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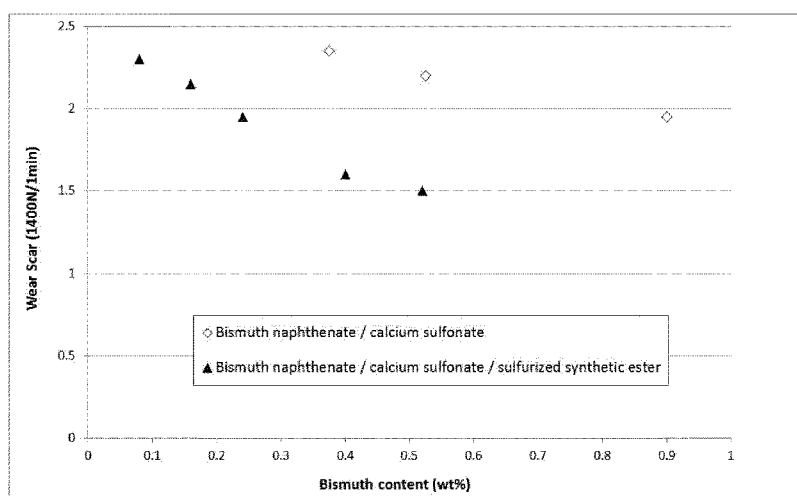
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(54) Title: GREASE COMPOSTION AND METHOD FOR MAKING THE SAME

Figure I. Wear scar



(57) Abstract: The present invention relates to a grease composition comprising a lubricating base oil, a polymeric thickener which comprises a polymer of propylene and a metal sulfonate. The present invention further provides a method for preparing the grease composition, the use of the grease composition for lubricating a mechanical component having a metal surface, and the use of a metal sulfonate in a grease composition which contains a polymeric thickener comprising a polymer of propylene for reducing friction on a mechanical component which has a metal surface.

GREASE COMPOSTION AND METHOD FOR MAKING THE SAME

FIELD OF THE INVENTION

The present invention relates to a grease composition, a method for preparing the grease composition, the use of the grease composition for lubricating a mechanical component having a metal surface, and the use of a metal sulfonate in a grease composition for reducing friction on a mechanical component having a metal surface.

BACKGROUND OF THE INVENTION

Grease compositions are widely used for lubricating bearings and other structural components. A grease is an essential product to reduce, for example, wear, friction, corrosion, running temperatures and energy losses.

Greases are materials which comprise a base oil that is thickened, for example using a metal soap or calcium sulfonate as thickening agent. This provides greases with the desired physical and chemical structure needed for sustained lubrication of machine elements under rolling or sliding conditions, as is the case in rolling bearings. There are a number of grease thickeners available, each with its own strengths and weaknesses. Briefly, typical lithium-based greases (the most common) are made from a fatty acid, usually 12-hydroxystearic acid, and a lithium base to produce a simple soap which acts as the grease thickener. In lithium-complex greases, part of the fatty acid is replaced with another acid (usually a diacid), which makes the complex soap. Calcium sulfonate greases can be used as an alternative for soap-based greases. They have the potential of providing high performance without the presence of additives.

Components are added to grease to provide essential extreme-pressure/anti-wear performance, and other desirable properties that allow equipment to run at peak performance. The function of such additives is to minimize wear, and to prevent scuffing and welding between contacting surfaces. Additives may also form a friction-reduction film following the physical-chemical reaction of the additives on the lubricated metal surface, resulting in desired properties of reducing friction and operating temperature.

An important performance benefit of grease compositions lies in the use of synergetic components. It is highly desirable that the additives incorporated, but also the thickening agent, (i) provide a synergetic improvement of different properties such as extreme
5 pressure/anti-wear properties, friction reduction, and corrosion protection; (ii) prevent a negative impact on other properties, for example lubricant film formation, or grease mechanical stability, or low temperature performance, (iii) achieve the desired performance at the lowest possible overall additive concentration.

10 In many applications, exposure to water or high humidity levels requires the use of greases that are highly effective in protecting against corrosion. Anti-corrosion additives are often surfactants that neutralize acids on the surface of metal. These can also repel water by creating absorption to form an oil-like surface, or by providing a barrier through incorporation in a physical-chemical surface-film.

15 Conventional greases such as lithium 12-hydroxide stearate-based grease compositions leave room for improvement in terms of anti-friction and anti-corrosion properties. Due to the strong polar interaction between thickener and lubricated surface, the effectiveness of grease additives is reduced, or alternatively, effective performance can only be achieved by
20 increasing the additive concentration.

Calcium sulfonate thickened greases can be used as an alternative for soap-based greases. They have the potential of providing high performance without the presence of additional additives, owing to the interaction with the metal surface, and the neutralizing ability, of the
25 calcium sulfonate thickener. They combine properties of a good mechanical stability, very strong extreme-pressure/anti-wear performance, and excellent rust protection. Although calcium sulfonate greases have desirable properties, the downside is the high concentration of calcium sulfonate concentration needed to thicken the grease, as well as raw material cost. The thickener concentration may vary to values as high as 20 to 50 percent in greases.

A further downside in calcium sulfonate grease performance is found to be inferior low temperature performance and limited pumpability due to high thickener content used to make calcium sulfonate greases. Another downside of the performance of calcium sulfonates relates to water sprayoff. In the ASTM D4049 sprayoff test, a thin layer of grease is placed on a panel and sprayed with water. After the test is completed, the percent of grease lost is calculated. Many calcium sulfonate greases typically show significant spray off.

Calcium sulfonate greases are made by converting a fluid detergent that contains amorphous calcium carbonate, to a grease containing calcite particles. Because of the lubricating properties of the calcite particles, performance additives containing sulfur, phosphorous or zinc may not be needed. In general, the art in preparing this class of greases involves converting an overbased colloidal dispersion of amorphous calcium carbonate in oil stabilized by surfactants, into an overbased grease consisting of a colloiddally stable thickener structure of calcite crystals in oil.

The degree of conversion of the amorphous calcium carbonate into the calcite form can greatly influence the properties of the finished grease and therefore the art lies how best one controls the process parameters and incorporate the other performance enhancing ingredients during processing stage.

In lubricating oils, calcium sulfonate is widely used as detergent, inhibitor, neutralizer, and exteme pressure agent. Suitable applications are engine oils, metalworking, automatic transmission fluid, industrial and automotive gear oil additives, as well as other applications. In engine oils, it is economically advantageous to incorporate as much neutralizing power in the sulfonate molecule as possible, which is accommodated by the use of highly overbased sulfonates. Generally, the type of sulfonates marketed can be divided into neutral sulfonates (TBN 1-10), slightly overbased sulfonates (TBN 15-30) and highly overbased sulfonates (TBN 300-400).

Processes for the production of overbased calcium sulfonates are described in British Patent specification Nos. 1299253 and 1309172. U.S. patent 3.365.396 describes a method of preparing an overbased calcium sulfonate concentrate with a base number greater than 250,

suitable for use as a lubricating oil additive. With “overbased” metal sulfonate is meant that a stoichiometric excess of the metal is present over that required to neutralize the anion of the salt. The excess metal from overbasing has the effect of neutralizing acids which may be build up in the lubricant. Typically, the excess metal will be present over that which is required to neutralize the anion at 10:1 to 30:1 on an equivalent basis.

In the art of grease lubrication, it would be highly desirable to combine the advantageous properties of metal-based soap greases with those of calcium sulfonate greases, and simultaneously enable the performance characteristics of calcium sulfonate in oil-lubricated applications. The use of calcium sulfonate additives in lithium-based greases is as such known. Where metal-based soap greases containing calcium sulfonate components lead to improved corrosion protection, they do not lead to substantial friction reduction, and the additive concentrations required are high. Therefore, the advantage of calcium sulfonate components in for instance lithium-based greases cannot be easily recognized when compared with lithium-based greases as such.

SUMMARY OF THE INVENTION

Object of the present invention is to provide grease compositions that display improved lubricant properties when compared with conventional such as lithium 12-hydroxy stearate-based grease compositions and lithium-complex greases that contain calcium sulfonate.

It has been found that grease compositions with improved lubricating properties can be provided when the grease composition comprises in an addition to the lubricating base oil, a particular polymeric thickener and a metal sulfonate.

Accordingly, the present invention relates to a grease composition comprising a lubricating base oil, a polymeric thickener which comprises a polymer of propylene, and a metal sulfonate.

The present grease composition displays improved lubricating properties in terms of friction behaviour, corrosion protection and anti-wear behaviour when compared with conventional

greases such as lithium 2-hydroxy stearate-based grease compositions that contain a metal sulfonate such as calcium sulfonate.

DETAILED DESCRIPTION OF THE INVENTION

- 5 The present invention relates to a grease composition comprising a lubricating base oil, a polymeric thickener which comprises a polymer of propylene, and a metal sulfonate.

Preferably, the present grease composition comprises:

- (a) 1-99 wt% of the lubricating base oil;
- 10 (b) 1-20 wt% of the polymeric thickener; and
- (c) 0.01-15 wt% of the metal sulfonate, all weight percentages based on the total weight of the grease composition.

- 15 The present invention also relates to a grease composition comprising a lubricating base oil, a polymeric thickener which comprises a polymer of propylene, a metal sulfonate, an organometallic compound, and a sulphur-containing organic compound.

- 20 Preferably, the present grease composition comprises:

- (a) 1-99 wt% of the lubricating base oil;
- (b) 1-20 wt% of the polymeric thickener;
- (c) 0.01-15 wt% of the metal sulfonate;
- (d) 0.01-10 wt% of the organometallic compound; and
- 25 (e) 0.01-10 wt% of the sulfur-containing organic compound, all weight percentages based on the total weight of the grease composition.

More preferably, the present grease composition comprises:

- (a) 74-86 wt% of the lubricating base oil;
- 30 (b) 12-16 wt% of the polymeric thickener;
- (c) 2-5wt% of the metal sulfonate;

(d) 0.5-2.5wt% of the organometallic compound; and
(e) 0.5-2.5wt% of the sulfur-containing organic compound, all weight percentages based on the total weight of the grease composition.

- 5 The grease composition according to the present invention comprises a polymeric thickener which comprises a polymer of propylene. The polymeric thickener preferably comprises a first component and a second component, with the first component having a higher weight average molecular weight than the second component.
- 10 Preferably, the polymeric thickener comprises a high molecular weight component and a low molecular weight component, characterized in that the thickener comprises a mixture of (1) a (co- or homo-)polymer of propylene with a weight average molecular weight of more than 200.000 and (2) a (co- or homo-)polymer of propylene with a weight average molecular weight of less than 200.000.
- 15 The polymeric thickener to be used in accordance with the present invention contains a high molecular weight component comprising a (co- or homo-)polymer of propylene with a weight average molecular weight of more 200.000, preferably 200.000-350.000 and a low molecular weight component comprising a (co- or homo-) polymer of propylene with a weight average
- 20 molecular weight of less than 100.000, preferably 50.000-100.000. The weight ratio between the high molecular weight component and the low molecular weight component in the polymeric thickener can be 1:40 - 3:1, suitably 1:40-1:1, preferably 1:40 - 1:5, more preferably 1:25 - 1:15, and most preferably 1:18-1:20. Outside this preferred range for the weight ratio between the high and low molecular weight components the final lubricating
- 25 grease composition will generally not have desired application properties, in particular mechanical stability and consistency, i.e. be too "rubbery/elastic" and/or too "buttery". However, as the properties of the final composition are also dependent on the lubricant base oil and additives incorporated in grease compositions, as well as on the way the composition is prepared, other ratios may also be used for obtaining the desired properties of the final
- 30 composition, as is well known to a man skilled in the art.

According to the present invention, the low molecular weight component is preferably a polypropylene homopolymer, more preferably a polypropylene homopolymer with a melt flow rate of 500-1500 dg/min., especially 750-1250 dg/min. as determined by test ASTM D 1238 L.

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The high molecular weight component preferably has a melt flow rate (ASTM D-1238) of 1.5-15, more preferably 1.5-7, especially 3-5. The low molecular weight component is preferably a polypropylene homopolymer. Preferably, the high molecular weight component is a polypropylene homopolymer or a propylene/ethylene-copolymer.

10

The polymer thickener is suitably used in the present grease composition in an amount in the range of from 1-20, preferably in an amount in the range of from 5-15, based on the total weight of the grease composition. Other amounts can be used if desired.

15 Apart from the polymeric thickeners mentioned in detail hereinabove, the present grease composition may also contain other polymeric thickeners.

It has been discovered that the grease composition in accordance with the present invention which comprises a polymeric thickener which comprises a polymer of a propylene, and a
20 metal sulfonate exhibits unexpected enhancement of corrosion protection, extreme pressure/anti-wear performance, and friction reduction. In addition, the bearings tested using the grease composition of the invention, showed strongly improved film-building properties, and even the formation of permanent protective films.

25 The present grease composition comprises a metal sulfonate. Suitably, the metal of the metal sulfonate is an alkali metal or an alkaline metal of Groups 1 and 2 of the Periodic Table. Preferably, the metal of the metal sulfonate component is a metal of Group 2 of the Periodic Table. Preferably, the metal sulfonate is oil-soluble Group 2 metal salt of a synthetic sulfonic acid or a natural sulfonic acid. Any metal sulfonate with a metal of Group 2 can be used in
30 accordance with the present invention. Preferably, a calcium sulfonate or magnesium sulfonate is used. More preferably, a calcium sulfonate is used.

The metal sulfonate is suitably used in the present grease composition in an amount in the range of from 0.01-15 wt%, preferably in an amount in the range of from 2-6 wt%, based on the total weight of the total grease composition. Other amounts can however also be used, if
5 desired.

The metal sulfonate components in which the metal is a metal of Group 2 of the Periodic Table are surface active and have the ability to lower the surface tension of liquids in which they are incorporated. An outstanding characteristic of these metal sulfonates is their capacity
10 to hold in stable suspension dispersed salts of metals of Group 2. Relatively high concentrations of basic metal salts in which the metal is a metal of Group 2 can thus be used in addition to lubricants to neutralize acidity, improve extreme pressure/anti-wear performance, and provide protection against corrosion. It is therefore preferred that the present metal sulfonate component in which the metal is a metal of Group 2 incorporates
15 therein a basic metal inorganic salt in which the metal is a metal of Group 2. Preferably, the metal sulfonate to be used in accordance with the present invention is an overbased metal sulfonate, more preferably, an overbased calcium sulfonate. The meaning of "overbased" has been given hereinabove.

In accordance with the present invention use is made of an organometallic component. Suitable organometallic components are those that contain zinc, lead, tin, tungsten, molybdenum, niobium, lanthanum, antimony, bismuth, chromium, or vanadium. Any organometallic compound which is suitable for use as an additive, especially an extreme pressure additive, in lubricant grease or lubricant oil compositions can be used in accordance
20 with the present invention. The organic moiety of the organometallic component may include alkyl, alkaryl, or aralkyl groups. The organic moiety may also include sulfur and/or phosphorus.

Preferably, the organometallic compound comprises a metal carboxylate. The metal of the
30 metal carboxylate is suitably an alkali metal or an alkaline metal of Groups 1 and 2 of the Periodic Table, bismuth, or zinc. Preferable, the metal of the metal carboxylate is bismuth or

zinc. Mixtures of bismuth and/or zinc carboxylates are also suitable. The carboxylates are of the formula $(R-CO_2)_x-M$, in which M represent the metal component, and x represents the number of carboxylate groups bounded to the metal component. R may be a branched, straight, or cyclic alkyl group with 1-30 carbon atoms or an aryl, alkaryl or aralkyl group with 5-20 carbon atoms. Metal carboxylates with 6-10 carbon atoms or metal naphthenic carboxylates are preferred. Preferred metal carboxylates include metal naphthenate, metal octoate, and mixtures thereof. The value of x may be in the range of from 1-6. When x is 2 or more, the respective R's may be the same. They can be chosen from the group consisting of phenyls, o-alkylphenyls, and p-alkylphenyls. The alkyl groups of the alkylphenyls contain preferably 1-6 carbon atoms.

When the organometallic compound contains molybdenum, the most preferred molybdenum-containing organometallic component is an oil-soluble decomposable organo molybdenum compound. For instance, dithiophosphomolybdate, sulfonated oxymolybdenum dialkyldithiophosphate, Molybdenum dithiocarbate, molybdenum ditridecyldithyocarbonate, Molybdenum octoate, or molybdenum naphthenethiooctoate. Most preferred are organic thio and phospho compounds.

The organometallic compound is suitably used in the present grease composition in an amount in the range of from 0.01-10%, preferably in an amount in the range of from 0.5-2.5%, based on the total weight of the total grease composition. Other amounts can be used, if desired.

The present grease composition comprises a sulfur-containing organic compound. The sulfur-containing organic compound is suitably a polysulfide, a sulfurized olefin, a sulfurized ester, or a sulfurized oil. Other suitable sulfur-containing compounds are thiols, a thiophosphates, and carbamates. A sulfur substituted fatty acid, or other sulfur-containing components may also be used.

In accordance with the present invention also a mixture of organic sulfides can be used. The polysulfides to be used suitably have the formula $R_2-S_X-R_3$, wherein R_2 and R_3 may

independently be a hydrocarbyl group as described below and x is equal to or greater than about 2. The organic polysulfides may be derived from an olefin or a mercaptan. The olefins, which may be sulfurized, contain at least one olefinic, i.e., a non- aromatic, double bond. Olefins having from 2 to about 30 carbon atoms, or from about 3 to about 16 (most often less than about 9) carbon atoms are particularly useful. Isobutylene, propylene and their dimers, trimers and tetramers, and mixtures thereof are especially preferred olefins. Of these compounds, isobutylene and diisobutylene are preferred. The mercaptans used to make the polysulfide may be hydrocarbyl mercaptans, such as those represented by the formula R-S-H, wherein R is a hydrocarbyl group as defined above. In one embodiment according to the present invention, each R is independently an alkyl, an alkenyl, cycloalkyl, or cycloalkenyl group. Each R independently may be a haloalkyl, hydroxyalkyl, or hydroxyalkyl substituted (e.g., hydroxymethyl, hydroxyethyl, etc.) aliphatic group. R generally contains 2-30 carbon atoms, preferably from 2-24 carbon atoms, and more preferably 3-18 carbon atoms. Suitable examples include butyl mercaptan, amyl mercaptan, hexyl mercaptan, octyl mercaptan, 6-hydroxymethyloctanethiol, nonyl mercaptan, decyl mercaptan, 10-aminododecanethiol, dodecyl mercaptan, 10-hydroxymethyl-tetradecanethiol, and tetradecyl mercaptan.

The polysulfides according to the present invention provide extreme pressure protection. The polysulfides have certain disadvantages including copper corrosion, oxidation stability, thermal instability and seal compatibility problems. Additionally, polysulfides may improve one performance parameter, e.g., wear resistance, or may introduce a deleterious performance characteristic, e.g., bearing surface damage under severe application conditions, or attack of elastomeric seals. It is therefore desirable to use a polysulfide which, when used alone or in combination with other additives, provides good extreme pressure properties to lubricants without adverse effects.

In accordance with the present invention also sulfur-containing compounds can be used that contain in addition phosphorus. Suitable examples of such compounds are sulfur-containing compounds that are free from heavy metals. Examples of such compounds include the phosphorus sulfides, such as P₈S₈ (P₈S₈ and corresponding polysulfides containing additional sulfur, also thiophosphates in which phosphorus is directly bound to sulfur. Sulfur

may be replaced in these compounds partly or entirely by selenium or tellurium. Preferred compounds of this type are obtained by sulfurization and/or phosphorization of organic substances containing one or more olefinic double bonds, e.g. sperm oil butadienes or terpenes. Sulfurized sperm oil esterified with dithiophosphate, sulfurized terpene esterified with dithiophosphate, and sulfurized sperm oil phosphated by reaction with phosphorus pentoxide are among the more complex compounds free from heavy metals which constitute the second component of the synergistic mixtures of this invention.

Suitable examples of thiophosphates include ashless thiophosphates and metal thiophosphates. Preferably the ashless thiophosphate is an ashless dithiophosphate.

Preferably, the metal thiophosphate is metal ditriphosphate. More preferably, the metal triphosphate is zinc ditriphosphate. Suitable examples of carbamates include ashes carbamates and metal carbamates. Preferably, the ashless carbamate is an ashless dithiocarbamate. Preferably, the metal carbamate is metal dithiocarbamate. More preferably, the metal carbamate is molybdenum dialkyl dithiocarbamate.

The sulphur-containing organic compound metal is suitably used in the present grease composition in an amount in the range of from 0.01-10, preferably in an amount in the range of from 0.5wt%-2.5wt%, based on the total weight of the total grease composition. Other amounts can be used, if desired.

The present grease composition comprises a lubricating base oil. As the lubricating base oil any lubricating oil known per se may be used, such as mineral oils, synthetic hydrocarbons, ester oils, vegetable oils and mixtures thereof, of different viscosity. The type of base oil and viscosity can be selected to suit specific applications.

Furthermore, additives known per se may be incorporated in the lubricant grease composition, as long as they do not have a detrimental effect on the thickener composition, the base oil and/or the final grease composition. The grease composition may additionally comprise at least one additive component which is selected from the group consisting of antioxidants, corrosion inhibitors, anti-wear agents and pressure tolerance-increasing

additives, and wherein the total content of the additive component(s) is in the range between 0.2 and 15% by weight, and preferably between 1 and 8% by weight, based on the total weight of the grease composition.

5 In a particular attractive embodiments of the present invention, the present grease composition comprises:

(a) 74-86 wt% of a lubricating base oil;

(b) 12-16 wt% of a polymeric thickener;

(c) 2-5wt% of a metal sulfonate;

10 (d) 0.5-2.5wt% of a metal naphthenate; and

(e) 0.5-2.5wt% of a sulfurized ester, all weight percentages based on the total weight of the grease composition.

In addition, the present invention relates to a method for preparing the present grease composition, comprising the steps of:

15 (a) mixing the polymeric thickener which comprises a polymer of propylene and the lubricating base oil at a temperature above the melting point of the polymer of propylene;

(b) cooling the mixture as obtained in step (a) to a temperature in the range of from 0-120 °C in less than 3 minutes;

(c) mixing the mixture as obtained in step (b) with the metal sulfonate, organometallic
20 compound, and sulphur-containing organic compound in any possible order to obtain the grease composition.

Preferably, in step (a) the polymeric thickener is heated above the melting point of the polymer of propylene.

25 Suitably, during step (a) one or more anti-wear additives, anti-fretting additives, anti-corrosion additives, anti-oxidants, inert powder(s) and/or other additives are additionally mixed with the other components.

Preferably, a final mixing is carried out in step (a) using a three-roll mill or a ball-mill.

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The polymeric thickener composition according to the invention can be prepared by mixing

the polymers in a manner known per se, which can optionally involve heating and/or the use of suitable solvents.

The polymeric thickener of the subject invention is mixed with a lubricating base oil and optional additives by means of conventional techniques known per se resulting in the grease composition according to the invention.

The mixing in step (a) is carried out at a temperature above the melting point of the polymer of propylene contained in the polymeric thickener. Preferably, step (a) is carried out at a temperature of 150- 250 °C more preferably 190-210 °C, although other temperatures may be used if required. Step (a) is preferably carried out under a protective atmosphere, such as a nitrogen gas flow, for avoiding oxidation of the oils during heating. In step (a), the mixture is prepared by mixing the polymers which constitute the components of the polymeric thickener in a manner known per se, which will involve heating and, if desired, the use of one or more suitable oils. The polymeric thickener is mixed with the lubricating base oil, and optionally also additives are mixed in by means of conventional techniques known in the art.

In step (b), the mixture as obtained in step (a) is suitably cooled from the mixing temperature as used in step (a) to room temperature. Suitably, the cooling step is a rapid cooling step or a so-called quenching step. The cooling can be carried out in a period of time between 1 sec. - 3 min., preferably 5 sec. - 1 min. More preferably, the cooling is carried out in less than 30 sec, even more preferably between 5 and 25 seconds. The rapid cooling can be carried out, for instance, by pouring the grease composition on a metal plate, although any other suitable rapid cooling method may also be used, such as spraying. The rapid cooling step as used in accordance with the present invention has a major influence on the grease structure, giving significant improvement of the properties of the final grease compositions compared to both conventional lubricating greases, as well as lubricating greases according to the invention which are cooled slowly, e.g. in approximately 1 degree per minute by the use of conventional cooling methods, such as simply keeping the grease in the reaction vessel with external/internal cooling. In the grease composition according to the invention, the polymeric thickener forms a sponge-like structure, which gives the grease its appearance and structure.

The lubricating base oil is kept within the pore-like spaces within the thickener structure, and bleeds out during service of the grease. The thickener-structure is very irregular with large pores as well as very small pores. The above indicated quenching of the lubricant grease composition provides a grease according to the invention with a smoother and more uniform structure of the polymeric thickener, with more uniformly distributed spaces for keeping the lubricant oil.

During service of the lubricant grease, the oil bleeds out of the oil/thickener-structure onto the surfaces of the bearing, thereby providing the lubricating action. The oil bleeding characteristics at the service temperature of the lubricant grease composition (i.e. the running temperature of the bearing, as well as the "start-up" temperature) are therefore critical for obtaining the lubricating action of the composition.

In step (c), the cooled mixture as obtained in step (b) is mixed with the metal sulfonate, organometallic compound and sulfur-containing organic compound in any possible order to obtain the grease composition. Step (c) can suitably be carried out by means of a first mechanical treatment, to obtain an intermediate grease. The intermediate grease has a first consistency, which is stiffer than a desired consistency of the final grease product to be obtained. The first mechanical treatment in step (c) may be carried out using e.g. a three-roll mill or other suitable milling apparatus. Other methods of mechanical shearing may be applied. The first mechanical treatment step is suitably carried out at ambient temperature, and is a treatment which is conventionally applied in the manufacture of grease products to obtain e.g. a homogenous mixture. Also, the addition of grease additives, such as anti-wear and/or anti-corrosion and/or extreme-pressure additives, may take place during the first mechanical treatment. The final grease product has a desired consistency. In a preferred example, where the grease composition has a polymer thickener content of approx. 13%, the final grease product has a consistency which lies in NLGI class II. This is achieved by subjecting the intermediate grease to a second mechanical treatment in a step (d), which is suitably carried out at a temperature in the range of from 50-90 °C. Preferably, the mechanical treatment in step (d) is carried out at a temperature in the range of from 70-90 °C, more preferably in the range of from 75-85 °C. The mechanical treatment in step (d) may be

carried out using a planetary mixer with heating means, although also other shearing methods may be applied. After step (d), the grease composition is ready for use. The mechanical stability of the grease is dependent on the polymer thickener used, the lubricating base oil used, as well as the additives used. Further, the mechanical properties of the grease can be influenced by "working" the grease after the thickener is mixed with the lubricating base oil, as is well known to a man skilled in the art of lubricants. Preferably, the grease is "worked" to a consistency desired and/or required for its intended use.

The mechanical stability of the grease can be ascertained by means of tests known in the art, such as the Shell roll stability test. Preferably, the grease will have a penetration after the Shell roll stability test (24 hrs at 80 °C, 165 rpm), of max. 430.

The consistency of the grease can be classified by means of the NLGI-class. According to the present invention the grease can usually be prepared to a NLGI-class range 00 to 4. An NLGI-class of 0 or 00 can be made, resulting in a lubricant composition. Also, the viscosity of the separated oil must be acceptable, and preferably be constant.

The grease composition according to the present invention can be used for all conventional applications for lubricant grease compositions. The present grease composition can be used for lubricating bearings, couplings, toothed transmission gears, chutes or other instruments. The mechanical component having a metal surface to be treated with the grease composition according to the present invention is preferably a bearing, bearing component or a bearing application system. The bearing component may be inner rings, outer rings, cages, rollers, balls and seal-counter faces. The bearing application system in accordance with the present invention comprises bearing housings, mounting axles, shafts, bearing joints and shields. Further uses of the lubricant grease compositions according to the present invention are e.g. agricultural machinery, bearings in dam-gates, low noise electric motors, large size electric motors, fans for cooling units, machine tool spindles, screw conveyor, and offshore and wind turbine applications.

The present invention therefore also relates to the use of a grease composition according to the present invention for lubricating a mechanical component having a metal surface. In particular, the present invention relates to the use of the present grease composition for protecting a mechanical component having a metal surface against corrosion, wear and/or fretting.

Further, the present invention relates to the use of a metal sulfonate, preferably calcium sulfonate, for reducing friction on a mechanical component having a metal surface.

Preferably, the mechanical component comprises a bearing, bearing component or gear box component.

The invention will now be further illustrated by the following Examples, which do not limit the invention in any way.

EXAMPLES

The grease compositions used in the examples below are shown in Table 1 and Table 2.

Grease compositions 1 – 7 were synthesized using a polypropylene thickener. Grease composition 1 was prepared having the following composition: 13wt% polypropylene, 0.2wt% anti-oxidant (Irganox L57), and 86.8wt% PAO base oil. The PAO base oil had a viscosity of 68cSt at 40°C.

Grease composition 2 was prepared identically to grease composition 1 followed by addition of 3.5% calcium sulfonate concentrate in mineral oil (12% calcium content). Grease composition 2 so obtained had a calcium content of 0.42%. Grease compositions 3 – 7 were prepared identically to Grease composition 2 followed by addition of 1 – 2.75 wt% bismuth naphthenate concentrate in mineral oil (8-16% Bismuth content), and 1 – 2.5wt% sulfurized synthetic ester concentrate in mineral oil (10% inactive sulphur content). In grease compositions 2 – 7 the initial concentration of PAO base oil was adjusted compared to grease composition 1, such that the overall polypropylene concentration after additive addition and grease processing was 13wt%.

The grease compositions were produced by mixing the polypropylene and the PAO base oil at a temperature of 195 °C, and quenching the mixture so obtained in 20 seconds to a temperature of 23 °C (room temperature). The anti-oxidant, calcium sulfonate, bismuth naphthenate and sulfurized synthetic ester were added to the grease so obtained during the shearing and milling procedure which was carried out at 80 °C using a Bear mixer, and using a 3-roll mill.

For reference, grease compositions 1 – 7 were compared with lithium-based grease compositions 8-10. These are shown in Table 2. Grease compositions 8 - 10 were synthesized as lithium-12-hydroxystearate equivalents of grease compositions 1 – 3 respectively, based on the polymeric thickener.

Grease 11 is LESA 2, an SKF after-market grease based on a special lithium thickener and a PAO base oil having a viscosity of 18.5cSt at 40°C. It is designed for low-friction performance.

Grease 12 is Mobil grease XHP 222, a high performance lithium complex grease with a mineral base oil having a viscosity 220cSt at 40 °C, intended for protection under severe operating conditions and against highly corrosive environments.

Example 1

Greases selected from Table 1 and Table 2 were used in 4-ball wear scar test experiments according to DIN 51350/5 (1 minute at 1400 N), and 4-ball weld load testing according to DIN 51350/4. The results of these experiments are shown in Table 3. Also, a comprehensive overview of the anti-wear trend is shown in Figure 1.

It should be clear from Table 3 that grease composition 2, comprising the polymeric grease and the calcium sulfonate only, offers little anti-wear and extreme pressure performance. It should also be clear that for grease compositions containing bismuth naphthenate, the anti-wear and extreme pressure performance can only be improved substantially if sulfurized

synthetic ester is also present. The synergy between metal carboxylates and sulfurized components is well established and described in prior art. It is unexpected though, that the anti-wear performance of grease compositions 5 and 7 is achieved at very low effective contents of bismuth and sulfur.

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Composition 5 shows a better performance, both in terms of wear scar and welding load, compared to grease composition 12, representing a benchmark lithium-grease.

Figure 1 shows the correlation between composition and wear scar (the graph includes additional compositions to emphasize the trend). Clearly, the wear-scar decreases linearly with increasing bismuth content, however the off-set for such behaviour is governed by the present of the sulfurized content, and presumably the calcium sulfonate. It allows the formulator to optimize the grease composition according to the present invention such, that the anti-wear and extreme pressure properties are optimized depending on the severity of the application, or the desire to minimize the overall additive concentration.

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Example 2

Greases selected from Table 1 and Table 2 were used in SKF EMCOR corrosion testing according to DIN 51802 in 3% salt water. The results are shown in Table 3. Under the severe corrosion conditions of exposure to 3% salt water, grease composition 4, 5, and 6 show outstanding resistance against corrosion. This is remarkable, considering that under these conditions, the benchmark grease composition 12 achieves a rating of 3-3.

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Example 3

Greases selected from Table 1 and Table 2 were evaluated in tapered rolling bearing testing. Experiments were performed up to 24 hours, to evaluate the initial friction coefficient and self-induced temperature peak during running-in, and the friction coefficient and self-induced temperature after prolonged operation. Testing was performed using 30204 J2/Q bearings under axial load, under a maximum contact pressure of 1.3GPa. The lubrication conditions corresponded to kappa values of 0.5 – 2. The kappa value represents the ratio of the actual

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lubricant viscosity in the rolling contact over the required lubricant viscosity needed to achieve minimum separation of the contacting surfaces by a lubricant film.

The results are shown in Table 4. It should be clear that during the initial phase, the friction coefficient and self-induced temperature are highest during the bearing testing. The highest self-induced temperature and overall friction, both during start-up and prolonged operation, is observed for Grease composition 1 based on the polymeric thickener, without additives present. Remarkably, Grease composition 2 based on the polymeric thickener containing only the calcium sulfonate additive, shows a much lower overall friction coefficient and self-induced temperature. Grease compositions 8 based on the lithium-12-hydroxystearate thickened grease without additives shows a high self-induced temperature and overall friction. In comparison, Grease composition 9 based on the lithium-12-hydroxystearate thickened grease containing only the calcium sulfonate additive, does not show an improvement, rather, friction is further increased compared to Grease composition 8. This shows that in correspondence with the grease composition of this invention, the friction can be reduced in polymeric greased compared to lithium-based greases, using calcium sulphate. The ability of grease composition 2 to reduce friction and operating temperature is remarkable, especially when compared to grease composition 11, representing a lithium-grease optimized for low-friction performance. Whereas composition 11 achieves the lowest overall friction coefficient of 0.0013, this is largely due to the use of a very low base oil viscosity ($\nu = 18 \text{ cSt at } 40^\circ$) in the grease composition. In contrast, the use of composition 2, having a much higher base oil viscosity ($\nu = 68 \text{ cSt at } 40^\circ\text{C}$), reduces friction to an overall friction coefficient of 0.017, which is merely 30% higher. In contrast, the use of composition 9 results in an overall friction coefficient of 0.0052, thus increasing friction by >300% compared to the low-friction performance grease.

The results for grease compositions 3 and 5 indicate that the reduction of the friction coefficient and self-induced temperature as observed for grease composition 2, can also be achieved after addition of bismuth naphthenate and sulfurized synthetic ester. Even so, grease composition 5 shows the lowest overall self-induced temperature of all compositions tested.

Combined with the ability to provide excellent anti-corrosion protection, and optimized anti-wear and extreme pressure performance, this indicates that the compositions within the accordance of the present invention provided a remarkable improvement in the simultaneous improvement of anti-corrosion, anti-wear and extreme pressure, and friction and temperature reduction properties of polymeric greases, compared to, e.g., lithium-based greases.

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Table 1. Polymeric grease composition

Grease composition	Composition of polymeric grease
Grease No. 1	13% polypropylene 0.2wt% anti-oxidant 86.8% PAO base oil, viscosity is 68cSt at 40°C
Grease No. 2	13% polypropylene 0.2wt% anti-oxidant 3.5% calcium sulfonate in mineral oil (TBN 300 mg KOH/g, calcium content 12%) 83.3% PAO base oil, viscosity is 68cSt at 40°C
Grease No. 3	13% polypropylene 0.2wt% anti-oxidant 2.5wt% Bismuth naphthenate in mineral oil (bismuth content 16 wt. %), 2.5wt% Sulphurized synthetic ester in mineral oil (inactive sulphur content 10 wt%) 81.8% PAO base oil, viscosity is 68cSt at 40°C
Grease No. 4	13% polypropylene 3.5% calcium sulfonate in mineral oil (TBN 300 mg KOH/g, calcium content 12%) 0.2wt% anti-oxidant 1wt% Bismuth naphthenate in mineral oil (bismuth content 16%), 1wt% Sulphurized synthetic ester in mineral oil (inactive sulphur content 10%) 81.3% PAO base oil, viscosity is 68cSt at 40°C
Grease No. 5	13% polypropylene 3.5% calcium sulfonate in mineral oil (TBN 300 mg KOH/g, calcium content 12%) 0.2wt% anti-oxidant 2.5wt% Bismuth naphthenate in mineral oil (bismuth content 8%), 2.5wt% Sulphurized synthetic ester in mineral oil (inactive sulphur content 5%) 78.3% PAO base oil, viscosity is 68cSt at 40°C
Grease No. 6	13% polypropylene 3.5% calcium sulfonate in mineral oil (TBN 300 mg KOH/g, calcium content 12%) 0.2wt% anti-oxidant

	3wt% Bismuth naphtenate in mineral oil (bismuth content 16%) 80.3% PAO base oil, viscosity is 68cSt at 40°C
Grease No. 7	13% polypropylene 3.5% calcium sulfonate in mineral oil (TBN 300 mg KOH/g, calcium content 12%) 0.2wt% anti-oxidant 2.75wt% Bismuth naphtenate in mineral oil (bismuth content 10.5%), 1.25wt% Sulphurized synthetic ester in mineral oil (inactive sulphur content 5%) 79.3% PAO base oil, viscosity is 68cSt at 40°C

Table 2. Lithium-based grease compositions

Grease composition	Composition of lithium-based grease
Grease No. 8	11% Lithium 12-hydroxystearate 0.2wt% anti-oxidant, Irganox L57 88.8% PAO base oil, viscosity is 68cSt at 40°C
Grease No. 9	11% Lithium 12-hydroxystearate 3.5% calcium sulfonate in mineral oil (TBN 300 mg KOH/g, calcium content 12%) 0.2wt% anti-oxidant, Irganox L57 85.3% PAO base oil, viscosity is 68cSt at 40°C
Grease No. 10	11% Lithium 12-hydroxystearate 2.5wt% Bismuth naphthenate in mineral oil (bismuth content 16 wt. %), 2.5wt% Sulphurized synthetic ester in mineral oil (inactive sulphur content 10 wt%) 0.2wt% anti-oxidant, Irganox L57 83.8% PAO base oil, viscosity is 68cSt at 40°C
Grease No. 11	SKF grease LESA 2: Low friction grease Special lithium-thickener PAO base oil, viscosity 18 cSt at 40°C
Grease No. 12	Mobil grease XHP 222 high performance lithium complex grease Applied under severe operating conditions and corrosive environments Mineral base oil, viscosity 220cSt at 40 °C

Table 3. Wear scar, Weld load, and EMCOR results

Grease composition	Bismuth content (%)	Sulfur content (%)	Wear Scar (1400N/1min)	Weld load (N)	EMCOR (3% salt water)
Polymeric grease					
Grease No. 2	0	0	2.9	2000	
Grease No. 4	0.16	0.1	2.1	2000	0-0
Grease No. 5	0.4	0.25	1.6	3200	1-1
Grease No. 6	0.45	0	2.2	2200	0-0
Grease No. 7	0.42	0.125	1.9	2800	
Lithium grease					
Grease No. 12	NA	NA	1.8	3150	3-3

Table 4. Friction and self-induced temperature in bearing testing

Grease composition	Friction coefficient		Self-induced temperature (°C)	
	Initial peak	After >6h	Initial peak	After >6h
Polymeric grease				
Grease no. 1	0.010	0.0063	145	113
Grease no. 2	0.008	0.0017	102	66
Grease no. 3	0.010	0.0025	120	79
Grease no. 5	0.009	0.0027	110	62
Grease no. 10	0.009	0.0032	111	75
Lithium grease				
Grease no. 8	0.009	0.0037	132	85
Grease no. 9	0.009	0.0053	130	115
Grease no. 10	0.009	0.0033	112	75
Grease no. 11	0.008	0.0013	99	60

CLAIMS

1. A grease composition comprising a lubricating base oil, a polymeric thickener which comprises polymer of propylene, and a metal sulfonate.

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2. The grease composition according to claim 1 comprising:

(a) 1-99wt% of the lubricating base oil;

(b) 1-20 wt% of the polymeric thickener; and

(c) 0.01-15 wt% of the metal sulfonate,

10 all weight percentages based on the total weight of the grease composition.

3. The composition according to claim 1 or 2, wherein the polymer of propylene comprises a mixture of (1) a (co- or homo-)polymer of propylene with a weight average molecular weight of more than 200.000 and (2) a (co- or homo-)polymer of propylene with a weight average
15 molecular weight of less than 100.000.

4. The composition according to claim 3, wherein the (co- or homo-)polymer of propylene with a weight average molecular weight of less than 100.000 is a polypropylene homopolymer.

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5. The composition according to claim 3 or 4, wherein the (co- or homo-)polymer of propylene with a weight average molecular weight of more than 200.000 is a polypropylene homopolymer or a propylene/ethylene-copolymer.

6. The composition according to any one of claims 1-5, wherein the metal of the metal
25 sulfonate is an alkali metal or an alkaline metal of Groups 1 and 2 of the Periodic Table, bismuth, or zinc.

7. The composition according to any one of claims 1-6, wherein the metal of the metal sulfonate is calcium.

8. A grease composition according to any one of claims 1-7 which in addition comprises an organometallic compound and a sulfur-containing organic compound.

9. The composition according to claim 8, wherein the metal of the organometallic compound is an alkali metal or an alkaline metal of Groups 1 and 2 of the Periodic Table, bismuth or zinc.

10. The composition according to claim 8 or 9, wherein the metal of the organometallic compound is bismuth or zinc.

11. The composition according to any one of claims 8-10, wherein the sulfur-containing organic compound is a polysulfide, a thiol, a thiophosphate, a carbamate, a sulfur-substituted fatty acid, or a sulfurized olefin.

12. The composition according to claim 11, wherein the sulfur-containing organic compound is an ashless dithiophosphate, a metal dithiophosphate, an ashless dithiocarbamate or a metal dithiocarbamate.

13. The composition according to claim 12, wherein the sulfur-containing organic compound is zinc dithiophosphate or molybdenum dialkyl dithiocarbamate.

14. The composition according to any one of claims 8-13, wherein the organometallic compound is a metal carboxylate, preferably a metal naphthenate, a metal octoate, or a mixture thereof.

15. A method for preparing the grease composition according to any one of claims 1-14, comprising the steps of:

(a) mixing the polymeric thickener which comprises a polymer of propylene and the lubricating base oil at a temperature above the melting point of the polymer of propylene;

(b) cooling the mixture as obtained in step (a) to a temperature in the range of from 0-120 °C in less than 3 minutes;

(c) mixing the mixture as obtained in step (b) with the metal sulfonate, organometallic compound and sulfur-containing organic compound in any possible order to obtain the grease composition.

5 16. Use of a grease composition according to any one of claims 1-14 for lubricating a mechanical component having a metal surface.

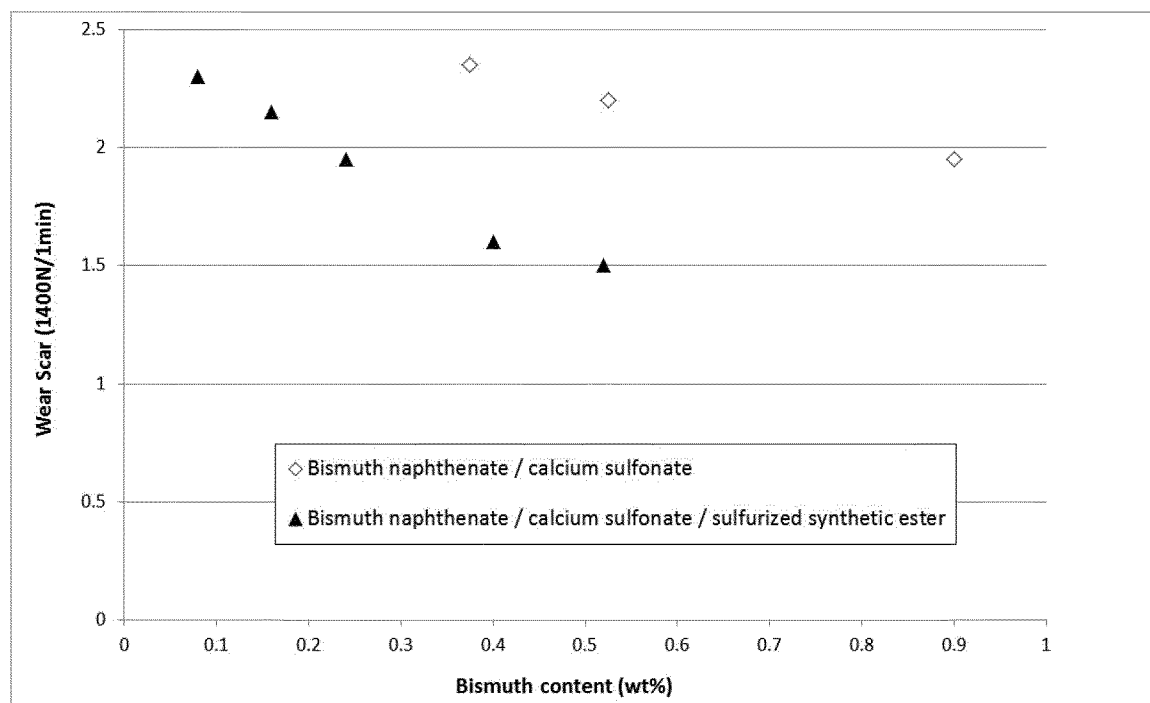
17. Use of the grease composition according to any one of claims 1-14 for protecting a mechanical component having a metal surface against corrosion, wear and/or fretting.

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18. Use of the grease composition according to claim 16 or 17, wherein the mechanical component comprises a bearing, bearing component or gear box component.

15 19. Use of a metal sulfonate in a grease composition which contains a polymer thickener comprising a polymer of propylene for reducing friction on a mechanical component which has a metal surface.

Figure 1. Wear scar



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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ADD. C10N30/06 C10N30/12 C10N40/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2014/108438 A1 (SKF AB [SE]) 17 July 2014 (2014-07-17) page 9, lines 27-32; claims 1,8 -----	15
X	US 2008/108531 A1 (BURREINGTON JAMES D [US] ET AL) 8 May 2008 (2008-05-08) claims 17-18; table 1 -----	1-13, 16-18
X	US 2 901 432 A (MORWAY ARNOLD J ET AL) 25 August 1959 (1959-08-25) column 2, lines 47-50; claim 1 -----	1-3,6-8, 16-18
Y	US 5 874 391 A (MEIJER DICK [NL] ET AL) 23 February 1999 (1999-02-23) claim 1; example 1 -----	1-14, 16-19
	----- -/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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