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(54) WATER RESISTANT GREASE COMPOSITION

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(57) ABSTRACT

A grease with improved water resistance is based on a combination of a polyamide thixotrope with a water insoluble thickener, preferably a lithium soap/complex thickener and an antioxidant/corrosion inhibitor/antiwear additive package. The improvement is maintained when highly effective or aggressive rust inhibitors which normally tend to degrade water wash out resistance are present in the grease. Another advantage is that resistance to fretting is significantly improved to the extent that the greases containing these components are capable of achieving a high level of resistance to false brinelling. The greases are particularly useful for application in wind turbine bearings.

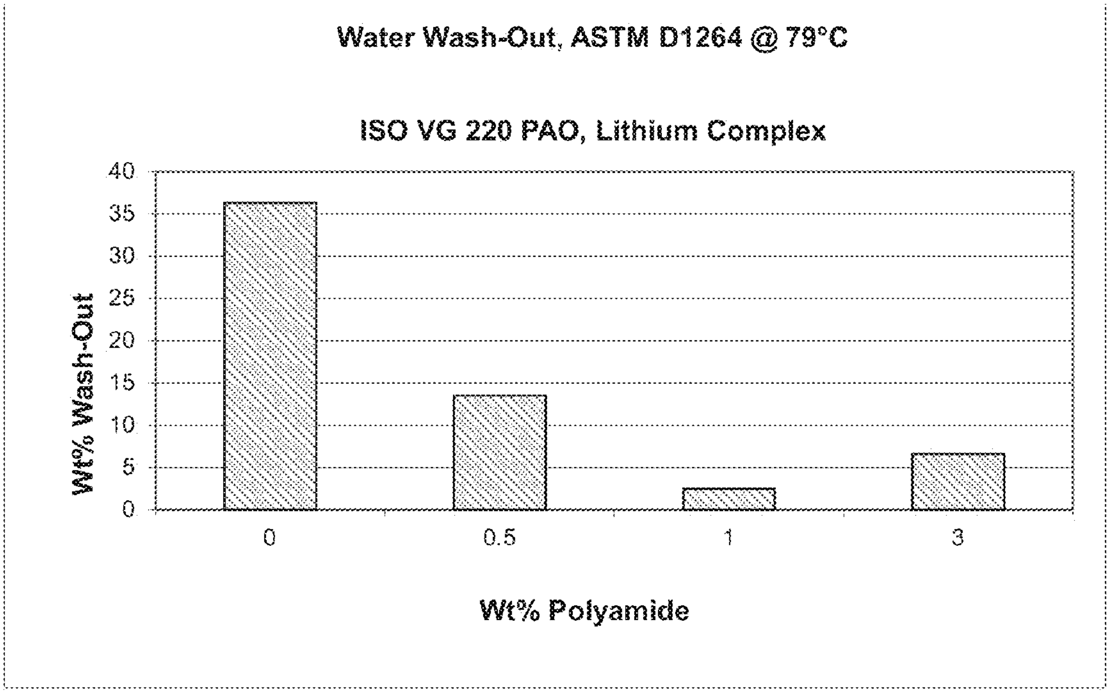

Water Wash-Out, ASTM D1264 @ 79°C
ISO VG 220 PAO, Lithium Complex
40
35
30
25
20
15
10
5
0
Wt% Wash-Out
0
0.5
1
3
Wt% Polyamide

Figure 1

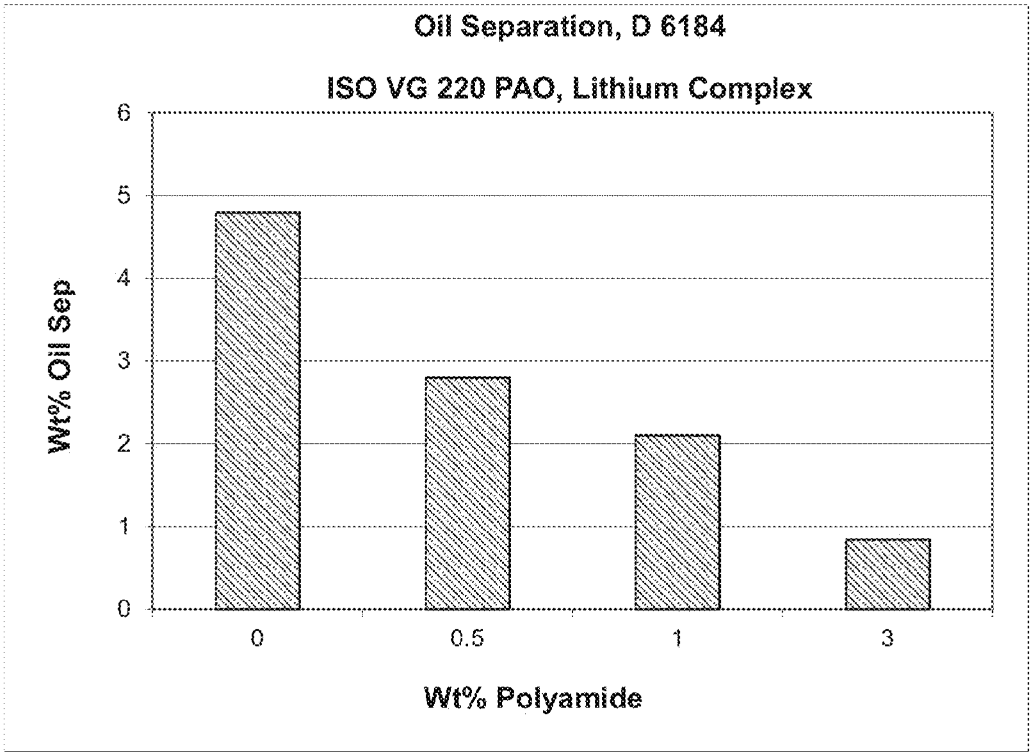

Oil Separation, D 6184
ISO VG 220 PAO, Lithium Complex
Wt% Oil Sep
6
5
4
3
2
1
0
0
0.5
1
3
Wt% Polyamide

Figure 2

WATER RESISTANT GREASE COMPOSITION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 61/557,002 filed on Nov. 8, 2011, which is incorporated herein in its entirety by reference.

FIELD

[0002] This disclosure relates to a grease composition with improved water and corrosion resistance which is particularly useful for use in wind turbine gearboxes and bearings as well as in other applications where heavy loads are encountered in adverse environments, especially when high loadings may prevail. In addition, improved low temperature performance and stability have been demonstrated.

BACKGROUND

[0003] The use of polymers to impart desirable properties to greases is known and widely practiced by grease manufacturers; see, for example, the description of various thickeners in *Manufacture and Application of Lubricating Greases* (1954), Reinhold, N.Y. 1954 and *Alteration of Grease Characteristics with New Generation Polymers,* G. D. Hussey, NLGI Spokesman, August 1987. Oil soluble polymers have been used, for example, to increase the structural stability of greases and to confer reduced oil separation, and increased water resistance. Although these benefits could be obtained without polymers by using lubricating oils having high viscosity basestocks, the resulting debit on low temperature mobility (i.e., pumpability) severely limits a non-polymer approach.

[0004] Water resistance is a property desirable in grease for many industrial applications; for example, in papermaking machinery and gearboxes, power transmissions and other bearings used in wet environments such as the slewing bearings in large outdoor antenna mountings and cranes on offshore oil rigs. It has been previously found that polymers may be effective in improving the water resistance of industrial and automotive greases. U.S. Pat. No. 5,110,490 (Pink), for instance, discloses a grease composition with enhanced water resistance containing an ethylene copolymer with amine functionality. The copolymer is produced by reaction of a polyamine such as ethylene diamine with an ethylene copolymer grafted with carboxylic moieties by reaction with and unsaturated carboxylic acid or anhydride group, for example, maleic anhydride. Amine functionalized ethylene copolymers of this type are described in U.S. Pat. No. 4,517,104 (Bloch) to which reference is made for a description of them.

[0005] Polymer additives are well established for enhancing enhance grease performance at low treatment levels as reported in NLGI Paper *Benefits of Polymer Additives in Grease,* Larson, et al, NLGI Spokesman, ISSN: 00276782, Vol: 73, Issue 7. As discussed in that paper, the challenges facing grease manufacturers face can be addressed with the inclusion of polymer additives in a variety of grease types. The benefits of polymer additives in this study are shown to include improved shear stability, enhanced water resistance, and increased yield. In addition to performance enhancements, selected polymer additives may provide economic benefits through increased grease yields of up to 17%.

[0006] Polymers that have been studied as grease additives include polyisobutylene (PIB), ethylene-propylene copolymers (OCP), styrene-hydrogenated butadiene (SBR), styrene-hydrogenated isoprene (SI), radial hydrogenated polyisoprene (star), acid functionalized polymers (FP), polymethacrylate (PMA), styrene ester copolymers (SE), and styrene ethylene butylene copolymers (SEBCP). These polymers have been used as co-thickeners e.g. with a calcium soap as described in U.S. Pat. No. 5,084,193 (Waynick) or as the sole thickener as in U.S. Pat. No. 5,874,391 (Meijer).

[0007] One application where water resistance is of major importance in grease formulations is wind turbine lubrication, especially in the stewing (pitch and yaw) bearings. Other significant factors include the life of the grease since the nacelles of the turbines are usually inaccessible for maintenance as well as elastomer and paint compatibility. Another and potentially more serious factor in the formulation of wind turbine greases is the need to provide protection against false brinelling which is the wear by fretting which occurs in bearings which are subjected to vibration in the absence of rotation. When the bearing is not turning, the minute oscillations which take place displace the grease from the bearing contact surfaces without allowing it to flow back, resulting in metal to metal contact, wear and damage which will cause the bearing to fail. In addition, capillary action, or damaged seals may allow water to enter the bearing, creating the potential for corrosion which further accelerates the damage. The bearing damage which occurs appears as “ripple” formations in the bearing surfaces. False brinelling is likely to be encountered in wind turbine pitch and yaw bearings as a result of the turbine being stationary either in low wind conditions or, contrarily, when high winds speeds necessitate shut down to avoid over-speeding. When this occurs, the bearings are subject to wind-induced vibrations which may accelerate escape of the lubricant from the bearing contact surfaces, creating the potential for fretting and bearing failure.

[0008] Along with water resistance, corrosion resistance is another highly important performance characteristic in wind turbine greases given the service conditions under which the turbines operate, often in remote wind- and rain-swept locations and often at sea. Corrosion inhibitors therefore form a necessary part of the additive package and in view of the harsh operating environments, it may be necessary to resort to the most effective types of corrosion inhibitors. Anti-wear performance is also significant in view of the heavy loadings to which wind turbine bearings are exposed for extended periods of time without the opportunity for routine maintenance.

SUMMARY

[0009] We have now found that improved water resistance in greases provided by a unique combination of a thickener, preferably a lithium salt soap thickener in combination with an oil insoluble polyamide thixotrope as a co-thickener; the improvement is, moreover, maintained when highly effective or aggressive rust inhibitors which normally tend to degrade grease stability and water wash out resistance are present in the grease. Another advantage which we have found is that resistance to fretting is significantly improved to the extent that the greases containing these components are capable of achieving good ripple protection in the Riffel Test.

[0010] According to the present disclosure the greases have a grease base of a lubricating base oil, a water- and oil-insoluble thickener, and an oil insoluble, thixotropic polyamide co-thickener. To this base formulation, additives including at least antioxidants, corrosion inhibitors and anti-wear agents will normally be added to obtain the desired final combination of properties. These greases, when fully formulated, exhibit a highly advantageous combination of properties including good water resistance as well as mechanical stability in wet conditions and good low temperature properties; this combination makes them eminently suitable for use in wind turbine bearings.

BRIEF DESCRIPTION OF E DRAWINGS

[0011] FIG. **1** is a bar graph of water wash-out versus wt % polyamide of Example 2.

[0012] FIG. **2** is a bar graph of oil separation versus wt % polyamide of Example 1.

DETAILED DESCRIPTION

[0013] All numerical values within the detailed description and the claims herein are modified by "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

Lubricating Base Oil

[0014] The present greases are preferably synthetic greases, that is, greases which are based on a synthetic liquid lubricating component but mineral oil lubricating bases may also be used. If a mineral oil base is used, it will typically be a neutral (paraffinic) base stock with a viscosity from 2 to 500 cSt, more usually 2 or 4 to 300 cSt, (40° C.) although for some power transmission applications, heavier base stocks may also be used. Blends of low viscosity oils, e.g. 2 to 10 cSt with higher viscosity oils e.g. 100 cSt or higher, are likely to be particularly favorable. One class of base oils derived from mineral oil sources which are potentially useful are the high viscosity index hydrocracked, catalytically dewaxed oils of API Groups II, II Plus, III and III Plus. These oils, especially the higher end Group II oils with viscosity indices of 110 to 120 (SAE) and the Group III oils with viscosity indices over 120 and higher, e.g 130 or 140, approaching those of the totally synthetic poly alpha olefins are particularly desirable base stocks for the greases whether used on their own or in combination with a synthetic base stock component, e.g. a poly alpha olefin (PAO) stock. Another class of useful base oils is the synthetic Fischer-Tropsch oils, especially those derived from waxy, Fischer-Tropsch (F-T) synthesized tube range fractions by hydroisomerization and catalytic dewaxing to improve the low temperature flow properties of the oil and improve its viscosity index. The F-T process used to form the initial waxy hydroisomerization feed is preferably one produced with a slurry F-T process using a cobalt catalyst. Lube base stocks of this kind are described in US 2002/0086803. Hydroisomerization over zeolite catalysts is a particularly preferred hydroisomerization/dewaxing technique.

[0015] Among the synthetic base oils, the poly alpha olefins (PAOs) constitute the most preferred class, having excellent oxidation stability and resistance to hydrolytic attack. Blends of the PAOs with either the high VI hydroisomerized mineral oils or the F-T lube stocks mentioned above are also especially favorable for their rheolology characteristics, especially VI and low temperature fluidity. The synthetic esters oils such as the Type I (dibasic acid, e.g. sebacic acid, azelaic, acid esters such as dicotly sebacate) and the Type II (polyol/monobasic acid esters, especially the neopentyl polyol esters e.g. the trimethylopropane, pentaerythritol of C_8-C_{10} acids) are not generally favored in view of their susceptibility to hydrolytic attack but they may be present in minor amounts to promote good seal swell and additive solvency, if needed. Other synthetic base stocks include the alkylbenzenes, carbonate esters (e.g., the product of reacting C_8 oxo alcohol with ethyl carbonate to form a half ester followed by reaction of the latter with tetraethylene glycol, etc.), polyphenyl ethers, e.g., those having from about 3 to 7 ether linkages and about 4 to 8 phenyl groups polyalkylene glycols and the polyphenyl ethers. Synthetic components such as the long chain alkylated naphthalenes may be used as blend components, e.g. for added additive solvency, if required.

[0016] Normally, the lubricating oil will comprise a major amount of the grease composition. Typically, the amount of lubricating oil will range from above about 50 to about 90 wt %, preferably from about 70 to about 85 wt %, of the grease composition.

Grease Thickener

[0017] The grease will contain an essentially water- and oil-insoluble thickener to provide the desired grease consistency and structure (cone penetration, dropping point, etc). Thickeners may be of the soap or non-soap types. Non-soaps are based on organic or non-organic solids such as bentonite clay, polymers such as the polyureas or silica aerogels and may be used where their particular properties so indicate. The preferred thickeners for the present greases are the metal salt/soap thickeners, including the complex soap thickeners based on metals including aluminum, barium, calcium, lithium, sodium, with the lithium salt/soap complex thickeners being the most preferred. These types of thickeners are well established and are described in numerous publications. See, for example, Boner op cit, *Lubricants and Related Products,* Klamann, Verlag Chemie, 1984, ISBN 3-527-26022-6, ISBN 0-89573-177-0 to which reference is made for a description of suitable thickeners and the manufacture of grease incorporating them.

[0018] The complex grease thickeners are made by combining the conventional metallic soaps with a complexing agent. The soaps are typically a metal salt of a long chain fatty acid having from 8 to 24 carbon atoms such as decanoic acid, myristic acid, palmitic acid or stearic acid. Particularly preferred is a lithium or lithium complex thickener that incorporates an hydroxy fatty acid having from 12 to 24 (preferably from 16 to 20) carbon atoms. A preferred hydroxy fatty acid is an hydroxy stearic acid, e.g., 9-hydroxy or 10-hydroxy stearic acid, with 12-hydroxy stearic acid being the most preferred. Other hydroxyl fatty acids which may be used include ricinoleic acid (12-hydoxystearic acid unsaturated at the 9,10 position), 12-hydroxybehenic acid and 10-hydroxypalmitic acid. The complex salt/soap thickeners are made with a combination of conventional lithium soap such as lithium 12-hydroxystearate and a complexing agent which may vary with the type of thickener, e.g. calcium complex thickeners may be formulated with acetic acid and hydroxy-substituted acids; boric acid may be used with lithium soaps. Low molecular-weight organic acid, typically C_4 to C_{12} dibasic acids such as glutaric, azelaic, pimelic, suberic, adipic or sebacic acids, are generally favored as the complexing agents with lithium greases. The complexes are formed by the introduction of the complexing agent or its metal salt into the lattice of the metal salt. Examples of metal salt/soap complex thickeners are described in U.S. Pat. No. 3,929,651; 3,940, 339; 4,410,435; 4,444,669 and 5,731,274. The complexing agent may be added as the free acid, a salt e.g, the lithium salt or as an ester such as an alkyl ester, e.g. methyl glutarate or methyl adipate, which will undergo hydrolysis to the acid in the presence of the added alkali, e.g. lithium hydroxide, to form the complexing agent.

[0019] The amount of thickener in the lubricating composition will typically range from about 1 to about 20 wt %. For most purposes, between about 6 to about 14 wt %, preferably between about 8 to about 10 wt %, of the thickener will be present in the composition. PAO bases may require a higher proportion of thickener than mineral oil basestocks.

Polyamide Co-Thickener

[0020] The present greases contain a polyamide thixotrope as a co-thickener which contributes to the formation of the thickener matrix. The thixotrope is essentially insoluble in water and oil in order to maintain the grease structure and the desired resistance to water wash out. Thixotropes create a viscosity increase that is reversed during shearing but then reforms when the shear forces are removed. This characteristic has been found to provide advantageous properties when used in combination with the remaining grease components.

[0021] The polyamides used in the present formulations have two or more amide groups [R—CO—NR'—R'] in their structure formed by reaction of a diamine, with a carboxylic entity. The diamine reactant will have two or more amine groups which may be either primary or secondary amine groups. Typical preferred amine compounds include the alkylene diamines of the formula:

$$H—NR'\text{-}[\text{-alkylene-}NR'—]_x—H$$

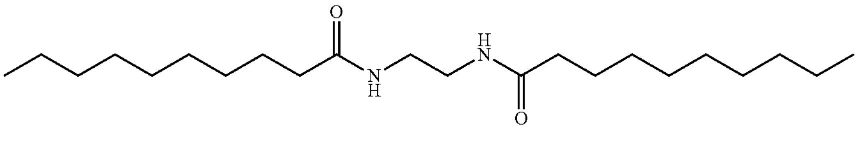
where R and R' which may be the same or different and may each be H or alkyl groups, typically of 2 to 6 carbon atoms and alkylene has 2 to 6 carbon atoms and x is an integer of about 1 to 10, preferably about 2 to 7, and the alkylene radical is a straight or branched chain alkylene group or substituted alkylene group having 2 to 10, preferably 2 to 7, more preferably 2 to 4, carbon atoms; the primary amities are preferred (R' is H).

[0022] Examples of the alkylene diamines of the above formula include ethylene diamine, propylene diamines, butylene diamines, pentylene diamines, hexylene diamines, heptylene diamines, dioctylene amines, other polymethylene amines, e.g. hexamethylene diamine. Polyamines e.g. triamines, etc are not generally favored in view of their tendency to form polymers which do not possess the desired thixotropic properties.

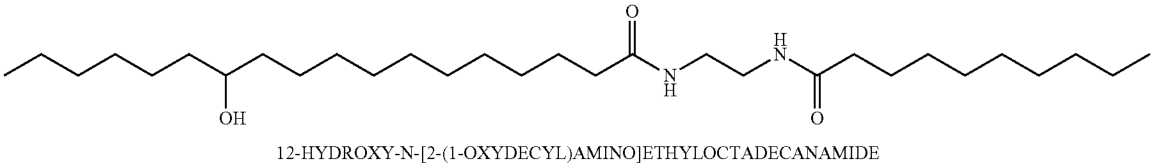
[0023] The preferred amines for the synthesis of the present thixotropes are the straight chain alkylene diamines which produce polyamides of substantially linear structure consistent with the thixotropic character. Examples of such diamines include ethylene diamine, 1,3-propylene diamine, 1,4-butylene diamine, hexamethylene diamine with special preference for ethylene diamine and hexamethylene diamine for their commercial availability.

[0024] The carboxylic component includes C_4+ monocarboxylic acids, typically long chain fatty acids from 8 to 20 carbon atoms and their derivatives including anhydrides, acyl halides and other entities capable of reaction with the primary amine groups of the polyamine to form the amide linkages. Polycarboxyylic acids are not favored in view of their tendency to react with the diamine reactant to form the undesired higher molecular weight condensation polymers which are not thixotropes; the molecular weight of the polyamide should not exceed about 800 and in most cases, not more than 650 for good thixotropic properties. Preferably, the molecular weight should be in the range of 250 to 630. The hydrocarbon groups attached to the carboxyl moiety may typically be alkyl, alkenyl, aryl, alkaryl, aralkyl and may be substituted by heteroatoms or other groups such as hydroxyl or hydroxyalkyl groups. The preferred carboxyl reactants are essentially aliphatic and include alkenyl and alkyl groups with straight chain alkyl groups and hydroxylalkyl groups being preferred. Particularly preferred carboxyl compounds are the C_8 to C_{20} alkyl and hydroxyalkyl monocarboxylic acids. The carboxyl component may contain hydrocarbon and substituted hydrocarbon groups of varying chain length, for example, a mixture of C_{10} and C_{18} alkyl and hydroxyalkyl acids.

[0025] A currently preferred carboxyl component comprise a combination alkanoic and hydroxyalkanoic acids, preferably a mixture of a C_8 to C_{18} alkanoic acid with a C_8 to C_{18} hydroxyalkanoic acid. The alkanoic acid is preferably the major component of the mixture with the hydroxyalkanoic acid being present in a lesser amount. A particularly preferred carboxylic reactant is a mixture of decanoic acid and 12-hydroxystearic acid. With ethylene diamine as the amine component, the polyamide formed from these two acids will be a mixture of three individual diamides with the formulae:

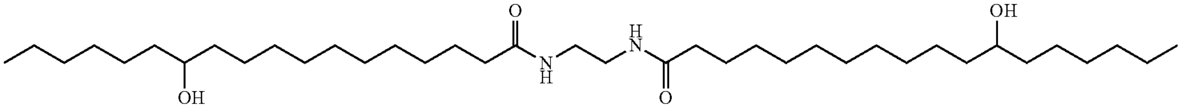


N,N'-ETHANE-1,2-DIYLBIS(DECANAMIDE)



12-HYDROXY-N-[2-(1-OXYDECYL)AMINO]ETHYLOCTADECANAMIDE

-continued



N,N'-ETHANE-1,2-DIYLBIS(12-HYDROXYOCTADECANAMIDE)

Preferably, the mol ratio between these reactants will be from 0.2 to 1 mol of the alkanoic acid and 0.1 to 1 mol of the hydroxyalkanoic acid per mol of the diamine. Polyamides of this type are disclosed in U.S. Re 41,588.

[0026] The carboxyl-donating component may be used in the form of a salt or other derivative, e.g. ester, anhydride or halide which is capable of reacting with the diamine to form the desired amide,

[0027] The amine and acid component will generally be prereacted to form the polyamide prior to admixing with the other grease components. Typically the amount of the polyamide will range from about 0.01 to about 4 wt %, preferably from about 0.1 to about 2 wt %, based on weight of the grease, although larger amounts could be used if desired.

Grease Manufacture

[0028] The grease making procedures either in a hatch process with contactor followed by finishing kettle or in a continuous greasemaking process are well known and widely used. In batch greasemaking, the grease is usually prepared by chemically reacting and mechanically dispersing the thickener components in the lubricating oil for from about 1 to about 8 hours or more (preferably from about 3 to about 6 hours) followed by heating at elevated temperature (e.g., from about 140 to about 225° C. depending upon the particular thickener used) until the mixture thickens. In sonic cases (e.g. a simple lithium grease), a preformed thickener can be used. The mixture is then cooled to ambient temperature (typically about 60° C.) during which time additive package is added.

[0029] The polyamide thixotropes may be incorporated into a semi-finished grease containing the base oil and thickener possibly with the additive package present or added earlier as a blend component. The polyamides are typically viscous liquids, semi-liquids or, quite often powders and in order to facilitate blending into the grease base, it may be necessary in the case of the powder materials or, in the case of the liquids, desirable, to heat the polyamide prior to incorporation into the other grease components. In a batch type process, the polyamide may be liquefied prior to being added to the contactor in which the components of the thickener are to be reacted in the presence of the base oil although it has been found preferable to add powdered thixotrope to the finishing kettle that is at a high enough temperature to melt the thixotrope but sufficiently low to avoid exposure to the higher temperatures typically prevailing in the contactor during the soapmaking step; in addition, this sequence avoids subjecting the thixotrope to high temperature/high shear conditions of the contactor likely to degrade the thixotropic properties. The temperatures in the finishing kettle will typically be 120° C. or higher so as to preclude separation of the polyamide before it becomes incorporated into the grease mass. In a continuous greasemaking process, the polyamide may be added as one of the blend components to where the line where the temperature/shear regime is suitable for the particular thixotrope.

[0030] A continuous greasemaking process for making lithium complex greases is described to U.S. Pat. No. 7,829,512.

[0031] The grease composition can be mixed, blended, or milled in any number of ways including external mixers, roll mills, internal mixers, Banbury mixers, screw extruders, augers, colloid mills, homogenizers, and the like.

Additives

[0032] The grease composition will typically contain small amounts of additives such as anticorrosive agents, extreme pressure and antiwear agents, pour point depressants, tackiness agents, oxidation inhibitors, dyes, and the like. The amounts of individual additives will vary according to the additive and the level of functionality to be provided by it. The total amount of these additives will typically range from about 2 to about 5 wt % based on total weight of the grease composition. In addition, solid lubricants such as molybdenum disulfide and graphite may be present in the composition, typically from about 1 to about 5 wt % (preferably from about 1.5 to about 3 wt %) for molybdenum disulfide and from about 3 to about 15 wt % (preferably from about 6 to about 12 wt %) for graphite.

[0033] When the additives are described below by reference to individual components used in the formulation, they will not necessarily be present or identifiable as discrete entities in the final product but may be present as reaction products which are formed during the grease manufacture or even its use. This will depend on the respective chemistries of the ingredients, their stoichiometry, and the temperatures encountered in the greasemaking process or during its use. It will also depend, naturally enough, on whether or not the species are added as a pre-reacted additive package. For example, the acid amine phosphates may be added as discrete amines and acid phosphates but these may react to form a new entity in the final grease composition under the processing conditions used in the grease manufacture.

[0034] At least one antioxidant will be present to retard oxidative degradation of the grease while in storage and use. Typically, these additives will be either aminic antioxidants or phenolic antioxidants; antioxidants of these two classes may be used together. Aminic antioxidants are generally aromatic amines of which the naphthylamines are in common use, e.g. alpha.-naphthylamine, phenyl-alpha.-naphthylamine, butylphenyl-.alpha.-naphthylamine, pentylphenyl-.alpha.-naphthylamine, hexylphenyl-.alpha.-naphthylamine, heptylphenyl-.alpha.-naphthylamine, octylphenyl-.alpha.-naphthylamine and nonylphenyl-.alpha.-naphthylamine; the monoalkylphenyl alpha-naphthylamines e.g. tert.-octyl-phenyl-α-naphtylamine and mononoyldiphenylamine are particular common. Other classes of aromatic amines include the dinuclear aromatic amines such as the dialkyl-diphenylamines, e.g. 4,4'-dibutyldiphenylamine, 4,4'-dipentyldiphenylamine, 4,4'-dihexyldiphenylamine, 4,4'-diheptyldiphenylamine, 4,4'-dioctyldiphenylamine and 4,4'-

dinonyldiphenylamine; polyalkyldiphenylamines such as tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine and tetranonyldiphenylamine. Amities of both types may be used singly or in combination with one another. The combination of tert.-octyl-phenyl-α-naphtylamine and dioctyl-diphenylamine is common Amine antioxidants are generally used in amounts from about 0.01 to 5 wt %, more usually from 0.5 to 1.5 wt %. Phenolic antioxidants, typically used in amounts from about 0.01 to 5 wt %, more usually from 0.5 to 1.5 wt %., are typified by the alkylated hydroxytoluenes, e.g. butylated hydroxytoluene.

[0035] Other types of antioxidant may also be considered, including the sulfur-containing antioxidants, for example, dialkyl thiodipropionates such as dilauryl thiodipropionate and distearyl thiodipropionate, dialkyldithiocarbamic acid derivatives (excluding metal salts), bis(3,5-di-t-butyl-4-hydroxybenzyl)sulfide, mercaptobenzothiazole, reaction products of phosphorus pentoxide and olefins, and dicetyl sulfide,

[0036] Given the necessity of securing good corrosion resistance, the grease will include a corrosion inhibitor of a type which is effective for rust inhibition; non-ferrous metal, especially copper, passivation functionality may also be useful. Corrosion inhibitors are a well-established class of additives and may typically be physical inhibitors which form a barrier type film on the metal or chemical type inhibitors which react on the metal surface to form a protective coating. Physical type inhibitors include the metal naphthenates and petroleum sulfonates, e.g barium petroleum sulfonates, zinc naphthenate and the like with preference for the zinc and calcium salts for their improved environmental acceptability.

[0037] The metal sulfonates and naphthenates are very effective and favored in many applications as corrosion inhibitors and have been found to be effective in wet tests but some greases formulated with the polyamide thixotrope and this class of corrosion inhibitors have been found to be subject to failure in corrosion testing. For this reason, the metal sulfonate/naphthenate corrosion inhibitors are not preferred in the current formulations.

[0038] The more aggressive chemical type inhibitors including the amine phosphates and imidazolines, are known to confer good corrosion (rust) inhibition in the conventional grease compositions even though these greases with alternative types of thickener system have been found to undergo degradation of the grease structure with these additives. The present greases, however, have been found to possess excellent mechanical stability even in the presence of water and under wet agitation (churning).

[0039] The amine rust inhibitors will generally contain from 8 to 24 carbon atoms and can be primary, secondary, tertiary, acyclic or cyclic, mono or polyamines. They can also be heterocyclic. The amine containing components can also contain other substituents, e.g, ether linkages or hydroxyl moieties. The preferred amines are generally aliphatic in nature. Some specific examples include: octylamine, decylamine, C_{10}, C_{12}, C_{14} and C_{16} tertiary alkyl primary amines (or combinations thereof), laurylamine, hexadecylamine, heptadecylamine, octadecylamine, decenylamine, dodecenylamine, palmitoylamine, oleylamine, linoleylamine, di-isoamylamine, di-octylamine, di-(2-ethylhexyl)amine, dilaurylamine, cyclohexylamine, 1,2-propylene amine, 1,3-propylenediamine, diethylene triamine, triethylene tetraamine, ethanolamine, triethanolamine, trioctylamine, pyridine, morpholine, 2-methylpiperazine, 1,2-bis(N-piperazinyl-ethane), 1,2-diamine, tetraminooctadecene, triaminooctadecene, N-hexylaniline and the like. They may also be triazole or triazole derivatives, which are described elsewhere as a necessary ingredient in the composition according to the present disclosure.

[0040] A preferred group of amities for this disclosure to serve as rust inhibitors are the oil-soluble aliphatic amines in which the aliphatic group is a tertiary alkyl group. Primene™ 81R (a primary aliphatic amine in which the amino nitrogen atom is linked to a tertiary carbon with C_{12-14} highly branched alkyl groups) and Primene™ JMT (a primary aliphatic amine in which the amino nitrogen atom is linked to a tertiary carbon with C_{16-22} highly branched alkyl groups) amines are commercially available amines that fall into this category.

[0041] The amines are preferably used in the form of salts with acid phosphates, which are effective as antirust and antiwear agents. The salts of the phosphates and amines may for instance be formed prior to addition to the additive package or they may be formed in situ after the acid phosphate and amine is added to the package.

[0042] The amine derivatives of the mono-or dialkyl acid phosphate provide valuable antiwear functionality and should be chosen to be soluble in the selected base oil of the grease. The amines may be of the types described above with preference given to the tertiary amines such as e.g. Primene™ 81-R; (Primene™ JM-T) or Primene™ TOA (a primary aliphatic amine in which the amino nitrogen atom is linked to a tertiary carbon with C_8 alkyl groups).

[0043] Preferred mono- and/or dialkyl-acid phosphate antiwear additives include at least one acid phosphate moiety derived from a phosphoric acid represented by the formula $R_1O(R_2O)P(O)OH$, where R_1 is hydrogen or hydrocarbyl and R_2 is hydrocarbyl. R_1 and R_2 may be the same or different, typically from 10 to 20 carbon atoms and preferably 10 to 12 carbon atoms.

[0044] The preferred hydrocarbyl groups for R_1 (if present) and R_2 are independently selected from C_1-C_{30} hydrocarbyls, preferably C_3-C_{20} alkyl, alkenyl, or aryl-containing hydrocarbyls, which may be straight chain, branched or cyclic, and may also contain heteroatoms such as O, S, or N. Suitable hydrocarbyl groups are alkyls of 1-40 carbon atoms, preferably 2-20 carbon atoms, more preferably 3-20 carbon atoms, alkenyls of 1-20 carbon atoms, cycloalkyls of 5-20 carbon atoms, aryls of 6-12 carbon atoms, alkaryls of 7-20 carbon atoms or aralkyls of 7-20 carbon atoms. Examples of suitable alkyl groups are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, methyl-decyl or dimethyl-decyl. Examples of suitable alkenyl groups are ethenyl, propenyl, butenyl, pentenyl or hexenyl. Examples of suitable cycloalkyl groups are cyclohexyl or methylcyclohexyl. Examples of suitable cycloalkenyl groups are 1-, 2-, or 3-cyclohexenyl or 4-methyl-2-cyclohexenyl. Examples of suitable aryl groups are phenyl or diphenyl. Examples of suitable alkaryl groups are 4-methyl-phenyl (p-tolyl) or p-ethyl-phenyl. Examples of suitable aralkyl groups are benzyl or phenethyl. It is possible to use a variety of acid phosphates, for example, one where R_2 is an aryl group, and the other where R_2 is an alkyl group like hexyl. The hydrocarbyl groups are typically selected from ethyl, iso-propyl, n-butyl, i-amyl, hexyl, 2-ethyl hexyl, n-octyl, nonyl, decyl, dodecyl, tridecyl, tetradecyl, hexadecyl, octadecyl, oleyl, linoleyl, linolenyl, phytol, myricyl, lauryl, myristyl, cetyl, stearyl, amyl phenol, nonyl phenol, methylcyclohexanol, alkylated napthol.

[0045] The acid phosphate esters for reaction with the amines may be conveniently formed by reaction of the corresponding alcohols, in the proper stoichiometric amounts, with phosphoric acid, to make the desired mono- or dialkyl phosphate. The preferred acid phosphates are selected from mono- and di-2-ethylhexyl acid phosphate, and mixtures of the two. Further description of useful amine phosphates is in US 2006/0223720 to which reference is made for a description of them.

[0046] The imidazolines which are useful as corrosion inhibitors are imidazolines with a long chain (C_8-C_{20}) alkyl, alkenyl or substituted alkyl or alkenyl substituent on one or both nitrogen atoms. A shorter chain substituent may be on the second nitrogen atom and this may be an alkyl group or substituted alkyl group. Exemplary useful imidazolines include 2-oleyl imidazoline, 1-hydroxyethyl-2-oleyl imidazoline and similar compounds.

[0047] Another useful class of corrosion inhibitors are the thiadiazoles, which are especially effective against copper corrosion. Preferably, the thiadiazole comprises at least one of 2,5-dimercapto-1,3,4-thiadiazole; 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles; 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles; 2,5-bis(hydrocarbylthio)- and 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles. The more preferred compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyldithio-5-mercapto-1,3,4-dithiadiazoles and the 2,5-bis(hydrocaroyldithio)-1,3,4-thiadiazoles, a number of which are available commercially from Afton Corporation as Hitec® 4313 or from Lubrizol Corporation as Lubrizol® 5955A.

[0048] Copper passivators include thiazoles, triazoles, and thiadizoles such as 2-mercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis-(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-bis-(hydrocarbyldithio)-1, 3,4-thiadiazoles. The imidazolines described above may also be suitable for providing copper passivation functionality.

[0049] The use of anti-wear/extreme pressure agents is favored in the present formulations in view of the severe loadings encountered in wind turbine bearings. Anti-wear and/or extreme pressure agents can be incorporated, typically in an amount from 0.1 to 5 wt %, more usually 0.5 to 2 wt %. Examples of anti-wear/extreme pressure agents include metal-free sulfur-containing species including sulfurized olefins, dialkyl polysulfides, diarylpolysulfides, sulfurized fats and oils, sulfurized fatty acid esters, phosphosulfur compounds, trithiones, sulfurized oligomers of C_2-C_8 monoolefins, sulfurized terpenes, thiocarbamate compounds e.g. metal or ash-free dithiocarbamates such as methylene bis (dibutyldithiocarbamate) or zinc dipentyldithiocarbamate; thiocarbonate compounds, sulfoxides, thiol sulfinates. Other examples include aryl phosphates and phosphites, thiophosphoric acid compounds e.g. zinc dialkyldithiophosphates metal-free phosphorus-containing additives such as esters of phosphorus acids, amine salts of phosphorus acids and phosphorus acid-esters, and partial and total thio analogs of these, for example, acid phosphate anti-wear agents, of the formula $R_1O(R_2O)P(O)OH$, where R_1 is hydrogen or hydrocarbyl and R_2 is hydrocarbyl.

[0050] Additive functionality may optionally be provided by multifunctional additives: antiwear agents, for example, will often provide EP activity; zinc diamyldithiocarbamate, for example, may be used as an oxidation inhibitor and metal deactivator with copper corrosion inhibition. Commercially available blends such as zinc dipentyldithiocarbamate with sulfurized isobutylenes may provide effective EP/antioxidant activity and the blend of methylene bis(dibutyldithiocarbamate) with tolutriazole derivative, is an ashless antioxidant which also exhibits extreme pressure performance alone or in combination with other additives.

[0051] Further examples of antiwear/EP agents and other additives are found in US 2007/0289897, to which reference is made for descriptions of them and exemplary methods for their preparation.

[0052] As noted above, the present grease formulations are characterized by a combination of properties including excellent water washout as measured by ASTM D 1264, low oil separation as measured by ASTM D 6184 as well as good low temperature properties including low starting torque as measured by ASTM D 1478 and the important property of corrosion resistance as measured by ASTM D 1743. Water washout (D 1264) is typically not more than 15% and in favorable cases less than 10%, e.g. less than 8 or even 6%; wet Shell roll (ASTM D 7342-2 (Procedure B) 10% DI at room temperature) may even show a negative change in penetration, i.e. become firmer after working. The oil separation is typically less than 8% and may be less than 5% and even less than 3 or 2%. The low temperature properties are also notable: in the Low-Temperature Torque test (ASTM D 1478), the starting torque (−40° C.) may be not more than 5,000 g-cm and typically is not more than 4,000 g-cms with values below 3,000 g-cms. being achievable; values at −30° C. are correspondingly better with a maximum of 2,000 g-cms, typically not more than 1500 g-cms.

[0053] A further advantage of the present formulations is that the greases are able to pass the Riffel Test (standard conditions), achieving a maximum scar depth of less than 10 microns (with up to 20 microns permitted in the region of salt water injection provided that the average is less than 2 microns), an average scare depth of less than 3 microns and corrosion less than or equal to a rating of 2. The Riffel Test (or Ripple Test) is a test developed by the IME, the German Institut für Mechanischenelemente und Mechanischengestaltung of Aachen (DE); the test can be carried out on request at the IME.

[0054] The following are examples of the present disclosure and are not to be construed as limiting.

EXAMPLES

Example 1

[0055] Evaluations of the effect of a polyamide thixotrope on grease performance were conducted using an additive-free lithium complex grease.

[0056] A series of grease formulations were made up using an ISO VG 220 PAO as the base oil with a lithium complex thickener and varying amounts of a water-/oil-insoluble polyamide co-thickener (from decanoic acid/12-hydroxystearic acid/ethylene diamine). The polyamide, when used, was added to the contactor during the thickener reaction at 188° C. in amounts of 0.5, 1.00 and 1.50 wt %, based on the weight of the base grease.

[0057] The test results of the greases are shown in Table 1 below and in FIGS. **1** and **2** for the water wash out and cone bleed (oil separation). The results show that the addition of the polyamide is effective to reduce oil separation and water wash out indicating good grease structural retention and excellent water washout: a value of 10-15 is conventionally considered acceptable for ASTM D1264.

TABLE 1

Effect of Polyamide Thixotrope						
Polyamide,	FM,	Penetration		Cone Bleed	Drop Pt.	Washout
wt. %	%	60X	100X	D6184	D2265	D1264
0	9.32	301	304	4.8	—	36.3
0.50	11.15	280	290	2.8	305	13.5
1.00	11.21	265	303	2.1	306	2.5
3.00	10.09	286	342	0.84	262	6.6

Example 2

[0058] ISO 460 grease formulations were prepared using a PAO blend base oil (6/150 cSt) and the same lithium complex thickener as in Example 1. A standard antioxidant/corrosion-rust inhibitor package (4.10 wt. %) containing an amine phosphate and an alkyl imidazoline as corrosion inhibitors was used. To this basic grease formulation, the same thixotropic additive as in Example 1 was added to the finishing kettle in amounts of 0.5, 1.0 and 3.0 weight percent based on the total weight of the grease formulation. The four greases were subjected to the performance testing with the results in Table 2 below.

TABLE 2

		Polyamide Greases			
Polyamide, wt. %		0.0	0.5	0.95	3.0
Thickener, wt %		13	13	13	13
Test	Units	Results			
Penetration, U/W	mm/10	281/283	292/283	315/312	255/252
Mechanical/Structural					
CGOR wt % Bleed (1)	wt %	3.8	3.8	3.9	2.9
CGOR ½ Scale Pen	mm/10	145	154	157	138
Change in Penetration	mm/10	28	24	14	22
Water Resistance					
Water Washout, 79° C. (2)	wt %	71.6	1.4	8.7	6.6
Wet Roll (3)					
½ Scale Penetration After	mm/10	142	145	152	118
Change in Penetration	mm/10	22	6	2	−10
Wet Extended Penetration (4)					
Penetration After	mm/10	339	335	339	297
Change in Penetration	mm/10	56	52	2.7	45
Change in Penetration	%	19.8	18.4	8.6	17.8
Water Spray Resistance (5)					
Low Temperature					
USS Mobility @ −18° C.	g/min	9.9	10.2	13.7	4.85

Notes:
(1) Churned Grease Oil Release, internal dynamic bleed test
(2) ASTM D 1264
(3) 10% DI @ RT, ASTM D7342-2 (Proc. B)
(4) (10% DI, 100Kx) ASTM D7342-2 (Proc. A)
(5) ASTM D 4049

Example 3

[0059] This example compares a commercial ISO 460 grease using a synthetic hydrocarbon (SHC) with a comparison ISO 460 grease containing the same polyamide thixotrope as in Example 2 added to a batch contactor/finishing kettle; this grease also contained an amine phosphate/imidazoline antiwear package. The polyamide co-thickener was added to the new grease formulation in an amount of 0.83 wt %. The performance of the two formulations was then tested and the results are shown in Table 3 below.

TABLE 3

Grease	Units	ISO 460 Grease	ISO 460 Grease + Polyamide
Structural Stability			
Unworked Penetration (1)	mm/10	315	294
60X Worked Penetration (1)	mm/10	310	298
100K X Worked Penetration (1)	mm/10	345	305
Change in worked pen, 60x to 100Kx	mm/10	35	7
Change in worked pen, 60x to 100Kx	%	11.3	2.3
High Temperature & Oil Bleed			
Pressure Bleed, 168 hrs @ 80° C. (2)	%	9.4	5.7
Water Resistance			
Water Washout (3)	%	7.4	3.3
Wet Extended Penetration (4)			
Pen before		311	298
Pen after		342	309
Change in Pen	mm/10	31	11
Change in Pen	%	9.97	3.69
Wet Shell Roll (5)			
½ scale pen before		155	144
½ scale pen after		163	137
Change in Pen(full scale)	mm/10	16	−14
Change in Pen (full scale)	%	5.1	−4.8
Low-Temperature (6)			
Low Temp. Torque @ −40° C.			
Starting	g · cm	10700	2860
Running	g · cm	3480	676
Low Temp. Torque @ −30° C.			
Starting	g · cm	3130	1300
Running	g · cm	738	202
USS Mobility @ −18° C.	g/min	4.9	18.46
Corrosion			
EMCOR, 10% SSW (7)	rating	0, 2/2	0, 0

Notes:
(1) ASTM D-217
(2) IP121
(3) ASTM D1264, 79° C.
(4) ASTM D7342 - Proc. A, 100Kx (10% DI)
(5) ASTM D7342 - Proc. B, (10% DI)
(6) ASTM D1478
(7) ASTM D6138

Example 4

[0060] Two ISO 460 greases were prepared in a batch mode in a mini contactor/kettle, both using a 6/150 cSt PAO blend and the same lithium complex thickener system as in previous examples and the same additive package as in Example 2 with the exception that the grease with added polyamide (1.0 wt %), the amount of imidazoline in the corrosion inhibitor was reduced from 0.5 to 0.2 wt %. The two formulations were tested in the Riffel Test under standard conditions with the following results showing acceptable ripple (false brinelling) and corrosion resistance in spite of the lower level of inhibitor.

TABLE 4

Riffel Test	IME Test Limits	Units	ISO 460 Grease	ISO 460 Grease with Polyamide
Max Scar	<10	micron	3.33	4.4
Mean Scar	<3	micron	0.49	1
Corrosion	≦3	rating	1.5	2

[0061] Applicants have attempted to disclose all embodiments and applications of the disclosed subject matter that could be reasonably foreseen. However, there may be unforeseeable, insubstantial modifications that remain as equivalents. While the present invention has been described in conjunction with specific, exemplary embodiments thereof, it is evident that many alterations, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description without departing from the spirit or scope of the present disclosure. Accordingly, the present disclosure is intended to embrace all such alterations, modifications, and variations of the above detailed description.

[0062] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this invention and for all jurisdictions in which such incorporation is permitted.

[0063] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

What is claimed is:

1. A grease composition which comprises: a lubricating base oil, a water insoluble thickener, and a thixotropic polyamide.

2. The grease composition according to claim **1** in which the polyamide comprises a reaction product of (i) a long chain (C_8-C_{20}) carboxylic acid derivative and (ii) an alkylene amine having at least two primary amine groups.

3. The grease composition according to claim **2** in which the polyamide comprises a diamide which is a reaction product of a C_{10}-C_{20} carboxylic acid and a C_2-C_4 alkylene diamine.

4. The grease composition according to claim **3** in which the polyamide comprises a diamide which is a reaction product of a C_{10}-C_{20} straight chain fatty carboxylic acid and a C_2-C_4 alkylene diamine.

5. The grease composition according to claim **4** in which the polyamide comprises a diamide which is derived from ethylene diamine, decanoic acid and 12-hydroxyoctadeanoic acid.

6. The grease composition according to claim **4** in which the polyamide comprises a diamide which is mixture of N,N'-ethane-1,2-diylbis(decanamide), 12-hydroxy-N-[2(1-oxydecyl) amino]ethyloctadecanamide and N,N'-1,2-diylbis(12-hydroxyoctadecanamide).

7. The grease composition according claim **1** in which the thickener comprises an aluminum, barium, calcium or lithium soaps, or an aluminum, barium, calcium or lithium salt/soap complex.

8. The grease composition according claim **7** in which the thickener comprises a lithium salt/soap complex.

9. The grease composition according claim **1** in which the thickener comprises an inorganic clay thickener.

10. The grease composition according claim **1** in which the lubricating base oil comprises a poly alpha olefin.

11. The grease composition according claim **10** in which the lubricating base oil comprises a poly alpha (C_8-C_{12}) olefin.

13. The grease composition according claim **10** in which the lubricating base oil comprises a poly alpha (C_8-C_{12}) olefin having a kinematic viscosity of 2 to 10 cSt and a poly alpha (C_8-C_{12}) olefin having a kinematic viscosity of 100 to 200 cSt.

14. The grease composition according claim **1** which comprises at least one of a corrosion inhibitor, an antioxidant and an antiwear agent.

15. The grease composition according claim **14** in which the corrosion inhibitor comprises an amine phosphate derived from a tertiary alkylamine and acid phosphate moiety derived from a phosphoric acid represented by the formula. $R_1O(R_2O)P(O)OH$, where R_1 is hydrogen or C_{10}-C_{20} hydrocarbyl and R_2 is hydrocarbyl and R_1 and R_2 may be the same or different.

16. The grease composition according claim **14** which comprises an imidazoline rust inhibitor.

17. The grease composition according claim **16** in which the imidazoline rust inhibitor comprises a long chain alkyl or alkenyl (C_8-C_{20}) imidazoline.

18. The grease composition according claim **17** in which the imidazoline rust inhibitor comprises 2-oleyl imidazoline.

19. The grease composition according claim **1** which has a rating in the Riffel Test of maximum scar less than 10μ, average scar less than 3μ and corrosion not more than 3.

20. The grease composition according claim **1** which has a water resistance (ASTM D 1264) of not more than 10%.

21. The grease composition according claim **1** which has an oil separation (ASTM D 6184) less than 5%.

22. The grease composition according claim **1** which has a low-temperature starting torque (ASTM D 1478, −40° C.) not more than 4,000 g-cm.

23. A grease composition having improved water resistance, mechanical grease stability and low temperature performance which comprises:

(i) a synthetic hydrocarbon base oil,

(ii) a lithium complex thickener,

(iii) a thixotropic, water-insoluble, oil-insoluble polyamide co-thickener derived from at least one C_8-C_{20} monocarboxylic fatty acid and a C_2-C_6 alkylene diamine,

(iv) a corrosion inhibitor

(v) an antioxidant, and

(vi) an antiwear agent.

24. The grease composition according to claim **23** in which:

(i) the base oil comprises a polyalpha olefin),

(ii) the thixotropic polyamide co-thickener is derived from decanoic acid, 12-hydroxystearic acid and ethylene diamine, and

(iii) the corrosion inhibitor comprises an amine phosphate and/or an alkyl imidazoline.

25. The grease composition according to claim **24** which comprises:

(i) from 70 to 85 wt % of the base oil,

(ii) from 6 to 14 wt % of the lithium complex thickener,

(iii) from 0.1 to 5 wt % of the polyamide co-thickener.

26. A grease composition having improved water washout resistance and anticorrosion characteristics having a water washout resistance (D 1264) not more than 15%, low-temperature torque starting torque (ASTM D 1478, −40° C.) not more than 4,000 g-cm, and oil separation (ASTM D6184) less than 8.

27. The grease according to claim **26** having a water washout resistance (D 1264) not more than 10%, and low-temperature torque starting torque (ASTM D 1478, −40° C.) not more than 3,000 g-cm, and an oil separation (ASTM D 6184) less than 5%.

28. The grease according to claim **26** having a water washout resistance (D 1264) not more than 15%, low-temperature torque starting torque (ASTM D 1478, −30° C.) not more than 2,000 g-cm, and an oil separation (ASTM D 6184) less than 8%.

29. The grease according to claim **26** having an Oil separation (ASTM D 6184) less than 5%.

30. The grease according to claim **26** having a negative change in penetration in the Wet Roll test (ASTM D 7342-2 (Procedure B, 10% DI at room temperature).

31. A method of making a grease composition having improved water resistance, mechanical grease stability and low temperature performance which comprises providing the following components:

(i) a synthetic hydrocarbon base oil,
(ii) a lithium complex thickener,
(iii) a thixotropic, water-insoluble, oil-insoluble polyamide co-thickener derived from at least one C_8-C_{20} monocarboxylic fatty acid and a C_2-C_6 alkylene diamine,
(iv) a corrosion inhibitor
(v) an antioxidant, and
(vi) an antiwear agent,

and mixing the components to form a grease.

32. The method according to claim **31** in which:

(i) the base oil comprises a poly(alpha olefin),
(ii) the thixotropic polyamide co-thickener is derived from decanoic acid, 12-hydroxystearic acid and ethylene diamine, and
(iii) the corrosion inhibitor comprises an amine phosphate and/or an alkyl imidazoline.

33. The method according to claim **32** which comprises:

(i) from 70 to 85 wt % of the base oil,
(ii) from 6 to 14 wt % of the lithium complex thickener,
(iii) from 0.1 to 5 wt % of the polyamide co-thickener.

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