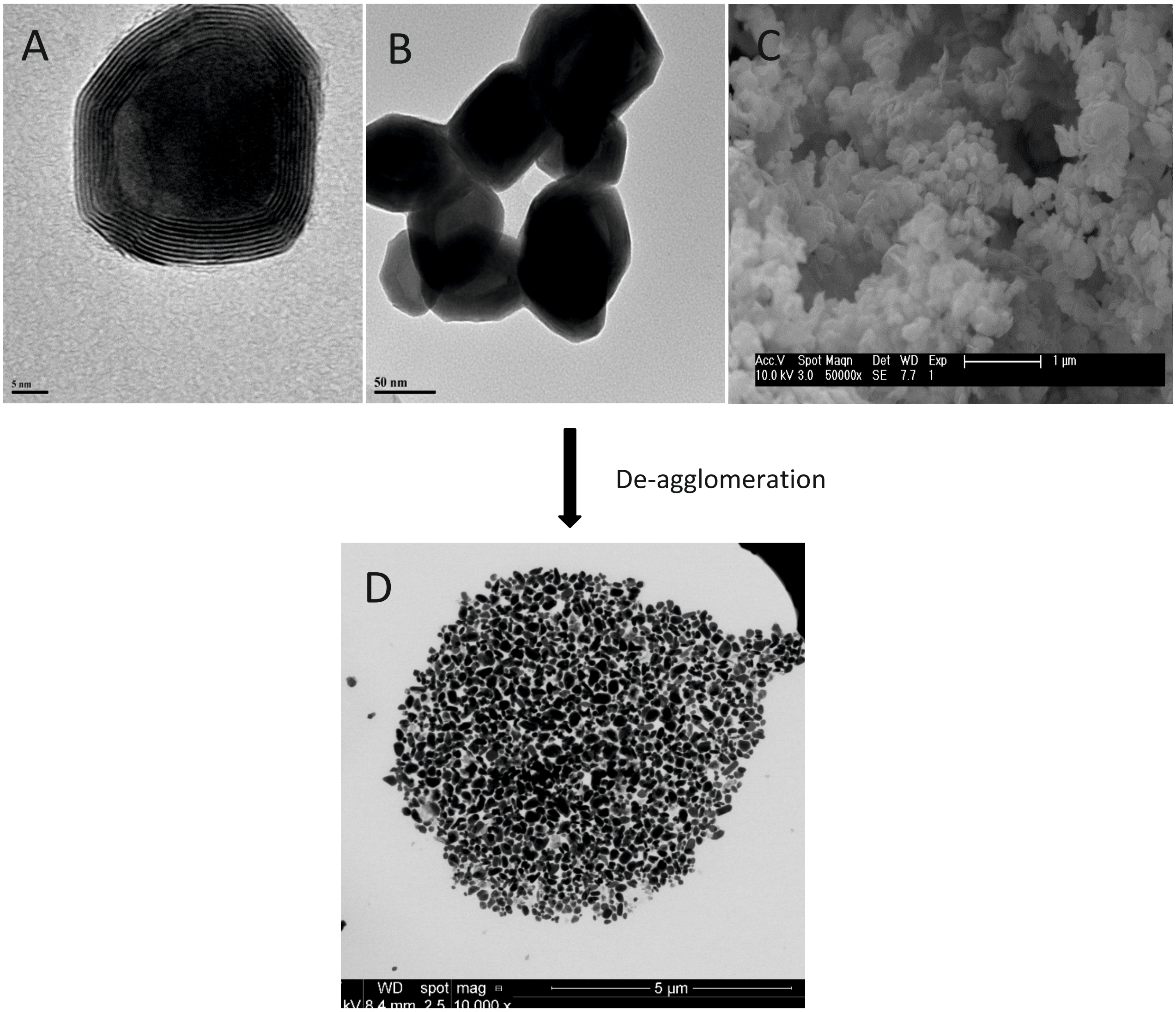

Fig.3. TEM image of (A) single *IF*-WS_2 nanoparticles (B) aggregate of nanoparticles and SEM images of (C) nanoparticle agglomeration (D) self-assembled nanoparticles after de-agglomeration process

Mechanism of IF-WS2 nanoparticles as friction and wear reduction

Lubricating mechanism of *IF*-WS_2 is widely investigated and several mechanism is proposed over the time. Unlike conventional platelet like particle which provide lubrication by sliding, fullerene-like IF-WS2 nanoparticle can lubricate the contact surfaces in various ways depending on lubricating environment including nature of contact surfaces. Initially, it was suggested that due to the spherical nature of the nanoparticle, rolling of the primary nanoparticles across the contact surfaces could be the key reason for lubrications (fig. 4). However, further research revealed several other mechanisms as well based on the operating conditions and nature of contact surfaces.

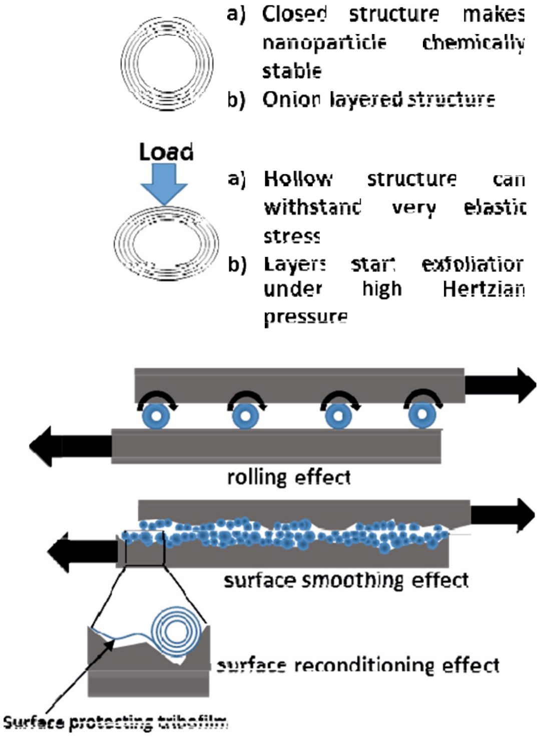

Fig. 4. Schematic of working mechanism of*IF*-WS_2 Nanoparticle as friction and wear reducer and increasing extreme pressure

Transfer of tiny nanoparticle into the asperities of the working metal surface during the process reduces the friction and wear. However, in some lubricating conditions, the spacing between the asperities of two working surfaces are smaller than the size of nanoparticle themselves. Under this condition, the IF nanoparticle are incapable of entering asperities and get partly deform under applied pressure. In this case, the gradual exfoliation (fig. 5) of the external layer of the fullerene-like nanoparticle undercompression and shear stress condition to form a tribofilm on the working surface is another reason for superior lubrication behaviour of the *IF*-WS_2 nanoparticles (13-15). The film formation on the surface shield the asperities, irregular and rough surfaces, thereby making the surface smoother and reduces the friction. Also, due to the unique fullerene-like layer structure with hollow core possessing high elasticity, these nanoparticle behave like tiny ball bearing on the sliding surfaces, thus lowering friction and wear.

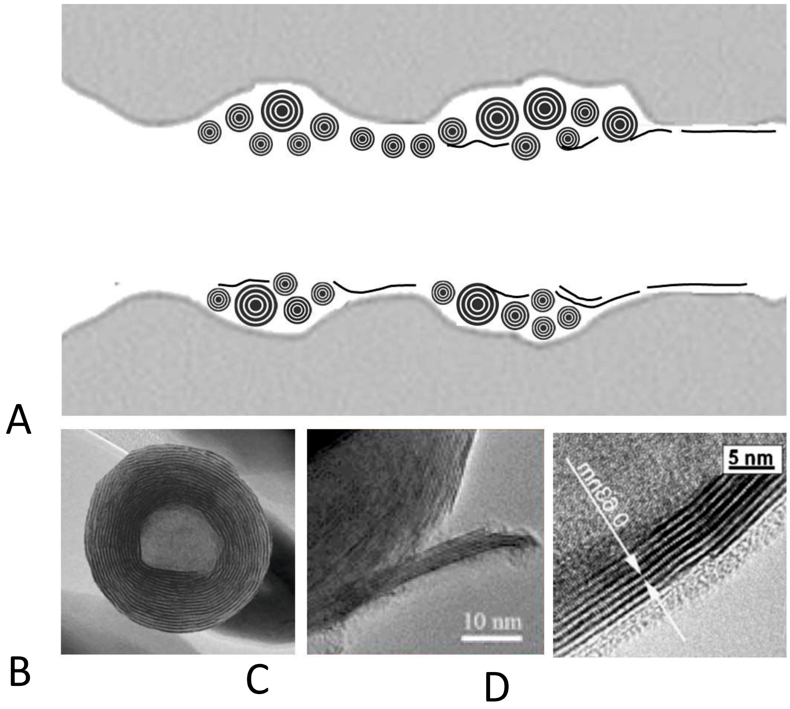

Fig. 5. (A) Schematic of tribofilm formation between metal surfaces. TEM images (B, C, and D) of IF-WS_2 nanoparticle showing tribofilm formation.

Experimental

Materials

Lithium (AP2) and Lithium Complex (LC2) greases were kindly supplied by RajPetro Specialties Pvt. Ltd. (India). Both, LC2 and AP2, greases were NLGI 2 consistency. The commercially available IF-WS_2 nanoparticle based greaseadditive (brand name GHX) and commercially available 2H-MoS_2 were used at different concentrations in abovementioned greases for comparison.

Test description

The mean primary particle size of IF-WS_2 was 100nm. The mean primary particle size for 2H-MoS_2 particle was 3µm. A concentration of selected solid additives in lubricating greases was 1% and 3%. The mixing procedures were conducted via dual asymmetric centrifugal speed mixer DAC150 (FlackTek Inc., USA). Greases and additives were mixed for 4 minutes at 4000rpm to obtain homogeneous solution as shown on Fig.6 .

Properties of lubricating greases were measured via series of tests shown in Table 1 below.

Table 1. Test methods to measure grease properties

Parameters	Test Methods, Ref.No.
Consistency (NLGI grade)	D217
Dropping point, ºC	D566
Four Ball Weld Load, kgs	D2596
Four Ball wear scar diameter, mm	D2266
Worked Penetration 60 Strokes @25ºC, dmm	D217
Copper corrosion Test, 24h @ 100ºC	D4048
Coefficient of Friction	

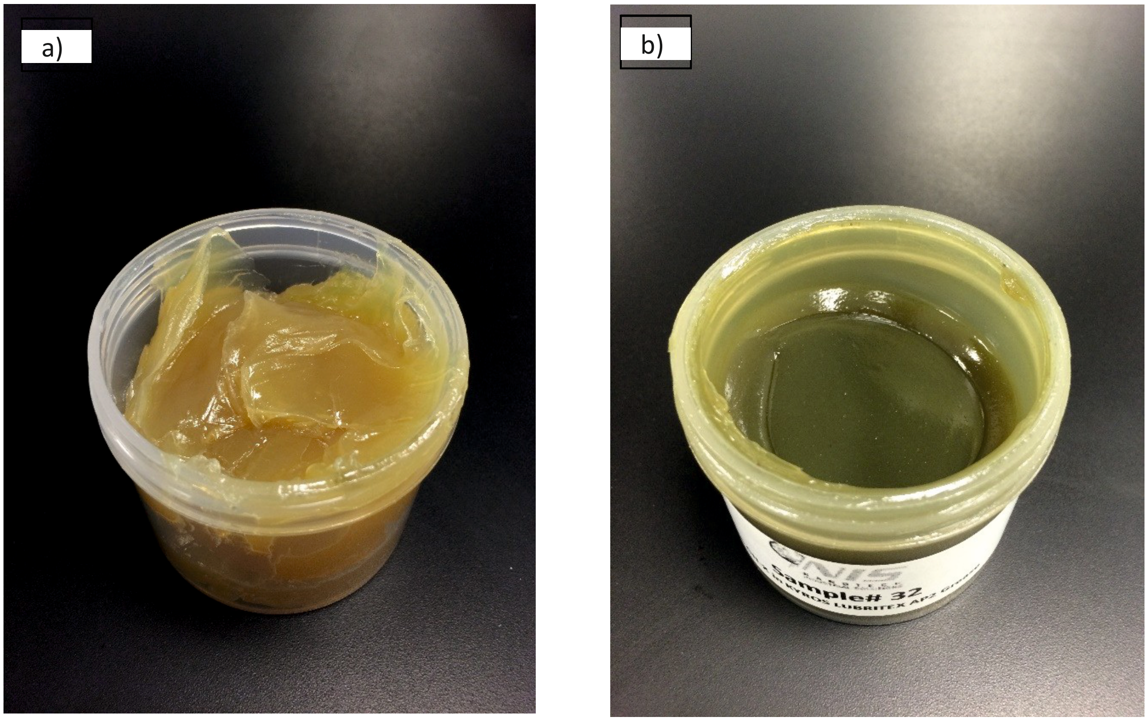

Fig.6. a) base grease b) base grease with 1% GHX after mixing

Results and discussions

Table 2 shows results for AP2 and LC2 greases with 1% and 3% concentrations of *IF*-WS$_2$ based additive and *2H*-MoS$_2$. Figures 7-10 are disclosing the variation of wear scar diameter and Extreme pressure properties as a function of solid particles concentrations. The addition of *IF*-WS$_2$ based solid additive clearly led to significant reduction of wear and increase of extreme pressure properties of both LC2 and AP2 greases.

There was 21%-24% less wear at 1% and 3% concentration of GHX in AP2 grease. There was not observed any anti-wear improvements between 1% and 3% concentration of GHX. On the other hand 1% of *2H*-MoS$_2$ did not improve anti-wear properties of grease and 3% of *2H*-MoS$_2$ gave 4% less wear.

Addition of 1% GHX in LC2 grease resulted in 13% reduction of wear, and 3% of GHX in LC2 grease gave 29.5% of wear reduction. On the other hand 1% of *2H*-MoS$_2$ particles did not result in any wear properties improvements and 3% of *2H*-MoS$_2$ resulted in 4.5% wear reduction.

Addition of *IF*-WS$_2$ or *2H*-MoS$_2$based additive both decreased dropping point of the greases at the same rate. On Lithium base grease (AP2) the dropping point got reduce from 194 ºC to 187 ºC at 1% concentration level and to 185 ºC at 3% concentration level. Further tests will be conducted to understand fundamentally effect of *IF*-WS2 based additive on dropping point.

Table 2. Test results

Parameters	Test Method, Ref. No.	AP2 Base	AP2 + 1% 2H-MoS_2	AP2 + 1% GHX	AP2+ 3% 2H-MoS_2	AP2+ 3% GHX	LC2 base	LC2 + 1% 2H-MoS_2	LC2 + 1% GHX	LC2 + 3% 2H-MoS_2	LC2 + 3% GHX
Consistency (NLGI grade)	D217	2	2	2	2	2	2	2	2	2	2
Dropping point, ºC	D566	194	187	187	185	185	267	245	245	240	240
Four Ball Weld Load, kgs	D2596	126	160	250	315	500	126	160	250	315	500
Four Ball wear scar diameter, mm	D2266	0.68±0.003	0.672	0.52±0.06	0.647	0.545±0.02	0.68±0.006	0.686	0.59±0.001	0.652	0.48±0.03
Worked Penetration 60 Strokes @25 ºC, dmm	D217	269	268	268	265	265	265	264	264	265	265
Copper corrosion Test, 24h @ 100 ºC	D4048	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a
Coefficient of Friction		0.15	0.14	0.13	0.13	0.12		0.15		0.14	
Rust Preventative	D1743			Passed		Passed			Passed		Passed

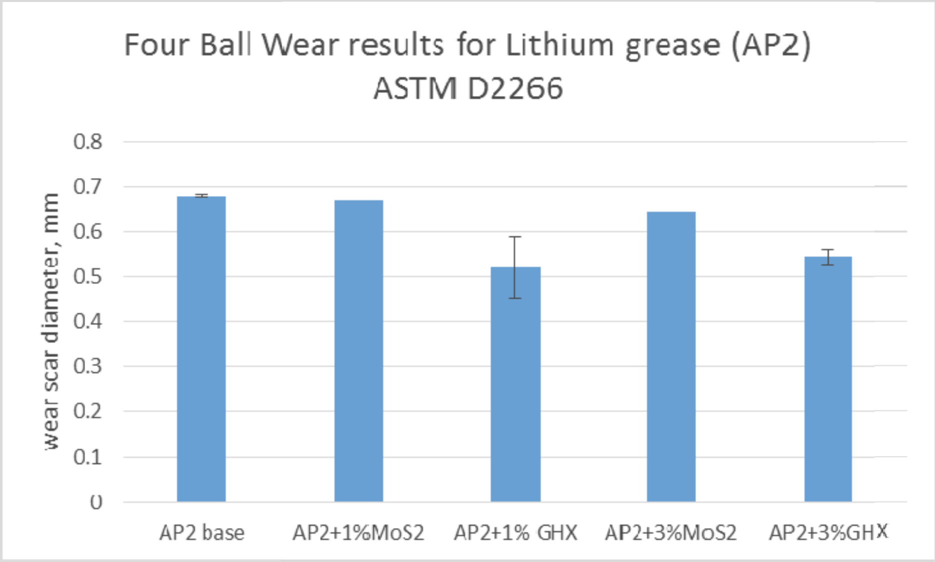

Fig.7. Wear scar diameter of AP2 grease as a function of additive concentration

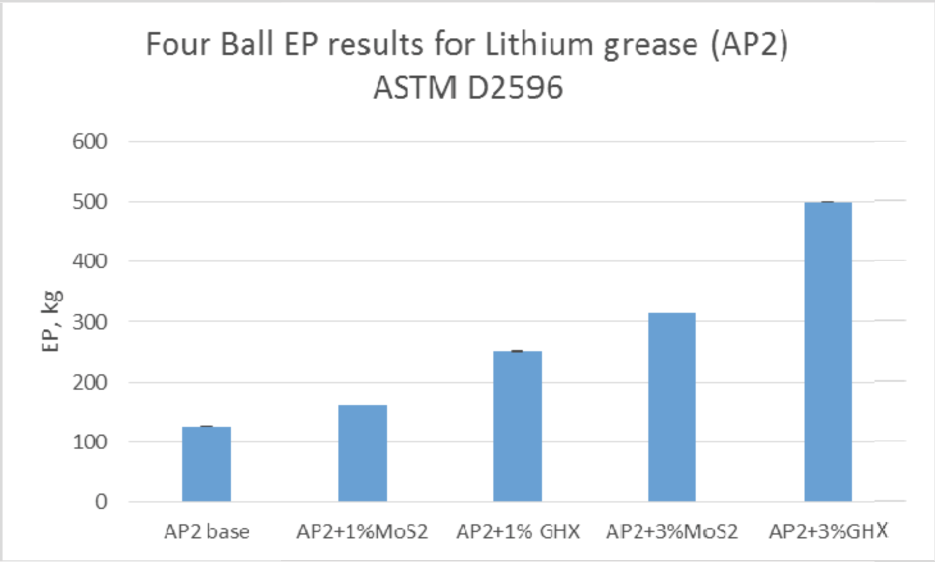

Fig.8. Extreme pressure properties of AP2 grease as a function of additive concentration

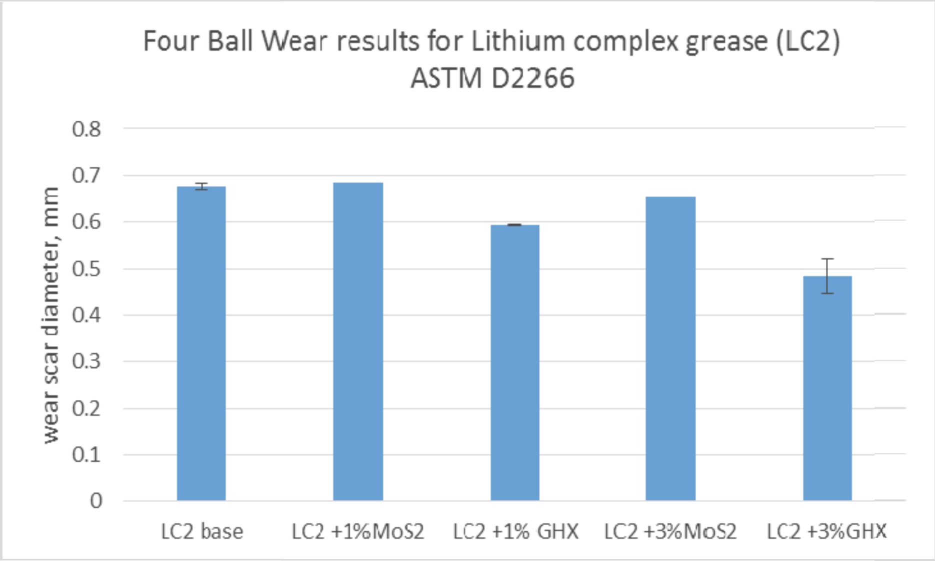

Fig.9. Wear scar diameter of LC2 grease as a function of additive concentration

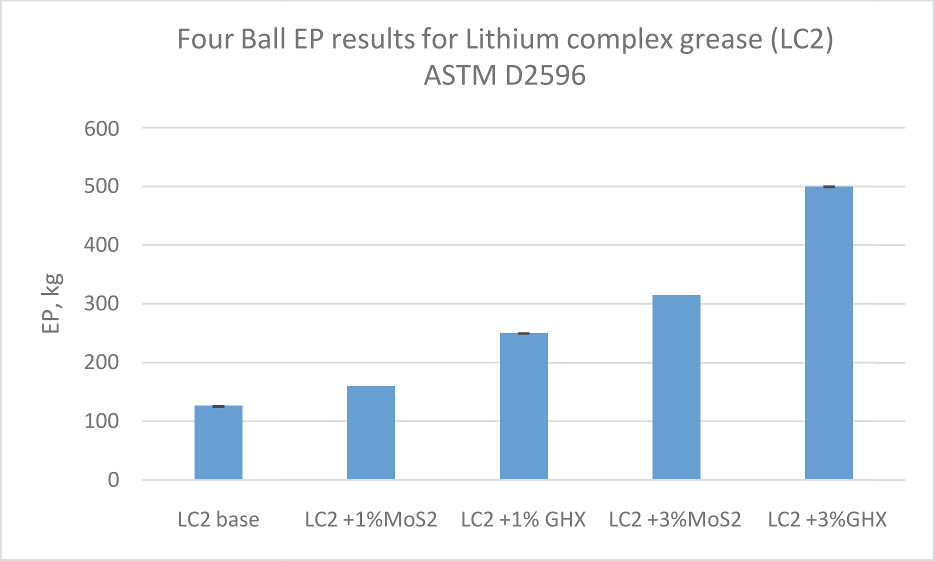

Fig.10. Extreme pressure properties of LC2 grease as a function of additive concentration

Conclusions

Lithium and Lithium Complex greases containing novel inorganic fullerene-like nanoparticles of tungsten disulfide (*IF*-WS_2) exhibit excellent wear reduction and extreme pressure increase properties. *IF*-WS_2 nanoparticles outperform platelet type particles (*2H* MoS_2) due to controlled morphology and size. For example, *IF*-WS_2basedLi and LiX greases exhibit wear scar diameter reduction up to 29.5% with significant improvement of EP properties up to 6 load stages reaching 500kg at 3% concentration.

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Intrinsic Antiwearand Extreme-Pressure Performance of Calcium Carbonate Micelles as Thickener – A Review on Overbased Calcium Grease Technology Ruiming

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Abstract: There are many versions of overbased calcium grease. Overbased calcium sulfonate complex grease is the one most popular and well-studied, while overbased calcium oleate complex grease has its unique advantages in terms of using renewable resources and environmental friendly nature of the thickener system. There are also reports on overbased calcium salicylate grease. In principle overbasedphenate grease should also be possible, though there are no major reports on overbased calcium phenate grease yet.

The common feature of all these overbased calcium greases is calcium carbonate micelles as the key components of the grease thickener system. The excellent antiwear and EP properties of these greases are intrinsic to the grease thickener instead of relying on performance additives. It is believed that such intrinsic antiwear and EP properties are derived from submicron or nano particles of crystalline calcium carbonate miclles either in the form of calcite or vaterite.

Present paper provides a review and comparison on antiwear and EP performance of several popular overbasedcalcium grease technologies and discussion on possible further improvement on the EP performance of such greases as well.

Introduction

There are many versions of overbased calcium grease. Overbased calcium sulfonate complex grease is the one most popular and well-studied, while overbased calcium oleate complex grease has its unique advantages in terms of using renewable resources and environmental friendly nature of the thickener system. There are also reports on overbased calcium salicylate grease. Though overbasedphenate grease might also be possible, so far the author is not aware of any major reports on overbased calcium phenate grease yet.

The common feature of all these overbased calcium greases is calcium carbonate micelles as the key components of the grease thickener system. The excellent antiwear and EP properties of these greases are intrinsic to the grease thickener instead of relying on performance additives. It is believed that such intrinsic antiwear and EP properties are derived from submicron or nano particles of crystalline calcium carbonate micelles either in the form of calcite or vaterite.

This present paper is aimed to provide an overall review on overbased calcium grease technology as an independent type of grease thickener system andthe term of overbased calcium grease is used to include various types and versions under this unique grease thickener system. Under this seemingly very broad subject, specific comparisons were made of the different types and version. Due to author's limited knowledge and experiences in the field, such a review is not an attempt to try to be inclusive, rather it probably be better considered as a current status summary of some random comparisons within this particular area.

Brief History

The first overbased calcium grease was developed almost 50 years ago as a gelled form of overbased calcium sulfonate from high TBN (300 to 500 mg KOH/g) liquid Newtonian calcium sulfonate (1-3). These early versions of overbased calcium sulfonate grease can be considered as simple form of calcium sulfonate grease since the gelation process only involves a simple conversion from amorphous calcium carbonate to crystalline calcium carbonate without any additional complex steps. These simple gelled form of calcium sulfonate more often used in other applications rather than lubricating greases, such as rust inhibition for vehicle undercoating (4) or as bearing cleaning compound (5), utilizing the excellent rust inhibition or detergency properties of such thickened compositions.

Today, the widely known and most popular form of overbased calcium grease is the calcium sulfonate complex grease. Calcium sulfonate complex greases were developed from the simple calcium sulfonate grease and introduced to the market more than 20 years ago (6-10). It has gained significant commercial interest and popularity in recent years. It is the only grease thickener system which has enjoyed a more than 30% annual growth rate by a recent grease production survey (11), albeit from a relatively small base. Expiration of certain key calcium sulfonate complex grease patents, and improved availability of key raw materials, i.e. high TBN Newtonian calcium sulfonate suitable for grease making, may explain partially the trend. However, the real driving force for the popularity of this relatively new grease thickener technology is the fact that the thickener system can also provide several key intrinsically superior grease performance functionalities without any or with minimal use of grease performance additives. The thickener system for the calcium sulfonate complex grease probably can be considered as one of the most complex among all complex greases. It is believed that the main component of this thickener system, i.e. calcium sulfonate covered crystalline calcium carbonate in micelle form is the key to its inherent high load carrying or extreme pressure capability, excellent water resistance and rust inhibition performance. The pseudo particle nature of calcium sulfonate covered calcite micelle further explains its high temperature performance similar to most particle thickened greases like bentonite clay or fumed silica thickened greases.

Traditionally, the key raw material used in making overbased calcium sulfonate grease was obtained through overbasing of natural or petroleum sulfonate. Natural or petroleum based sulfonates are either a by-product of API group I base oil refining process or a co-product of the white oil refining process. But the availability ofsuch petroleum sulfonate for grease making is in serious doubt either due to major trend inshifting from group I base oil group II and III base oil or complete shutdown of such refining unit due to corrosive nature and environmental concerns. The closure of Shell Martinez Refinery's sulfonation unit in 2003 was a typical example of such trend.Today most high TBN calcium sulfonates used for grease making are probably synthetic in nature and obtained through several synthetic process from alkylation of benzene, sulfonation of alkylbenzene to overbasing of alkylbenzen sulfonate.

Thickening mechanism (Soap fiber thickening vs. particle thickening)

When we look at grease thickener systems, traditionally we can divide it into two families, metallic soap thickened and non-soap thickened. One can also divide grease thickener system based on the interaction between the thickener and base oil. Then it can be divided into fiber thickened and particle thickened. Most metallic soap thickened greases are fiber thickened, in which the soap fiber forms a three dimensional web structure so that it acts like a sponge which adsorb and hold the base oil and additives inside this three dimensional web structure. But if we look at purely at fiber thickening mechanism, then polyurea and polymer thickened greases should also be considered as fiber thickened. In these system, instead of metallic soap fiber forms a three dimensional web, it is the organic polymer which forms a three dimensional web which in turn absorbs oil just like metallic soap fiber does. On the other hand, the particle thickener system relies on fine particle size and ability of such particle to adsorb oil. The typical particle thickened greases include organophilic clay based thickens like bentonite clay, fumed silica thicken grease and micronized and activated PTFE particle thickened PFPE grease. Here the high surface area and surface affinity to oil molecules are the key factors for these particle thickened greases. All soap fiber thickened grease has a well-defined dropping point while most particle chickened greases do not have a well-defined dropping point or no dropping point at all. Try to determine which category that overbased calcium grease will belong might be tricky. It contains crystalline calcium carbonateparticles at its core of the micelles, but these are not purely solid particles in this strict physical meaning. On the other hand, so far there isno evidence of any fibrous structure being observed in any overbased calcium greases, even when additional 12-hydroxystearic acid is added as the complexing agent in the case of calcium sulfonate complex grease.

Therefore, overbased calcium greases are neither particle thickened nor fiber thickened. It is a hybrid of both particle thickener and soap fiber thickener system. Many advantages of this grease technology can be attributed to this hybrid thickener system. Its high dropping point is more similar to a particle thickened grease while its stable thixotropic property is a reflection of similar interaction between the thickener and base oil close to those of soap fiber thickened greases.

Calcium Sulfonate Complex Grease vs. CalciumOleate Complex Grease

Calcium sulfonate complex greases made either from high TBN petroleum sulfonate or synthetic high TBN sulfonate have many desirable performance attributes. But due to the availability of petroleum sulfonate and relatively high cost of the synthetic high TBN sulfonate, there is always a need if a grease technology, in this case thickener system in particular, is based on readily available materials from renewable resources rather than based either directly or indirectly from petroleum. Calcium oleate complex grease was developed in this background to meet the needs in terms of both environment friendly nature and from the renewable resources since most high oleic acid was derived from various high oleic vegetable oils instead of based on petroleum.

First overbased calcium carboxylates grease was introduced by Reddy et al (12) in 2005 as a novel grease technology to meet such challenging demands. This new technology based on nano-particles of calcium carbonate had the potential as an alternative to the high performance overbased calcium sulfonate complex grease technology. Like any new technology in its embryonic stage, it takes time and resources to grow, to materialize and hopefully to reach final perfection. After couple years of continuous efforts for further improvement and debugging, a modified version of overbased calcium carboxylate grease precursor was developed in early 2008 (13). The modified version is still based on oleic acid derived from either vegetable oils or animal fats. But it is more concentrated and has a higher Total Base Number (TBN at about 330 mgKOH/g) for better grease thickening efficiency.

Along with the modified version of overbased calcium oleate grease precursor, several different ways to make high performance overbased calcium oleate grease were also developed (14).

When overbased calcium carboxylates grease precursors were first introduced, the suggested grease making procedure follows a simple conversion from the Newtonian liquid grease precursor to Non-Newtonian thixotropic grease. During such conversion, amorphous calcium carbonate particles about 30 nm in size contained in the grease precursor are converted to micelles of crystalline calcium carbonate (12). Attendant to this morphological change is the rheological change, i.e. the grease precursor as Newtonian liquid changes into a non-Newtonian thixotropic gel or grease. The thickened composition generated from this simple morphological change can be called simple overbased calcium carboxylate grease, similar to simple overbased calcium sulfonate grease first developed in 1960s and early 1970s (1-3). These earlier versions of simple calcium sulfonate grease were more often used in other applications rather than lubricating greases, such as rust inhibitor for vehicle undercoating (4) or as bearing cleaning compound (5), utilizing the excellent rust inhibition or detergency properties of such thickened compositions.

Simple overbased calcium greases, either based on calcium sulfonates or calcium carboxylates, have their own intrinsic deficiencies. Such deficiencies limit their wide spread use as high performance lubricating greases. These deficiencies are manifested either in their poor thickening efficiency, i.e. low oil incorporation or poor shear stability, to just name a few.

In order to overcome such deficiencies intrinsic to simple overbased calcium greases, especially those for a simple version of overbased calcium oleate greases, a reaction step involving a complexing agent is introduced into the grease making procedures (14). The complex reaction step involves additional reaction between the gelled thickener elements with additional 12-hydroxystearic acid either alone or in combination with some other inorganic acids, such as phosphoric acid or boric acid. It is believed that the hydrogen bonding provided by 12-hydroxystearic acid adds additional bonding between grease thickener elements. Such hydrogen bonding makes thickener structure more robust and more shear resistant.

In the case of simple overbased calcium oleate grease, the thickener element is composed of each individual micelle of crystalline calcium carbonate dispersed in the oil phase with calcium oleate as dispersant. After the complexing reaction, calcium carbonate micelles covered by calcium oleate are essentially turned into calcium carbonate micelles covered both by calcium oleate and calcium 12-hydroxystearate. The hydrogen bonding between these crystalline calcium carbonate micelles partially covered by these mixed carboxylates makes the interaction between thickener and oil far more complex. Such complex interactions are well established in the existing grease technologies, such as aluminum complex grease, lithium complex grease and overbased calcium sulfonate complex grease as well. All these grease platforms involve hydroxyl group on the thickener molecules in one form or the other. To illustrate such differences and their effects on grease performance, comparison test data on simple and complex version of overbased calcium oleate grease are listed in Table 1 (16).

Table 1. Comparison of simple and complex version of overbased calcium oleate grease

Grease Characterization	**Grease Type**	**Experimental FG simple Ca oleatebase grease***	**Experimental FG Ca oleate complex base grease****
Thickener		**Ca Oleate simple**	**Ca Oleate Complex**
Base Oil, type		**600SUS white oil**	**600 SUS white oil**
Percent of precursor, %		**65%***	**34.5%****
Odor/Smell		**Typical**	**Typical**
Thickener Biobased		**Yes**	**Yes**

Grease Test	ASTM Method		
NLGI Grade	D217	2	2
Penetration 60 strokes, mm/10	D217	268	272
Penetration 10k strokes, mm/10	D217	291	269
Mechanical Stability 10k strokes, %change	D217	+8.6	-1
Roll Stability 2 hrs @ 77°F, %	D1831	12.85	N/A
Drop Point, °C (F)	D2265	288 (550)	349 (660)
Water Washout @ 175 °F, %lost	D1264	11.9	5.24

Timken OK Load,kg (LBS).	**D2509**	**13.6 (30)**	**20.4 (45)**
Four Ball Wear, mm	**D2266**	**0.44**	**0.43**
Four Ball EP	**D2596**		
Load Wear Index		**35**	**46**
Weld, kg		**315**	**400**
Oxidation Stability	**D942**		
100 hours kPa (PSI) loss		**18.5**	**70**
500 hours kPa (PSI) loss		**71.5**	**75**
Rust Inhibition/Bearing Corrosion	**D1743**	**1,1,0 Pass**	**1,1,0 Pass**
Copper Corrosion	**D4048**	**1b**	**1b**
Wheel Bearing Leakage, grams	**D1263**	**0.07**	**0.2**
Oil Separation, % Loss	**D1742**	**0.38**	**0.03**
Evaporation loss, % Loss @99°C	**D972**	**25.4***	**0.65**
Grease Mobility, g/min. -18°C	**USS**	**0.51**	**4.2**
Low Temperature Torque @ - 18°C	**D1478**		
Start, g-cm		**832**	**780**
60 minutes, g-cm		**221**	**260**

*Note: Based on overbased calcium oleate grease precursor with 10% calcium content with low viscosity diluent oil and volatile solvent.**Note: Based on overbased calcium oleate grease precursor has a calcium content of 15% with low volatility diluent oil.

The advantages of calcium oleate complex grease over the simple version are very obvious. Since all these grease performance tests were conducted on base greases without any performance additives, it is easy to draw the conclusion that these desirable grease performance attributes are provided by the complex thickener system. In other words, the complex thickener system in the calcium oleate complex grease is multifunctional. Not only does it act as an excellent thickener system for grease (higher dropping point and higher mechanical strength), it also provides the desirable functionalities such as good antiwear and excellent EP properties.

It would be very interesting to compare the grease performance between calcium sulfonate complex grease with the calcium oleate complex grease. Since only available performance data on the calcium oleate complex grease (COCG) was based on an experimental food grade version (2009) it is only fair to compare it withcommercial food grade calcium sulfonate complex grease (CSCG) (15, 16). Typical grease performance data are listed in Table 2 (15).

Table 2. Typical performance data on CSCG and COCG (both food grade type)

Grease Characterization	**Grease Type**	**Commercial FG CSCG grease (15,16)**	**Experimental FG COCG base grease**
Thickener		Ca sulfonate Complex	Ca Oleate Complex
Base Oil, type		95 cSt white oil	600 SUS white oil
Percent of precursor, %		N/A	34.50%
Odor/Smell		typical	typical
Thickener Biobased		No	Yes
Grease Test	**ASTM Method**		
NLGI Grade	D217	2	2
Penetration 60 strokes, mm/10	D217	280	272
Penetration 10k strokes, mm/10	D217	277	269
Mechanical Stability 10k strokes, %change	D217	-1	-1
Roll Stability 2 hrs @ 77°F, %	D1831	2.1 (50%H_2O)	N/A
Drop Point, °C (F)	D2265	318 (604)	349 (660)
Water Washout @ 175 °F, %lost	D1264	0.5	5.24
Timken OK Load,kg (LBS).	D2509	27.2 (60)	20.4 (45)
Four Ball Wear, mm	D2266	0.45	0.43
Four Ball EP	D2596		
Load Wear Index		62	46
Weld, kg		500	400
Oxidation Stability	D942		
100 hours kPa (PSI) loss		N/A	70
500 hours kPa (PSI) loss		6psi @1000hrs	2 (with 0.5% AO*)
Rust Inhibition/Bearing Corrosion	D1743	Pass	Pass
Copper Corrosion	D4048	1b	1b
Wheel Bearing Leakage, grams	D1263	1.0	0.2
Oil Separation, % Loss	D1742	0.1	0.03
Evaporation loss, % Loss @99°C	D972	N/A	0.65
Grease Mobility, g/min. -18°C	USS	19.3	4.2
Low Temperature Torque @ -18°C	D1478		
Start, g-cm		1404	780
60 minutes, g-cm		247	260

*Note: Food Grade aminic type antioxidant was used, treat rate 0.5% by weight.

From the performance data listed in Table 2, it is obvious that there are many desirable performance attributes associated to this novel calcium oleate complex grease. These include high dropping point, high mechanical strength (shear stability), good antiwear and load carrying capability for extreme pressure conditions, i.e. high EP performance, and good low temperature performance as manifested by the grease mobility and low temperature torque test results. Since all these tests were conducted on a base grease without any performance additives (except 500 hrs oxidation test), it is easy to draw the conclusion that these desirable attributes are provided by the thickener system. In other words, the thickener system in the calcium oleate complex grease is multifunctional. Not only does it act as an excellent thickener system for grease, it also provides the desirable functionalities such as antiwear and EP properties.

Origin of Antiwear and EP Performance in Overbased Calcium Greases

The intrinsic high performance of overbased calcium grease in antiwear and EP is believed to be derived from crystalline calcium carbonate. Micronized or nano particles of crystalline calcium carbonate in its most stable form of calcite is well known as one type of special EP additive called passive EP additive. Different from traditional EP chemistries of chlorine, phosphorous and sulfur, all rely on fast reaction with newly generate metal surface under EP conditions to prevent localized welding of metal surfaces, passive EP additive prevents welding by forming an inert physical barrier layer between two surfaces under EP conditions.

In cases of calcium sulfonate complex grease, the Newtonian overbased calcium sulfonate precursor is exclusively converted to Non-Newtonian semi-solid grease containing crystalline calcium carbonate in calcite form.On the other hand, foroverbased calcium oleate grease, such conversion results exclusively crystalline calcium carbonate in vaterite form.It is believed that the packing difference of a surface layer of calcium sulfonate or a surface layer of calcium oleate, which acts as a template for the formation of crystalline calcium carbonate. In other words, calcium sulfonate leads to calcium carbonate in calcite form and calcium oleate leads to calcium carbonate in vaterite form.

The formation of vaterite form of calcium carbonate in calcium oleate grease was reported in 2009 (15). In the case of oberbased calcium oleate grease, the conversion of the Newtonian overbased liquid grease precursor to Non-Newtonian semi-solid grease is a reflection of the morphological change associate with calcium carbonate contained in the grease precursor.

There are several analytical techniques which can be used to study this conversion from Newtonian overbased liquid to Non-Newtonian grease (12). Since the conversion is a reflection of morphological change, i.e. a phase transition from amorphous calcium carbonate to crystalline calcium carbonate, structural analysis techniques should be best suited for characterization of such change. X-ray Diffraction (XRD) and FTIR Infrared Analysis techniques have been employed to study the gellation process. As an example, X-ray diffraction patterns of non- crystalline overbased calcium oleate grease precursor, gelled thixotropic grease showing crystalline calcium carbonate in Vaterite form, and pure calcium carbonate powder in Vaterite crystal structure (prepared through wet chemistry method) are shown in Figure 1.

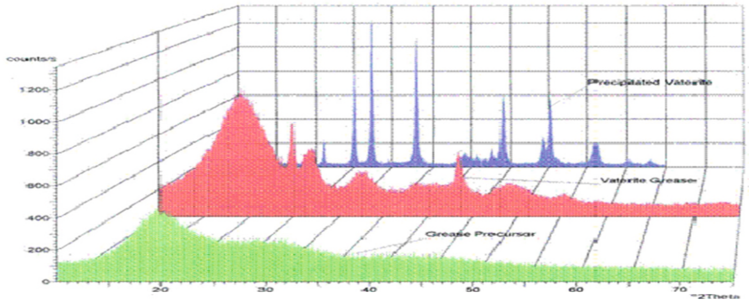

Figure 1. XRD patterns for amorphous grease precursor (lower spectrum), gelled grease containing Vaterite crystalline calcium carbonate (middle spectrum) and pure crystalline calcium carbonate precipitated through wet chemistry method (upper spectrum).

The lack of any sharp diffraction peaks for the grease precursor shown in Figure 4 clearly indicates the amorphous or non-crystalline nature of the liquid grease precursor. Once the grease precursor is converted to grease, diffraction peaks characteristic of Vaterite crystal form can be seen at 25 °2θ, 27 °2θ and 32.8 °2θ. These peaks match well with the XRD pattern obtained from pure Vaterite calcium carbonate powder precipitated through a wet chemistry method (upper spectrum of Figure 4). Since the diffraction peak at 29.2 °2θ is a dominant diffraction peak for the Calcite crystal form of calcium carbonate, the lack of diffraction peak at 29.2 °2θ indicates that when the amorphous grease precursor converts to crystalline calcium carbonate, it coverts exclusively to Vaterite crystal form.

This phenomenon is different than what is typically observed with overbased calcium sulfonate grease systems, where Calcite calcium carbonate will be the dominant crystal form. Due to the laminar structure of the Calcite calcium carbonate, each Calcite particle acts like a minute deck of cards which slides easily along the surface to provide protection and prevent direct surface to surface contact. It is generally believed that Calcite crystal form is more desirable in the calcium sulfonate grease thickener system, while Vaterite calcium carbonate is less desirable (12, 15). Such a conclusion might be true for the calcium sulfonate complex grease thickener system, but it certainly cannot be extended to the calcium oleate complex grease thickener system. The grease performance data on exclusively Vaterite particle based calcium oleate complex grease showed the same, if not better, high antiwear and high EP properties as calcium sulfonate complex grease. Therefore, if the visualized picture for Calcite particles to cover and protect the underlying metal surface is that each particle acts like a minute deck of cards, then due to the spherical crystal structure of Vaterite calcium carbonate, the nanometer sized Vaterite particles can be imagined as a group of miniature marble balls. An illustration for such group of miniature balls in between the two metal surfaces is given in Figure 2. Figure 2 showed groups of Vaterite micelle particles in between two metal surfaces in relative motion under normal load. When the load is increased from normal to extreme, the Vaterite micelle particles spread out on the surface and effectively cover the whole surfaces and prevent direct metal to metal contact, as shown in Figure 2. Though a quantitative comparison between the antiwear and EP properties of Calcite particles and Vaterite particles is beyond the scope of present study, nevertheless, the grease performance data indicates strongly that these nanometer sized marble balls are as effective as those minute decks of cards in terms of effectively separating the two metal surfaces in relative motion, reducing friction and wear (for simplicity, asperities on the surfaces are not shown).

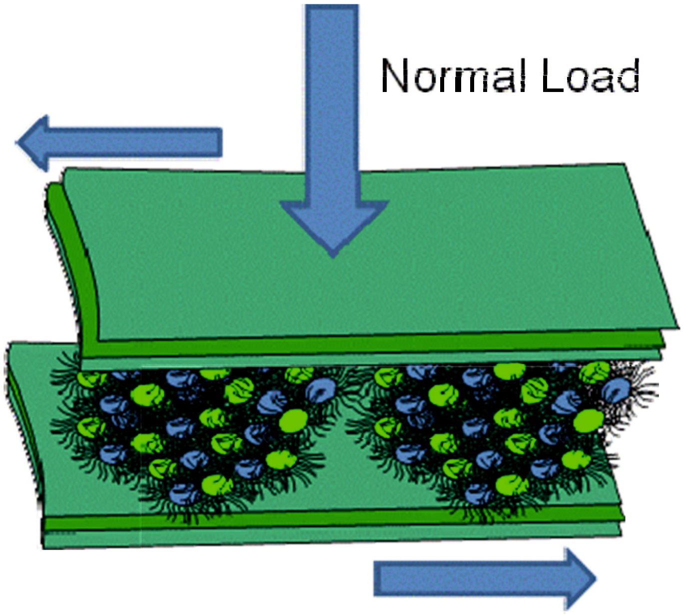

Figure 2.Group of Vaterite micelle particles in between two metal surfaces in relative motion under normal load.

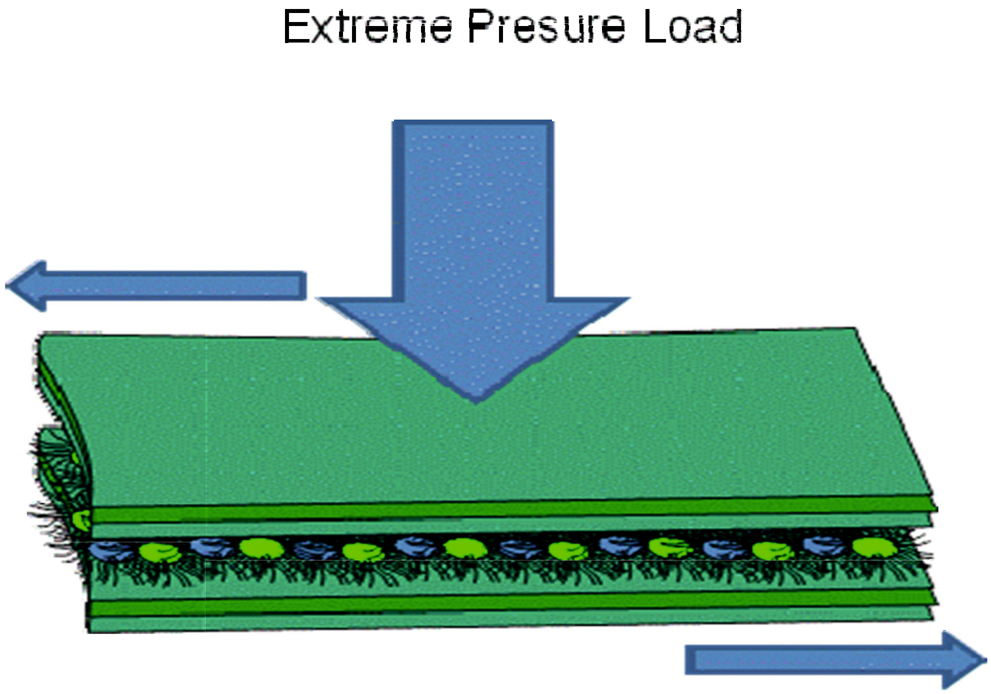

Figure 3.Vaterite micelle particles spread out in between two metal surfaces in relative motion under extreme pressure load.

Conclusion

The common feature of all overbased calcium grease is sub-micron crystalline calcium carbonate. The micelles of calcium carbonate either covered with calcium sulfonate in the case of calcium sulfonate complex grease or covered with calcium oleate are the main components of the grease thickener system. The type of ligand on the micelle will determine the crystal structure of these minute particles of calcium carbonate formed during the conversion reaction from amorphous calcium carbonate to crystalline calcium carbonate. In the case of calcium sulfonate complex grease, calcite is formed while in the case of calcium oleate complex grease, vaterite is formed exclusively as a stable form. The complex reaction after the conversion of Newtonian liquid overbased calcium grease precursor to semi-solid non-Newtonian grease further improves the rheological property of the grease. Such improvements are reflected in terms of higher thickening efficiency, higher dropping point, higher shear stability and higher EP performance. It is believed that complex reaction in combination of micelle nature of the sub-micron calcium carbonate makes this particular thickener system as a hybrid between particle thickener system and soap fiber thickener system.

It is also believed that these sub-micron calcium carbonate micelles are the origin of many of the desirable grease attributes, especially in terms of excellent antiwear and high EP performance.

These calcium carbonate micelles act as passive EP additive and effectively build a physical barrier between two metal surfaces under extreme pressure conditions.

With the further improvement on the availability of various high TBN overbased calcium grease precursors, either as synthetic calcium sulfonate dedicated for grease making only, or food grade version of calcium sulfonate, oroverbased calcium oleate, the overbased calcium grease will become more popular in the near future.

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