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(54) Title: LUBRICANTS OILS AND GREASES CONTAINING NANOPARTICLES

(57) Abstract: Lubricant oil compositions containing a base oil and an additive package comprising one or more wear-resistant additives. The wear-resistant additives can be (a) a Group 1a alkali metal carbonate, a Group 2a alkaline earth metal carbonate, or a mixture thereof; (b) Group 1a alkali metal sulfate, a Group 2a alkaline earth metal sulfate, or a mixture thereof; (c) a Group 1a alkali metal phosphate, a Group 2a alkaline earth metal phosphate, or a mixture thereof; (d) Group 1a alkali metal carboxylate, a Group 2a alkaline earth metal carboxylate; or (e) a combination of (a), (b), (c), and (d). The wear-resistant additives are in the form of nanoparticles.



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1 **LUBRICANT OILS AND GREASES CONTAINING NANOPARTICLES**

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4 This application claims priority to US provisional application serial
5 number 60/592,794, filed July 30, 2004, incorporated herein by reference.

6
7 **BACKGROUND OF THE INVENTION**

8 This invention pertains to lubricants and greases containing
9 nanoparticles of, for example, carbonate such as calcium carbonate, a
10 carboxylate such as calcium carboxylate, a phosphate such as tricalcium
11 phosphate, and/or calcium sulfate.

12 Lubricant oils and greases are commonly used for a variety of
13 applications. For example, lubricant oils are used as crankcase lubricants for
14 internal combustion engines, including gasoline and diesel engines. With the
15 current and anticipated emission regulations, automotive manufactures have
16 been conducting research to develop exhaust aftertreatment devices and
17 other mechanical features to meet the new lower emissions standards.
18 Engine oil is affected by these regulations in that it will need to have
19 significantly lower levels of phosphorous in order to avoid the harmful effects
20 over time on the new exhaust aftertreatment devices. This is a problem for
21 the engine oil formulator because for decades zinc dithiophosphates have
22 been the primary wear-resistant additive used for engine oils. Reducing the
23 level of phosphorous in engine oil requires a similar reduction in zinc
24 thiophosphates or other phosphorous-containing wear-resistant additives.
25 The inventor has identified that a need exists to provide a solution to this
26 problem.

1

SUMMARY OF THE INVENTION

2 An improved adherent, friction-reducing lubricant oil or grease
3 composition is provided which contains nanoparticles of a carbonate, a
4 carboxylate such as calcium acetate, a phosphate, a sulfate, or a combination
5 of two or more of these materials. As used herein, "nanoparticles" refers to
6 particles having a mean diameter generally less than 1,000 nanometers, more
7 typically less than 100 nanometers, and in one embodiment in the range from
8 1 to 100 nanometers. In one embodiment, the invention is a lubricant having
9 a low viscosity such as is used as engine oil for gasoline or diesel engines
10 used in automobiles and trucks. Fluid lubricants typically are Newtonian or
11 near-Newtonian whereas greases are non-Newtonian. A Newtonian fluid is
12 one in which the absolute viscosity is independent of the shear rate. A non-
13 Newtonian material is one which the absolute viscosity is dependent of the
14 shear rate. In general, the lubricant lacks a thickener. By contrast, in another
15 embodiment of this invention, the greases of this invention include a base oil
16 and a thickener.

17 It is believed that the lubricant and grease of this invention provides
18 good friction reduction and provides excellent adherence to the surfaces to be
19 treated, the exact amount of which can be controlled by variations in the
20 levels of the components of its novel composition. It is believed that the
21 lubricant and grease of this invention has outstanding extreme pressure and
22 wear resistance properties which are, advantageously, provided without
23 imparting any corrosivity and with limited amounts of phosphorous containing
24 additives commonly used in lube oils today. This invention provides
25 formulations which may contain phosphorous containing additives, but which
26 use such phosphorous materials in amount within regulatory guidelines and
27 which do not deleteriously impact the aftertreatment devices discussed above.
28 For instance, through the practice of this invention it may be possible to use a
29 zinc thiophosphate in an oil formulation in smaller amounts than previously
30 utilized but which amounts falls within acceptable ranges for regulatory
31 guidelines and the aftertreatment devices. Advantageously, the oils of this
32 invention employ additives of a size small enough to be permanently

1 suspended without settling out. Through use of the additives of this invention,
2 phosphorous containing additives used in the prior art can be limited or
3 omitted entirely. In addition, the nanoparticles would preclude any plugging of
4 oil filters. It is possible that through use of the additives of this invention,
5 frictional heat generated under high loads may be reduced relative to
6 traditional additives. With respect to the greases of this invention, the use of
7 nanoparticles may impart lower noise generation and smoother micro-
8 structure.

9 In one broad respect, this invention is a lubricant oil composition which
10 comprises: a base oil and an additive package comprising one or more wear-
11 resistant additives, wherein the wear-resistant additives comprise (a) a Group
12 1a alkali metal carbonate, a Group 2a alkaline earth metal carbonate, or a
13 mixture thereof; (b) Group 1a alkali metal sulfate, a Group 2a alkaline earth
14 metal sulfate, or a mixture thereof; (c) a Group 1a alkali metal phosphate, a
15 Group 2a alkaline earth metal phosphate, or a mixture thereof; (d) Group 1a
16 alkali metal carboxylate, a Group 2a alkaline earth metal carboxylate; or (e) a
17 combination of (a), (b), (c), and (d); and wherein the additives are in the form
18 of nanoparticles. In general, the base oil comprises a substantial proportion
19 of the lubricant oil, such as at least 50 percent of the composition. The
20 additive package is present in an amount sufficient to impart antiwear
21 properties to the lubricant, wherein the additive package is in the form of
22 nanoparticles. In general the wear-resistant additives are metal salts of
23 carbonates, sulfates, phosphates and/or carboxylates. The additive package
24 may also provide extreme pressure resistant properties to the compositions of
25 this invention. In one embodiment, the additive package comprises the
26 nanoparticles of a carboxylate such as calcium carboxylate, a carbonate such
27 as calcium carbonate, a phosphate such as monocalcium phosphate,
28 dicalcium phosphate, or tricalcium phosphate, and/or a sulfate such as
29 calcium sulfate. In one embodiment, the lubricant does not contain a
30 thickener such as used in the grease of this invention.

31 In another broad respect, this invention is a process for manufacturing
32 a lubricant oil composition, comprising: mixing an additive package into a

1 base oil, wherein the additive package comprises one or more wear-resistant
2 additives, and wherein the wear-resistant additives are (a) a Group 1a alkali
3 metal carbonate, a Group 2a alkaline earth metal carbonate, or a mixture
4 thereof; (b) Group 1a alkali metal sulfate, a Group 2a alkaline earth metal
5 sulfate, or a mixture thereof; (c) a Group 1a alkali metal phosphate, a Group
6 2a alkaline earth metal phosphate, or a mixture thereof; (d) Group 1a alkali
7 metal carboxylate, a Group 2a alkaline earth metal carboxylate; or (e) a
8 combination of (a), (b), (c), and (d); and wherein the wear-resistant additives
9 are in the form of nanoparticles.

10 In another broad respect, this invention is a method for lubricating an
11 internal combustion engine, comprising: using a lubricant oil composition as
12 the motor oil, wherein the lubricant oil composition comprises: a base oil and
13 an additive package comprising one or more wear-resistant additives, wherein
14 the wear-resistant additives are (a) a Group 1a alkali metal carbonate, a
15 Group 2a alkaline earth metal carbonate, or a mixture thereof; (b) Group 1a
16 alkali metal sulfate, a Group 2a alkaline earth metal sulfate, or a mixture
17 thereof; (c) a Group 1a alkali metal phosphate, a Group 2a alkaline earth
18 metal phosphate, or a mixture thereof; (d) Group 1a alkali metal carboxylate,
19 a Group 2a alkaline earth metal carboxylate; or (e) a combination of (a), (b),
20 (c), and (d); and wherein the wear-resistant additives are in the form of
21 nanoparticles.

22 In one broad respect, this invention is a lubricant grease composition
23 which comprises: a base oil, a thickener, and an additive package comprising
24 one or more wear-resistant additives, wherein the wear-resistant additives are
25 (a) a Group 1a alkali metal carbonate, a Group 2a alkaline earth metal
26 carbonate, or a mixture thereof; (b) Group 1a alkali metal sulfate, a Group 2a
27 alkaline earth metal sulfate, or a mixture thereof; (c) a Group 1a alkali metal
28 phosphate, a Group 2a alkaline earth metal phosphate, or a mixture thereof;
29 (d) Group 1a alkali metal carboxylate, a Group 2a alkaline earth metal
30 carboxylate; or (e) a combination of (a), (b), (c), and (d); and wherein the
31 additives are in the form of nanoparticles. In general the grease composition
32 contains a substantial proportion of a base oil and thickener. The thickener

1 can be, for example, polyurea, triurea, biurea, calcium soap thickener (simple
2 or complex), lithium soap thickener (simple or complex), aluminum soap
3 thickener (simple or complex), or combinations thereof. The additive package
4 is in general present in an amount sufficient to impart antiwear properties to
5 the grease. In one embodiment, the additive package in the grease
6 composition comprises the nanoparticles of a carboxylate such as calcium
7 carboxylate, a carbonate such as calcium carbonate, a phosphate such as
8 monocalcium phosphate, dicalcium phosphate, or tricalcium phosphate,
9 and/or a sulfate such as calcium sulfate, or a combination thereof.

10 The grease composition may optionally include a polymeric additive
11 that cooperates and is compatible (non-interfering) with the antiwear additive
12 package to provide retentivity, friction reduction, wear reduction, mobility, and
13 pumpability while also maintaining an environmentally safe product. The
14 polymeric additive can comprise: polyesters, polyamides, polyurethanes,
15 polyoxides, polyamines, polyacrylamides, polyvinyl alcohol, ethylene vinyl
16 acetate, or polyvinyl pyrrolidone; polyolefins (polyalkylenes), such as
17 polyethylene, polypropylene, polyisobutylene, ethylene propylene, and
18 ethylene butylene; or polyolefin (polyalkylene) arylenes, such as polymers of
19 ethylene styrene and styrene isoprene; polyarylene polymers such as
20 polystyrene; polyacrylate, or polymethacrylate; or combinations, or boronated
21 analogs (compounds) of the preceding. Preferably, the polymeric additive
22 comprises: polyolefins (polyalkylenes), such as polyethylene, polypropylene,
23 polyisobutylene, ethylene propylene, and ethylene butylene; or polyolefin
24 (polyalkylene) arylenes, such as ethylene styrene and styrene isoprene;
25 polyarylene polymers such as polystyrene. As used in this application, the
26 term "polymer" means a molecule comprising one or more types of
27 monomeric units chemically bonded together to provide a molecule with at
28 least six total monomeric units. The monomeric units incorporated within the
29 polymer may or may not be the same. If more than one type of monomer unit
30 is present in the polymer the resulting molecule may be also referred to as a
31 copolymer.

1 In another broad respect, this invention is a process for manufacturing
2 a lubricant grease composition, comprising: mixing an additive package with
3 a base oil and thickener, wherein the additive package includes one or more
4 wear-resistant additives, wherein the additive package comprises (a) a Group
5 1a alkali metal carbonate, a Group 2a alkaline earth metal carbonate, or a
6 mixture thereof; (b) Group 1a alkali metal sulfate, a Group 2a alkaline earth
7 metal sulfate, or a mixture thereof; (c) a Group 1a alkali metal phosphate, a
8 Group 2a alkaline earth metal phosphate, or a mixture thereof; (d) Group 1a
9 alkali metal carboxylate, a Group 2a alkaline earth metal carboxylate; or (e) a
10 combination of (a), (b), (c), and (d); and wherein the additives are in the form
11 of nanoparticles.

12 In another broad respect, this invention is a process for lubricating a
13 surface, comprising: applying a lubricant grease composition to the surface,
14 wherein the lubricant grease composition comprises a base oil, a thickener,
15 and an additive package, wherein the additive package includes one or more
16 wear-resistant additives, wherein the wear-resistant additives are (a) a Group
17 1a alkali metal carbonate, a Group 2a alkaline earth metal carbonate, or a
18 mixture thereof; (b) Group 1a alkali metal sulfate, a Group 2a alkaline earth
19 metal sulfate, or a mixture thereof; (c) a Group 1a alkali metal phosphate, a
20 Group 2a alkaline earth metal phosphate, or a mixture thereof; (d) Group 1a
21 alkali metal carboxylate, a Group 2a alkaline earth metal carboxylate; or (e) a
22 combination of (a), (b), (c), and (d); and wherein the additives are in the form
23 of nanoparticles. Typically the surface is made of a metal or metal alloy. In
24 one embodiment the surface is a part in an automobile, truck, train, tractor, or
25 other vehicle including but not limited to ships and airplanes.

26 The lubricant oil and grease of this invention may be optionally
27 augmented with other antiwear additives such as graphite and molybdenum
28 disulfide, as well as other additives commonly employed in lubricants and
29 greases. Alternatively, such other antiwear additives can be omitted. The
30 grease may be further augmented in its composition by a boron-containing
31 material to further inhibit oil separation.

1 The use of combinations of carboxylates, carbonates, phosphate,
2 and/or the sulfates may possibly produce good results over the use of
3 improved amounts of any of these additives alone.

4 In one embodiment, the compositions of this invention are formed in
5 the absence of halogenated materials. Halogenated materials should be
6 avoided when using the additive mixture comprising sulfates and carbonates.
7 Halogenated materials to be avoided include halogenated hydrocarbons,
8 particularly chlorinated paraffins. Such materials exhibit corrosive tendencies
9 at prolonged high temperatures and thereby result in chemical attack to
10 ferrous and non-ferrous metals. This corrosivity is greatly accelerated when
11 water is present. Even small levels of water such as the moisture levels
12 commonly found in air at room temperature are enough to cause catastrophic
13 ferrous corrosion. Furthermore, it is believed that the extremely large
14 synergistic improvement in antiwear properties produced by the
15 sulfate/carbonate mixture is decreased when chlorinated paraffins are also
16 present.

17 The non-corrosivity of the mixture of calcium sulfate and calcium
18 carbonate at very high temperatures is also in marked contrast to oil-soluble
19 sulfur-containing materials.

20 In another embodiment, the additive package comprises sulfates and
21 carbonates with a minor amount of hydroxides. The preferred hydroxide is
22 calcium hydroxide. The addition of calcium hydroxide to the sulfate/carbonate
23 mixture imparts improved wear resistance to the oil or grease and also
24 provides additional overbasing to neutralize acidic materials which form over
25 long periods of time as the oil or grease oxidizes.

1 **DETAILED DESCRIPTION OF THE INVENTION**

2 The lubricating oil of this invention, in general, comprises the base oil
3 and the additive package of nanoparticles. In general, the base oil is present
4 in an amount of at least about 75% by weight, alternatively at least 80%, and
5 in one embodiment at least 90%, based on the total weight of the lubricant oil
6 composition including all other components. In general, the base oil is
7 present in an amount of less than about 99% by weight, and in one
8 embodiment less than about 95% by weight. In general the additive package
9 is present in an amount up to 10% by weight, in one embodiment up to 8%.
10 In general the additive package is present in an amount of at least 0.1% and
11 in one embodiment at least 1%.

12 The grease of this invention, in general, comprises by weight: 45% to
13 90% base oil, 5% to 20% thickener, and 0.5% to 30% antiwear additives. If
14 present, the amount of the polymer is from 1% to 10% of adhesive polymer. In
15 one embodiment, the lubricating grease comprises by weight: at least 65%
16 base oil, at least 3% thickener, and 8% to 20% extreme pressure antiwear
17 additives. When the grease is thickened substantially by polyurea, triurea,
18 biurea, calcium soaps (simple or complex), lithium soaps (simple or complex),
19 or aluminum soaps (simple or complex), or combinations thereof, the
20 lubricating grease typically comprises by weight 3% to 14% of said thickener.
21 In one embodiment, the lubricating grease comprises by weight 4% to 8% of
22 said thickener.

23 The base oil can be naphthenic oil, paraffinic oil, aromatic oil, or a
24 synthetic oil such as a polyalphaolefin polyolester, diester, polyalkyl ethers,
25 polyaryl ethers, silicone polymer fluids, or combinations thereof. The viscosity
26 of the base oil can range from 50 to 10,000 SUS at 100 F.

27 Other hydrocarbon oils can also be used, such as: (a) oil derived from
28 coal products, (b) alkylene polymers, such as polymers of propylene,
29 butylene, etc., (c) olefin (alkylene) oxide-type polymers, such as olefin
30 (alkylene) oxide polymers prepared by polymerizing alkylene oxide (e.g.,

1 propylene oxide polymers, etc., in the presence of water or alcohols, e.g.,
2 ethyl alcohol), (d) carboxylic acid esters, such as those which were prepared
3 by esterifying such carboxylic acids as adipic acid, azelaic acid, suberic acid,
4 sebacic acid, alkenyl succinic acid, fumaric acid, maleic acid, etc., with
5 alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, etc., (e)
6 liquid esters of acid of phosphorus, (f) alkyl benzenes, (g) polyphenols such
7 as biphenols and terphenols, (h) alkyl biphenol ethers, and (i) polymers of
8 silicon, such as tetraethyl silicate, tetraisopropyl silicate, tetra(4-methyl-2-
9 tetraethyl) silicate, hexyl(4-methyl-2-pentoxy) disilicone, poly(methyl)siloxane
10 and poly(methyl)phenylsiloxane.

11 The preferred base oil comprises about 65% by weight of a refined,
12 solvent-extracted, hydrogenated, dewaxed base oil, preferably 850 SUS oil,
13 and about 35% by weight of another refined solvent-extracted dewaxed base
14 oil, preferably 150 SUS oil, for better results. Type II, II+, and III base are the
15 most preferred currently.

16 Thickeners useful in the lubricating grease include polyurea, calcium
17 soaps (simple and complex), lithium soaps (simple and complex), and
18 aluminum soaps (simple and complex). Polyurea thickeners are preferred
19 over other types of thickeners because they have high dropping points,
20 typically 460 F. to 500 F., or higher. Polyurea thickeners are also
21 advantageous because they have inherent antioxidant characteristics, work
22 well with other antioxidants, and are compatible with all elastomers and seals.

23 The calcium base material used in the thickener can be calcium oxide,
24 calcium carbonate, calcium bicarbonate, calcium hydroxide, or any other
25 calcium containing substance which, when reacted with a monocarboxylic
26 acid or monocarboxylic acid derivative, provides a calcium carboxylate
27 thickener.

28 In order to attain extreme pressure properties, antiwear qualities,
29 and/or friction reduction properties, as well as any elastomeric compatibility
30 which may be required, the additives in the additive package may comprise a

1 carboxylate, a sulfate, a phosphate and/or a carbonate. Each component, if
2 present, is in an amount of from 0.1 to 10% of the lubricant oil composition or
3 grease composition.

4 Desirably, the mean particle size of the carboxylate, carbonate,
5 phosphate, and sulfate is generally less than about 100 nanometers. In one
6 embodiment, the mean size is from 1 to 100 nanometers.

7 The preferred carbonate additive is calcium carbonate. While calcium
8 carbonate is preferred, other carbonate additives can be used, if desired, in
9 conjunction with or in lieu of calcium carbonate, such as the carbonates of
10 Group 2a alkaline earth metal, such as beryllium, magnesium, calcium,
11 strontium, and barium, or the carbonates of a Group 1a alkali metal, such as
12 lithium, sodium, and potassium. Desirably, calcium carbonate is less
13 expensive, less toxic, more readily available, safer, and more stable than
14 other carbonates. Calcium carbonate is also superior to calcium bicarbonate.
15 Calcium carbonate is also water insoluble. Calcium bicarbonate, however, has
16 an acidic proton which at high temperatures can corrosively attack metal
17 surfaces.

18 While calcium sulfate is preferred, other sulfate additives can be used,
19 if desired, in conjunction with or in lieu of calcium sulfate, such as the sulfates
20 of Group 2a alkaline earth metal, such as beryllium, magnesium, calcium,
21 strontium, and barium, or the sulfates of a Group 1a alkali metal, such as
22 lithium, sodium, and potassium. Desirably, calcium sulfate is less expensive,
23 less toxic, more readily available, and safer. Calcium sulfate is also superior
24 to calcium bisulfate. Calcium sulfate is also essentially water insoluble and will
25 not wash out of the grease when contamination by water occurs.

26 The carboxylates used in this invention are of a Group 2a alkaline earth
27 metal, such as beryllium, magnesium, calcium, strontium, and barium, or a
28 Group 1a alkali metal, such as lithium, sodium, and potassium. The
29 carboxylates are of a Group 2a alkaline earth metal or of a Group 1a alkali
30 metal such as those described above. Representative carboxylates include

1 acetates, proprionates and other carboxylates having up to 12 carbons. A
2 representative example of such carboxylates includes calcium acetate.

3 The phosphates used in this invention are of a Group 2a alkaline earth
4 metal, such as beryllium, manganese, calcium, strontium, and barium, or of a
5 Group 1a alkali metal, such as lithium, sodium, potassium, rubidium, cesium,
6 and francium. For example, monocalcium phosphate, dicalcium phosphate,
7 and tricalcium phosphate can be employed in the practice of this invention.

8 The additive package can further comprise calcium hydroxide. A
9 relatively minor level of calcium hydroxide, when added to the oil or grease,
10 may improve the wear resistance properties. Also, the calcium hydroxide
11 provides additional excess alkaline reserve which can be useful to help
12 neutralize any acidic products which may result from high temperature
13 oxidation of the grease over long periods of time. Preferably, the calcium
14 hydroxide, when present, should be present at 0.01% to 5% by weight of the
15 grease.

16 The additive package may be complemented by the addition of small
17 amounts of an antioxidant and a corrosion inhibiting agent, as well as dyes
18 and pigments to impart a desired color to the composition.

19 Antioxidants or oxidation inhibitors prevent varnish and sludge
20 formation and oxidation of metal parts. Typical antioxidants are organic
21 compounds containing nitrogen, such as organic amines, sulfides, hydroxy
22 sulfides, phenols, etc., alone or in combination with metals like zinc, tin, or
23 barium, as well as phenyl-alpha-naphthyl amine, bis(alkylphenyl)amine, N,N
24 diphenyl-p-phenylenediamine, 2,2,4 trimethyldihydroquinoline oligomer, bis(4
25 isopropylaminophenyl)-ether, N-acyl-p-aminophenol, N-acylphenothiazines, N
26 of ethylenediamine tetraacetic acid, and alkylphenol-formaldehyde-amine
27 polycondensates.

28 Corrosion inhibiting agents or anticorrosants prevent rusting of iron by
29 water, suppress attack by acidic bodies, and form protective film over metal
30 surfaces to diminish corrosion of exposed metallic parts. A typical corrosion .

1 inhibiting agent is an alkali metal nitrite, such as sodium nitrite. Other ferrous
2 corrosion inhibitors include metal sulfonate salts, alkyl and aryl succinic acids,
3 and alkyl and aryl succinate esters, amides, and other related derivatives.
4 Borated esters, amines, ethers, and alcohols can also be used with varying
5 success to limit ferrous corrosion. Likewise, substituted amides, imides,
6 amidines, and imidazolines can be used to limit ferrous corrosion. Other
7 ferrous corrosion inhibitors include certain salts of aromatic acids and
8 polyaromatic acids, such as zinc naphthenate.

9 Metal deactivators can also be added to further prevent or diminish
10 copper corrosion and counteract the effects of metal on oxidation by forming
11 catalytically inactive compounds with soluble or insoluble metal ions. Typical
12 metal deactivators include mercaptobenzothiazole, complex organic nitrogen,
13 and amines. Although such metal deactivators can be added to the grease,
14 their presence is not normally required due to the extreme nonreactive,
15 noncorrosive nature of the railroad track/wheel flange grease composition.

16 For the lubricant oil compositions, dispersants may optionally be
17 employed to add dispersion stability for the nanoparticles. Such dispersants
18 may be especially useful after the oil has been stressed during use, including
19 heat and cold cycles. The dispersants can be selected from conventional
20 dispersants and appropriately matched to the nanoparticles present in a given
21 formulation. When used, the amount of dispersant will typically be in the
22 range of 0.01 to 10 percent by weight of the total composition.

23 In any of the above described forms of the lubricating grease, boron-
24 containing oil separation inhibitors can be optionally added. It was found that
25 borates or boron-containing materials such as borated amine, when used in
26 greases in the presence of calcium phosphates and calcium carbonates, act
27 as an oil separation inhibitor, which is especially useful at high temperatures.
28 Such useful borated additives and inhibitors include: (1) borated amine, such
29 as is sold under the brand name of Lubrizol 5391 by the Lubrizol Corp., and
30 (2) potassium triborate, such as a microdispersion of potassium triborate in
31 mineral oil sold under the brand name of OLOA 9750 by the Oronite Additive

1 Division of Chevron Company. Other useful borates include borates of Group
2 1a alkali metals, borates of Group 2a alkaline earth metals, stable borates of
3 transition metals (elements), such as zinc, copper, and tin, boric oxide, and
4 combinations of the above. These borated materials may also be used when
5 soap thickeners or mixtures of polyurea and soap thickeners are used. When
6 boron-containing oil separation inhibitors are used in the grease they should
7 be present at 0.01% to 10%, preferably 0.1% to 5%, and most preferably
8 0.25% to 2.5%, by weight of the boron-containing material in the total grease.
9 Inorganic borate salts, such as potassium triborate, provide an oil separation
10 inhibiting effect similar to borated amines when used in polyurea greases in
11 which calcium phosphate and calcium carbonate are also present. It is
12 believed that the physio-chemical reason for this oil separation inhibiting effect
13 is similar to that for borated amines.

14 Other solid additives in nanoparticle form may be used in this invention
15 in addition to, or as an alternative to the carbonates, carboxylates, and
16 sulfates. Such other solid additives in nanoparticle form included but are not
17 limited graphite, molybdenum disulfide, and TEFLON polymers.

1 **WHAT IS CLAIMED IS:**

2

3 1. A lubricant oil composition, comprising: a base oil and an additive
4 package comprising one or more wear-resistant additives, wherein the wear-
5 resistant additives are (a) a Group 1a alkali metal carbonate, a Group 2a
6 alkaline earth metal carbonate, or a mixture thereof; (b) Group 1a alkali metal
7 sulfate, a Group 2a alkaline earth metal sulfate, or a mixture thereof; (c) a
8 Group 1a alkali metal phosphate, a Group 2a alkaline earth metal phosphate,
9 or a mixture thereof; (d) Group 1a alkali metal carboxylate, a Group 2a
10 alkaline earth metal carboxylate; or (e) a combination of (a), (b), (c), and (d);
11 and wherein the additives are in the form of nanoparticles.

12 2. The composition of claim 1, wherein the nanoparticles have a mean
13 diameter in the range from 1 to 100 nanometers.

14 3. The composition of claim 1, wherein the wear-resistant additives are
15 calcium salts.

16 4. The composition of claim 1, wherein the base oil is present in an
17 amount of least 90% by weight.

18 5. The composition of claim 1, wherein the additive package is present in
19 an amount in the range from about 0.1% to about 10% by weight.

20 6. The composition of claim 1, wherein a carbonate is present and the
21 carbonate is calcium carbonate.

22 7. The composition of claim 1, wherein a sulfate is present and the sulfate
23 is calcium sulfate.

24 8. The composition of claim 1, wherein a carboxylate is present and the
25 carboxylate is calcium carboxylate.

26 9. The composition of claim 1, wherein a phosphate is present and the
27 phosphate is calcium phosphate.

- 1 10. The composition of claim 1, further comprising calcium hydroxide.
- 2 11. The composition of claim 1, wherein a combination of two of (a)-(d) is
3 present.
- 4 12. The composition of claim 11, wherein the combination includes a
5 sulfate.
- 6 13. The composition of claim 11, wherein the combination includes a
7 carbonate.
- 8 14. The composition of claim 11, wherein the combination includes a
9 phosphate.
- 10 15. The composition of claim 11, wherein the combination includes a
11 carboxylate.
- 12 16. The composition of claim 11, wherein at least three additives are
13 present in combination.
- 14 17. A process for manufacturing a lubricant oil composition, comprising:
15 mixing an additive package into a base oil, wherein the additive package
16 comprises one or more wear-resistant additives, and wherein the wear-
17 resistant additives are (a) a Group 1a alkali metal carbonate, a Group 2a
18 alkaline earth metal carbonate, or a mixture thereof; (b) Group 1a alkali metal
19 sulfate, a Group 2a alkaline earth metal sulfate, or a mixture thereof; (c) a
20 Group 1a alkali metal phosphate, a Group 2a alkaline earth metal phosphate,
21 or a mixture thereof; (d) Group 1a alkali metal carboxylate, a Group 2a
22 alkaline earth metal carboxylate; or (e) a combination of (a), (b), (c), and (d);
23 and wherein the wear-resistant additives are in the form of nanoparticles.
- 24 18. The process of claim 17, wherein the nanoparticles have a mean
25 diameter in the range from 1 to 100 nanometers.
- 26 19. The process of claim 17, wherein the wear-resistant additives are
27 calcium salts.

- 1 20. The process of claim 17, wherein the base oil is present in an amount
2 of least 90% by weight.
- 3 21. The process of claim 17, wherein the additive package is present in an
4 amount in the range from about 0.1% to about 10% by weight.
- 5 22. The process of claim 17, wherein a carbonate is present and the
6 carbonate is calcium carbonate.
- 7 23. The process of claim 17, wherein a sulfate is present and the sulfate is
8 calcium sulfate.
- 9 24. The process of claim 17, wherein a carboxylate is present and the
10 carboxylate is calcium carboxylate.
- 11 25. The process of claim 17, wherein a phosphate is present and the
12 phosphate is calcium phosphate.
- 13 26. The process of claim 17, further comprising calcium hydroxide.
- 14 27. The process of claim 17, wherein a combination of two of (a)-(d) is
15 present.
- 16 28. The process of claim 27, wherein the combination includes a sulfate.
- 17 29. The process of claim 27, wherein the combination includes a
18 carbonate.
- 19 30. The process of claim 27, wherein the combination includes a
20 phosphate.
- 21 31. The process of claim 27, wherein the combination includes a
22 carboxylate.
- 23 32. The process of claim 17, wherein at least three additives are present in
24 combination.

1 33. A method for lubricating an internal combustion engine, comprising:
2 using a lubricant oil composition as the motor oil, wherein the lubricant oil
3 composition comprises: a base oil and an additive package comprising one
4 or more wear-resistant additives, wherein the wear-resistant additives are (a)
5 a Group 1a alkali metal carbonate, a Group 2a alkaline earth metal carbonate,
6 or a mixture thereof; (b) Group 1a alkali metal sulfate, a Group 2a alkaline
7 earth metal sulfate, or a mixture thereof; (c) a Group 1a alkali metal
8 phosphate, a Group 2a alkaline earth metal phosphate, or a mixture thereof;
9 (d) Group 1a alkali metal carboxylate, a Group 2a alkaline earth metal
10 carboxylate; or (e) a combination of (a), (b), (c), and (d); and wherein the
11 wear-resistant additives are in the form of nanoparticles.

12 34. A lubricant grease composition, comprising: a base oil, a thickener,
13 and an additive package comprising one or more wear-resistant additives,
14 wherein the wear-resistant additives are (a) a Group 1a alkali metal
15 carbonate, a Group 2a alkaline earth metal carbonate, or a mixture thereof;
16 (b) Group 1a alkali metal sulfate, a Group 2a alkaline earth metal sulfate, or a
17 mixture thereof; (c) a Group 1a alkali metal phosphate, a Group 2a alkaline
18 earth metal phosphate, or a mixture thereof; (d) Group 1a alkali metal
19 carboxylate, a Group 2a alkaline earth metal carboxylate; or (e) a combination
20 of (a), (b), (c), and (d); and wherein the wear-resistant additives are in the
21 form of nanoparticles.

22 35. A process for manufacturing a lubricant grease composition,
23 comprising: mixing an additive package with a base oil and thickener,
24 wherein the additive package includes one or more wear-resistant additives,
25 wherein the additive package comprises (a) a Group 1a alkali metal
26 carbonate, a Group 2a alkaline earth metal carbonate, or a mixture thereof;
27 (b) Group 1a alkali metal sulfate, a Group 2a alkaline earth metal sulfate, or a
28 mixture thereof; (c) a Group 1a alkali metal phosphate, a Group 2a alkaline
29 earth metal phosphate, or a mixture thereof; (d) Group 1a alkali metal
30 carboxylate, a Group 2a alkaline earth metal carboxylate; or (e) a combination

1 of (a), (b), (c), and (d); and wherein the additives are in the form of
2 nanoparticles.

3 36. A process for lubricating a surface, comprising: applying a lubricant
4 grease composition to the surface, wherein the lubricant grease composition
5 comprises a base oil, a thickener, and an additive package, wherein the n
6 additive package includes one or more wear-resistant additives, wherein the
7 wear-resistant additives are (a) a Group 1a alkali metal carbonate, a Group
8 2a alkaline earth metal carbonate, or a mixture thereof; (b) Group 1a alkali
9 metal sulfate, a Group 2a alkaline earth metal sulfate, or a mixture thereof; (c)
10 a Group 1a alkali metal phosphate, a Group 2a alkaline earth metal
11 phosphate, or a mixture thereof; (d) Group 1a alkali metal carboxylate, a
12 Group 2a alkaline earth metal carboxylate; or (e) a combination of (a), (b), (c),
13 and (d); and wherein the additives are in the form of nanoparticles.