

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 903 398 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

24.03.1999 Bulletin 1999/12

(51) Int. Cl.⁶: **C10M 133/08**, C10M 169/06

// (C10M169/06, 117:00,
119:24, 133:08), C10N30:12,
C10N50:10

(21) Application number: **98117874.2**

(22) Date of filing: **21.09.1998**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(72) Inventors:

- **Andrew, David Leslie**
R R 1 Arkona, Ontario, Canada N0M 1B0 (CA)
- **Moore, Garry George**
Sarnia, Ontario, Canada N7S 3H5 (CA)

(30) Priority: **23.09.1997 US 936036**

(74) Representative:

Somers, Harold Arnold et al
ESSO Engineering (Europe) Ltd.,
Patents & Licences,
Mailpoint 70,
Esso House,
Ermyn Way
Leatherhead, Surrey KT22 8XE (GB)

(71) Applicant:

**EXXON RESEARCH AND ENGINEERING
COMPANY**
Florham Park, New Jersey 07932-0390 (US)

(54) **Lubricating grease containing alkoxyated amine corrosion inhibitor**

(57) The invention relates to a lubricating grease having enhanced corrosion-resistance by means of a corrosion-inhibiting additive comprising one or more defined alkoxyated amines.

EP 0 903 398 A2

Description

[0001] The present invention relates to lubricating grease compositions which exhibit corrosion resistance performance and to a method for increasing the corrosion resistance performance of greases by use of additives.

[0002] The use of additives in lubricating oil based formulations to achieve particular performance characteristics associated with the use of specific additives and additive types is well known.

[0003] U.S. Patent 4,129,508 teaches lubricant and fuel compositions exhibiting improved demulsifying properties attributable to the use of a mixture of (1) one or more reaction products of a hydrocarbon substituted succinic acid or anhydride with one or more polyalkylene glycols or monoethers thereof and (2) one or more organic basic metal salts and (3) one or more alkoxyated amines. The aforesaid demulsifying combination of additives is recited as being useful in lubricant formulations as diverse as crankcase oils for internal combustion and diesel engines, gas turbine oils, automatic transmission fluids, trans axle lubricants, gear oils, metal working fluids, hydraulic oils, greases. The patent, however, contains no examples of the use of the combination in greases, but only as additives in crankcase lubricants, gear oils, automatic transmission fluids and in fuels.

[0004] U.S. Patent 3,711,406 teaches poly (hydroxylated) amines combined with alkaline earth metal carbonates dispersed in a hydrocarbon medium to provide rust protection in internal combustion engines, i.e., in crankcase lubricants.

[0005] U.S. Patent 3,398,197 describes various N-secondary alkyl tertiary amine compounds, including alkoxyated amines as new compositions of matter and as useful as fuel additives and bactericides.

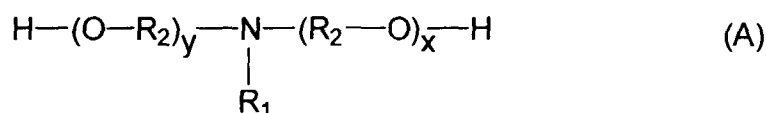
[0006] U.S. Patent 3,933,659 teaches a functional fluid useful in automatic transmissions containing, in addition to other additives, at least one material selected from N-fatty alkyl-N,N-diethanolamine; N-fatty alkyl-N, N-di(ethoxyethanol) amine, N-fatty alkyl-N,N-di-poly(ethoxy) ethanol amine.

[0007] U.S. Patent 4,382,006 claims lubricating composition comprising a major portion of an oil of lubricating viscosity or grease prepared therefrom and a minor portion of a friction-reducing compound, which is a borated adduct of an alkoxyated amine. The patent refers, in general, to the use of both borated and non-borated alkoxyated amines, but exemplifies such materials only in lubricating oils and only as friction-reducing additives.

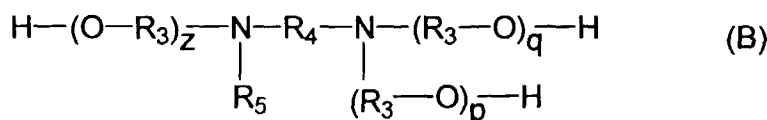
[0008] It would be an advance in grease technology if an improvement in rust and corrosion resistance could be achieved by use of an additive other than known rust and corrosion preventive additives, such as barium sulfonate, calcium sulfonates, amine phosphates, etc.

DESCRIPTION OF THE INVENTION

[0009] The present invention is a method for increasing the corrosion resistance of a base lubricating grease comprising a major portion of a base oil of lubricating viscosity, and a thickener by adding to said base grease a minor portion of one or more alkoxyated amine additive of the formula:



or

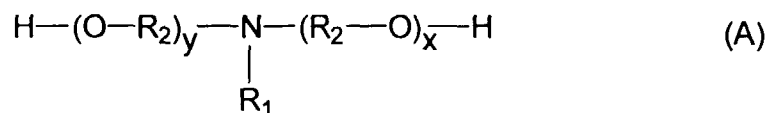


wherein R_1 and R_5 are independently C_1 to C_{30} hydrocarbyl radicals, R_2 and R_3 are independently C_2 to C_6 hydrocarbyl radicals, R_4 is a C_1 to C_6 hydrocarbyl radical, x and y are integers from 0 to 50 provided that $0 < (x + y) \leq 50$, and p , q and z are integers from 0 to 50 provided that $0 < (p + q + z) \leq 50$, in the absence of alkaline earth metal carbonates.

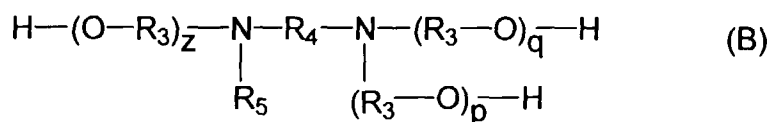
[0010] The amount of said alkoxyated amine additive added to the grease may be in the range 0.01 to 10 wt%. The invention also relates to corrosion resistant greases containing the alkoxyated amine additive described above.

DETAILED DESCRIPTION OF THE INVENTION

[0011] A method is disclosed for increasing the corrosion resistance of lubricating greases comprising a major portion of a base oil of lubricating viscosity, such base oil being any natural, synthetic or mixture of natural and synthetic oils, and a thickener which may be any of the conventional metal soaps and salts such as simple or complex lithium soap thickener, simple or complex calcium soap thickener, mixed lithium and calcium simple or complex soaps, aluminum soaps, urea, di-urea, tri-urea or polyurea thickener, by adding to the lubricating grease a minor amount of one or more additives of the formula



or



wherein R₁ and R₅ are independently C₁ to C₃₀ hydrocarbyl radicals, R₂ and R₃ are independently C₂ to C₆ hydrocarbyl radicals, R₄ is a C₁ to C₆ hydrocarbyl radical, x and y are integers from 0 to 50 provided that 0 < (x + y) ≤ 50, and p, q and z are integers from 0 to 50 provided that 0 < (p + q + z) ≤ 50, in the absence of alkaline earth metal carbonates.

[0012] Additional small quantities of other conventional additives may also be included in the grease formulation, those other additional additives being extreme pressure agents, anti oxidants, dyes, other rust and/or corrosion inhibitors, tackiness agents, oiliness agents, viscosity index improvers, etc.

[0013] The lubricating oil base stock that is used in preparing the grease compositions of this invention can be any of the conventionally used mineral oils, synthetic hydrocarbon oils or synthetic ester oils. In general, these lubricating oils will have a viscosity in the range of about 2 to 500 cSt (mm²/s) at 100°C. Mineral lubricating oil base stocks used in preparing the greases can be any conventionally refined base stocks derived from a paraffinic, naphthenic and mixed base crudes. Conventional refinery techniques include distillation, solvent or catalytic dewaxing, solvent extraction, hydrofinishing, hydrocracking, vis-breaking, etc. Synthetic lubricating oils that can be used include esters of di-basic acids, reacted with linear or branched aliphatic alcohols such as C₆-C₁₅ alcohols, such as di-2-ethylhexyl sebacate, esters of glycols such as C₁₃ oxo acid diester or tetraethylene glycol, or complex esters such as one formed from 1 mole of sebacic acid and 2 moles of tetraethylene glycol and 2 moles of 2-ethylhexanoic acid. Other synthetic oils that can be used include synthetic hydrocarbons such as alkyl benzenes, e.g., alkylate bottoms from the alkylation of benzene with tetrapropylene, or the copolymers of ethylene and propylene; silicone oils, e.g., ethyl phenyl polysiloxanes, methyl polysiloxanes, etc.; polyglycol oils, e.g., those obtained by condensing butyl alcohol with propylene oxide; carbonate esters, e.g., the product of reacting C₆ oxo alcohol with ethyl carbonate to form a half ester followed by reaction of the latter with tetraethylene glycol, etc. Other suitable synthetic oils include the polyphenyl ethers, e.g., those having from about 3 to 7 ether linkages and about 4 to 8 phenyl groups.

[0014] Other suitable oils are the polyol ester oils made by reacting an aliphatic polyol with carboxylic acid. Aliphatic polyols contain from 4 to 15 carbon atoms and has from 2 to 8 esterifiable hydroxyl groups. Examples of polyols are trimethylolpropane, pentaerythritol, dipentaerythritol, neopentyl glycol, tripentaerythritol and mixtures thereof. The carboxylic acid reactant is selected from aliphatic monocarboxylic acid or mixtures of aliphatic mono carboxylic acids or mixtures of aliphatic mono- and di-carboxylic acids. The carboxylic acids contain 4 to 12 carbons and include straight and branched chain carboxylic acids.

[0015] Included in the group of synthetic oils are those recovered from tar sands, shale oil, light hydrocarbons produced via, for example, the Fisher-Tropsch process for converting synthesis gas (CO and hydrogen) into hydrocarbons, wax isomerate oils produced by the catalytic hydroisomerization of natural petroleum waxes (i.e., slack wax) or synthetic waxes (i.e., Fischer-Tropsch waxes) or mixtures of such waxes. See USP 5,059,299 and USP 5,158,671 for description of wax isomerization and the oils produced thereby. Other synthetic oils include the polyolefins such as polybutene, polyisobutenes and especially the polyalphaolefins, i.e., fluids formed by the oligomerization of at least one 1-alkane hydrocarbon having from 6 to 20 carbons, preferable 8 to 16 carbons, more preferably 10 to 12 carbons, most

preferably 10 carbons. Hydrogenated oligomers are preferred and hydrogenated oligomers formed from 1-decene are particularly preferred.

[0016] Thickeners useful in the present grease formulation include simple and complex lithium soaps, preferably complex lithium soaps, simple and complex calcium soaps, mixed lithium-calcium soaps, and polyurea.

5 **[0017]** Polyurea thickeners are well known in the art. They are produced by reacting an amine or mixture of amines and a polyamine or mixture of polyamines with one or more diisocyanates and one or more isocyanates as appropriate. The reaction can be conducted by combining and reacting the group of reactants, taken from the above list in a reaction vessel at a temperature between about 15°C to 160°C for from 0.5 to 5 hours. The reaction is usually accomplished in a solvent, which in the case of grease production, is a quantity of the base oil to be used in the final grease formulation.

10 Detailed discussion of polyurea thickener production for greases can be found in USP 4,929,371.

[0018] Simple and complex lithium or calcium soaps for use as thickeners in grease formulations and their method of production are also well known to the grease practitioner. Simple soaps are produced by combining one or more fatty acid(s), hydroxy fatty acid(s), or esters thereof in a suitable solvent, usually the grease base oil, and reacting the acids or esters with the appropriate base, e.g., LiOH or CaOH. Complex lithium or calcium soap thickeners are prepared by

15 combining one or more fatty acid(s), hydroxy fatty acid(s) or esters thereof with an appropriate complexing agent in a suitable solvent, usually the grease base oil, and reacting the mixture with the appropriate base, e.g., LiOH or CaOH. The complexing agent typically consists of one or more dicarboxylic acids, or esters thereof, or one or more C₂ to C₆ short chain carboxylic acids, or esters thereof.

[0019] The fatty acid or hydroxy fatty acid used in the production of the thickeners employed in the grease of the present invention has 12 to 24 carbon atoms. Thus lithium or calcium salts of C₁₂ to C₂₄ fatty acids or of 9-, 10- or 12-hydroxy C₁₂ to C₂₄ fatty acids or the esters thereof are employed.

[0020] The lithium complex soaps are prepared by employing both the C₁₂-C₂₄ fatty acid, hydroxy fatty acid or esters thereof and a C₂-C₁₂ dicarboxylic acid complexing agent. Suitable acids, therefore, include the hydroxystearic acids, e.g., 9-hydroxy, 10-hydroxy or 12-hydroxystearic acid. Unsaturated fatty or hydroxy fatty acids, such as recinolic acid

25 which is an unsaturated form of 12-hydroxystearic and having a double bond in the 9-10 position, as well as esters of each acid, can also be used. The C₂-C₁₂ dicarboxylic acids employed will be one or more straight or branched chain C₂-C₁₂ dicarboxylic acids, preferably C₄-C₁₂, more preferably C₆ to C₁₀ dicarboxylic acids or the mono- or di-esters thereof. Suitable examples include oxalic, malonic, succinic, glutaric, adipic, suberic, pimelic, azelaic, dodecanedioic and sebacic acids and the mono- or di-esters thereof. Adipic, sebacic, azelaic acids and mixtures thereof preferably

30 sebacic and azelaic acids and mixture thereof are employed as the dicarboxylic acids used in the production of the complex lithium soap grease bases.

[0021] The calcium complex soaps are prepared by employing the C₁₂ to C₂₄ fatty acid, hydroxy fatty or ester or glyceride thereof and a C₂ to C₆ short chain carboxylic acid complexing agent. Suitable acids, therefore, include the hydroxystearic acids, e.g., 9-hydroxy, 10-hydroxy or 12-hydroxystearic acid. Unsaturated fatty acids or hydroxy fatty

35 acids, such as recinolic acid which is an unsaturated form of 12-hydroxystearic and having a double bond in the 9-10 position, as well as esters of each acid, can also be used. The short chain carboxylic acid can be straight chain or branched, preferably C₂ to C₆, and more preferably C₂, C₃ or C₄. Examples of short chain carboxylic acids include acetic acid, propanoic acid, butanoic acid, etc. Acetic acid is the preferred complexing acid in the production of calcium complex greases. Acetic acid can be added to the grease formulation in the form of the free acid and then neutralized

40 with CaOH along with the fatty acid, fatty acid ester or fatty acid glyceride, or alternatively, calcium acetate can be added to the grease directly.

[0022] Neutralization of the simple acid type soap (simple soap) or different acid-type acid mixture (complex soap) with the base is usually conducted at a temperature in the range of about 180 to 220°F. When the soap has thickened to a heavy consistency the temperature is raised to about 290-310°F to ensure elimination of water. Subsequent heating to a high temperature of about 380-420°F followed by addition of the balance of the oil used in preparing the grease and cooling to about 220°F can also be practiced.

[0023] While it is expected that the skilled practitioner of grease production will be familiar with the technique used to produce complex lithium or calcium greases, various of such production methods are presented in detail in USP 3,681,242, USP 3,791,973, USP 3,929,651, USP 5,236,607, USP 4,582,619, USP 4,435,299, USP 4,787,992. Mixed

50 lithium-calcium soap thickened greases are described in USP 5,236,607, USP 5,472,626. The particular techniques used to produce the simple or complex lithium or calcium soaps or lithium-calcium soaps are not believed to be critical in the present invention and do not form part of the present invention. The above is offered solely as illustration and not limitation.

[0024] In the present invention the preferred thickener, regardless of the technique used for its production, is complex

55 lithium soap.

[0025] The grease formulation of the present invention contains anywhere from 1 to 30 wt% thickener, preferably 5 to 15 wt% thickener, based on the finished formulation.

[0026] A preferred complex lithium grease base is disclosed and claimed in USP 3,929,651 which also teaches a

detailed procedure for its production. The teachings of that patent are incorporated herein by reference. Broadly that complex lithium grease base comprises a major amount of a base oil, a minor amount of a complex lithium soap thickener and a minor quantity of a lithium salt of a C₃-C₁₄ hydroxy carboxylic acid where in the OH group is attached to a carbon atom that is not more than 6 carbon atoms removed from the carbon of the carboxyl group.

5 **[0027]** In USP 3,929,651, the complex lithium soap is any of the conventional complex lithium soaps of the literature and typically comprises a combination of a dilithium salt of a C₂-C₁₂ dicarboxylic acid or the mono- or di-ester of such acids and a lithium salt of a C₁₂-C₂₄ fatty acid or of a 9-, 10- or 12- hydroxy C₁₂-C₂₄ fatty acid or the ester of such acid. These materials have been discussed in detail above. In addition, the grease also contains an additional lithium salt component, the lithium salt of a hydroxy carboxylic acid (s) or ester(s) thereof having an OH group attached to a carbon atom that is not more than 6 carbons removed from the carbon of the carboxyl group. This acid has from 3 to 14 carbon atoms and can be either an aliphatic acid such as lactic acid, 6-hydroxydecanoic acid, 3-hydroxybutanoic acid, 4-hydroxybutanoic acid, 6-hydroxy- α -hydroxy-stearic acid, etc., or an aromatic acid such as parahydroxybenzoic acid, salicylic acid, 2-hydroxy-4-hexylbenzoic acid, metahydroxybenzoic acid, 2,5-dihydroxybenzoic acid (gentisic acid); 2,6-dihydroxybenzoic acid (gamma resorcylic acid); 2-hydroxy-4-methoxybenzoic acid, etc., or a hydroxyaromatic aliphatic acid such as 2-(ortho hydroxyphenyl)-, 2-(meta hydroxyphenyl)-, or 2-(parahydroxyphenyl)-ethanoic acid. A cycloaliphatic hydroxy acid such as hydroxycyclopentyl carboxylic acid or hydroxynaphtheneic acid could also be used. Particularly useful hydroxy acids (or the esters thereof) are 2-hydroxy-4-methoxybenzoic acid, salicylic acid, and parahydroxybenzoic acid. Instead of using the free hydroxy acid of the latter type when preparing the grease, one can use a lower alcohol ester, e.g., the methyl, ethyl, or propyl, isopropyl, or sec-butyl ester of the acid, e.g., methyl salicylate. 20 The ester of the hydroxy carboxylic acid is hydrolyzed with aqueous lithium hydroxide to give the lithium salt. The monolithium salt or the dilithium salt of the C₃-C₁₄ hydroxy acid or ester thereof can be used, but the dilithium salt is preferred.

[0028] As taught in USP 3,929,651, these three component lithium salt thickeners can be formed in a number of different ways. One convenient way when the C₃-C₁₄ hydroxy carboxylic acid is salicylic acid is to co-neutralize the C₁₂-C₂₄ fatty acid or 9-, 10-, or 12-hydroxy C₁₂-C₂₄ fatty acid and the dicarboxylic acid in at least a portion of the oil with lithium hydroxide. This neutralization will take place at a temperature in the range of about 180°F to 220°F. When the soap stock has thickened to a heavy consistency, the temperature is raised to about 260°F to 300°F, to bring about dehydration. The soap stock is then cooled to about 190°F to 210°F, and the additional acid or ester of the C₃-C₁₄ hydroxy carboxylic acid, e.g., methyl salicylate is added; then, additional lithium hydroxide is added gradually to convert the acid or ester, e.g., methyl salicylate, to the dilithium salt, dilithium salicylate. Reaction is conducted at about 220°F to 240°F, preferably with agitation so as to facilitate the reaction. In this reaction, the alcohol is evolved, and dilithium salt of the acid or ester, e.g., salicylate, forms.

[0029] Dehydration is then completed at 300°F to 320°F, after which the grease is heated at 380-390°F for 15 minutes to improve its yield and is then cooled while additional oil is added to obtain the desired consistency. Alternatively, the additional oil can be added to the soap concentrate prior to the in situ formation of the dilithium salt of the appropriate acid or ester, e.g., the dilithium salt of salicylic acid.

[0030] An alternative method is to co-neutralize all three types of acid used in making the grease, or to saponify a lower ester of the hydroxy C₃-C₁₄ acid, e.g., methyl salicylate, simultaneously with the neutralization of the hydroxy fatty acid of the first type, e.g., hydroxystearic acid and the dicarboxylic acid. Still another alternative is to co-neutralize the hydroxy fatty acid and the ester of the hydroxy C₃-C₁₄ acid followed by neutralization of the dicarboxylic acid.

[0031] The greases contain, based on the finished grease mass, from about 2 to about 35 wt% and preferably about 10 to about 25 wt% of all three lithium salt components. The additional lithium salt of the C₃-C₁₄ hydroxycarboxylic acid (e.g., dilithium salicylate) is present in the grease in an amount in the range 0.05 to 10 wt% of the finished grease. The proportion of the lithium soap of C₁₂-C₂₄ fatty acid or 9-, 10- or 12- hydroxy C₁₂-C₂₄ fatty acid to the lithium soap of the dicarboxylic acid can be in the range of 0.5 to 15 parts by weight of the former to one part by weight of the latter, preferably in the range of 1.5 to 5 parts by weight of the soap of the C₁₂-C₂₄ fatty acid or 9-, 10- or 12- hydroxy C₁₂-C₂₄ fatty acid to one part by weight of the soap of the dicarboxylic acid. The proportion of the C₃-C₁₄ hydroxy carboxylic acid to the dicarboxylic acid will be from about 0.025 to 2.5 parts by weight of the hydroxy carboxylic acid to one part by weight of the dicarboxylic acid, preferably about 0.125 to 1.25 parts by weight of the hydroxy carboxylic acid to one part by weight of the dicarboxylic acid.

[0032] A preferred complex lithium grease base useful in the present member comprises a major amount of a base oil, a minor amount of the three component lithium salt thickeners described in the USP 3,929,651, discussed immediately above and thiadiazole. This particular grease is disclosed and claimed in copending U.S. Patent No. 5,731,274 granted March 24, 1998 in the name of David L Andrew.

55 **[0033]** The thiadiazol type materials used in that formulation are the general formula:



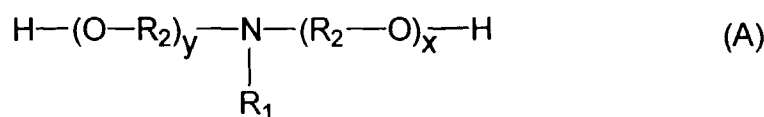
wherein Q is a 1,3,4-thiadiazole, 1,2,4-thiadiazole, 1,2,3-thiadiazole or a 1,2,5-thiadiazole heterocycle, "x" and "y" may be the same or different and are integers from 1 to 5 and R₁ and R₂ are the same or different and are H or C₁-C₅₀ hydrocarbyl, or (2)



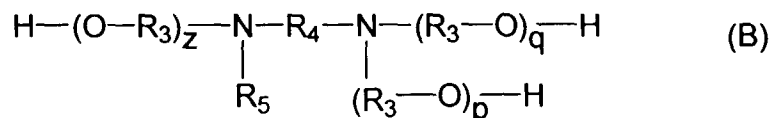
wherein Q₁ and Q₂ are the same or different and are 1,3,4-thiadiazole, 1,2,4-thiadiazole, 1,2,3-thiadiazole or 1,2,5-thiadiazole heterocycles, "x", "y", and "z" may be the same or different and are integers of from 1 to 5, and R₁ and R₂ are the same or different and are H or C₁-C₅₀ hydrocarbyl. The preferred thiadiazole has the structure 2 where x = 1, y = 1 and z = 2, R₁ = hydrogen, R₂ = hydrogen and Q₁ = Q₂ and is 1,3,4-thiadiazole. The preferred thiadiazole is available from R. T. Vanderbilt Company, Inc., under the trade name Vanlube 829.

[0034] In the preferred grease the thiadiazole material is present in the grease in an amount in the range 0.05 to 5 wt% of the finished grease. The thiadiazole material is added to the grease in U.S. Patent No. 5,731,274 for the purpose of enhancing the oxidation resistance of the grease.

[0035] The grease formulation of the present invention contains 0.01 to 10 wt%, preferably 0.05 to 5 wt%, more preferably 0.2 to 1.5 wt% of one or more alkoxyated amine(s) of the formula:



or



wherein R₁ and R₅ are independently C₁ to C₃₀ hydrocarbyl radicals, R₂ and R₃ are independently C₂ to C₆ hydrocarbyl radicals, R₄ is a C₁ to C₆ hydrocarbyl radical, x and y are integers from 0 to 50 provided that 0 < (x + y) ≤ 50, and p, q and z are integers from 0 to 50 provided that 0 < (p + q + z) ≤ 50.

[0036] Preferably, R₁ and R₅ are independently C₁ to C₃₀ straight or branch chain alkyl, alkenyl, alkynyl or an aryl substituted aliphatic chain where the aliphatic chains are attached to the nitrogen atom(s) in the molecule. More preferably R₁ and R₅ are C₁₂ to C₂₀ alkyl or alkenyl, even more preferably a mixture of C₁₄, C₁₆ and C₁₈ alkyl or alkenyl substituents.

[0037] Preferably, R₂ and R₃ are independently C₂ to C₆ straight or branched alkyl, alkenyl, alkynyl diradicals, more preferably a C₂ to C₄ alkyl diradical, most preferably a C₂ diradical.

[0038] Preferably, R₄ is a C₁ to C₆ alkyl, alkenyl, alkynyl diradical, more preferably R₄ is a C₂ to C₄ alkyl diradical, most preferably a C₃ alkyl diradical.

[0039] Preferably, x and y are integers from 1 to 25, provided 1 ≤ (x + y) ≤ 25, more preferably 1 to 15 provided 1 ≤ (x + y) ≤ 15.

[0040] Preferably p, q and z are integers from 1 to 25 provided 1 ≤ (p + q + z) ≤ 25, more preferably 1 to 15, provided 1 ≤ (p + q + z) ≤ 15.

[0041] A particularly preferred alkoxyated amine is ETHOMEEN T/15 (commercially available from Akzo Chemical). ETHOMEEN T/15 has Structure A wherein R₁ is representative of a tallow amine derivative which typically contains a mixture of C₁₄, C₁₆ and C₁₈ unsaturated and saturated straight chain hydrocarbon substituents, R₂ is CH₂CH₂, and x + y is approximately 5. This particular ethoxylated amine is much more effective in preventing corrosion in salt water environments than conventional barium sulfonate or calcium sulfonate rust inhibitors. In addition, the effective treat cost of the ETHOMEEN T/15 compound is substantially lower than barium sulfonate rust inhibitors. Barium sulfonate rust inhibitors such as Nasul BSN (supplied by King Industries) and Lockguard 3655 (supplied by Lockhart Chemicals) are currently used rust inhibitors in lithium complex greases; the use of alkoxyated amines as rust inhibitors as described herein can be employed in place of such conventionally used rust inhibitors to achieve equivalent or superior corrosion resistance performance.

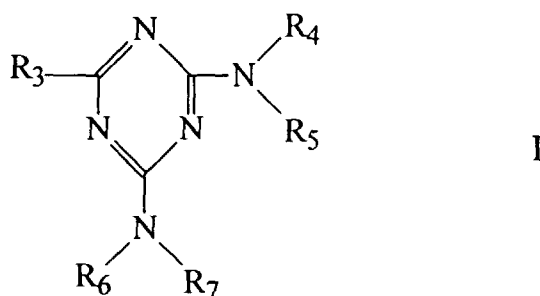
[0042] Further, the grease of the present invention can contain any of the typical grease additives including conventional antioxidants, extreme pressure agents, tackiness agents, dyes, etc. Such typical additives and their functions are described in "Modern Lubricating Greases" by C. J. Bone, Scientific Publication (G.B.) Ltd., 1976.

[0043] Examples of antioxidants include the phenolic and aminic type antioxidants and mixture thereof.

[0044] The amine type anti-oxidants include diarylamines and thiodiaryl amines. Suitable diarylamines include diphenyl amine; phenyl- α -naphthylamine; phenyl- β -naphthylamine; α - α -di-naphthylamine; β - β -dinaphthylamine; or α , β -dinaphthylamine. Also suitable antioxidants are diarylamines wherein one or both of the aryl groups are alkylated, e.g., with linear or branched alkyl groups containing 1 to 12 carbon atoms, such as the diethyl diphenylamines; dioctyldiphenyl amines, methyl phenyl- α -naphthylamines; phenyl- β (butylnaphthyl) amine; bis(4-methyl phenyl) amine or phenyl (3-propyl phenyl) amine octyl-butyl-diphenylamine, dioctyldiphenyl amine, octyl-, nonyl-diphenyl amine, dinonyl diphenyl amine and mixtures thereof.

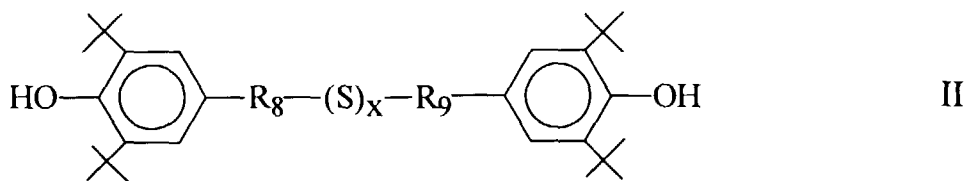
[0045] Suitable thiodiarylamines include phenothiazine, the alkylated phenothiazines, phenyl thio- α -naphthyl amine; phenyl thio- β -naphthylamine; α - α -thio dinaphthylamine; β - β -thio dinaphthylamine; phenyl thio- α (methyl naphthyl) amine; thio-di (ethyl phenyl) amine; (butyl phenyl) thio phenyl amine.

[0046] Other suitable antioxidants include triazines of the formula



where R_4 , R_5 , R_6 , R_7 , are hydrogen, C_1 to C_{20} hydrocarbyl or pyridyl, and R_3 is C_1 to C_8 hydrocarbyl, C_1 to C_{20} hydrocarbylamine, pyridyl or pyridylamine. If desired mixtures of antioxidants may be present in the lubricant composition of the invention.

[0047] Phenolic type anti-oxidants include 2,6-di-*t*-butyl phenol, 2,6-di-*t*-butyl alkylated phenol where the alkyl substituent is hydrocarbyl and contains between 1 and 20 carbon atoms, such as 2,6-di-*t*-butyl-4-methyl phenol, 2,6-di-*t*-butyl-4-ethyl phenol, etc., or 2,6-di-*t*-butyl-4-alkoxy phenol where the alkoxy substituent contains between 1 and 20 carbons such as 2,6-di-*t*-butyl-4-methoxyphenol; materials of the formula



where x is zero to 5, R_8 and R_9 are the same or different and are C_1 - C_{20} hydrocarbyl which may contain oxygen or sulfur or be substituted with oxygen or sulfur containing groups; and materials of the formula

TABLE 1 - FORMULATIONS AND TEST RESULTS

COMPONENT (in wt%)	Comp. Example A	Comp. Example B	Comp. Example C	Comp. Example D	Comp. Example E	Example 1	Example 2	Example 3	Example 4
Total Base Oils (mineral oils)	78.50	78.50	78.50	78.50	78.50	78.89	78.89	78.89	78.89
Lithium Complex thickener system	16.52	16.52	16.52	16.52	16.52	16.61	16.61	16.61	16.61
Glycerine	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
EP and antiwear additives	1.80	1.80	1.80	1.80	1.80	1.81	1.81	1.81	1.81
dialkyldiphenyl amine antioxidant	0.45	0.45	0.45	0.45	0.45	0.46	0.46	0.46	0.46
polymeric tackifier	1.28	1.28	1.28	1.28	1.28	1.28	1.28	1.28	1.28
RUST INHIBITORS									
NASUL BSN (barium sulfonate)	1.00								
LOCKGUARD 3655 (barium sulfonate)		1.00							
LOCKGUARD 6942 (calcium sulfonate)			1.00						
NASUL CA-50 (basic calcium sulfonate)				1.00					
NASUL 729 (neutral calcium sulfonate)					1.00				
ETHOMEEN T/15 (Structure A, R ₁ =tallow, R ₂ =CH ₂ CH ₂ , x+y=5)						0.50			
ETHOMEEN S/15 (Structure A, R ₁ =soya, R ₂ =CH ₂ CH ₂ , x+y=5)							0.50		
ETHODUOMEEN T/13 (Structure B, R ₅ =tallow, R ₄ =CH ₂ CH ₂ , p+q+z=3)								0.50	
ETHOMEEN C/12 (Structure A, R ₁ =coco, R ₂ =CH ₂ CH ₂ , x+y=2)									0.50

TABLE 1 - FORMULATIONS AND TEST RESULTS
(continued)

TESTS	Comp. Example A	Comp. Example B	Comp. Example C	Comp. Example D	Comp. Example E	Example 1	Example 2	Example 3	Example 4
Base oil viscosity @ 40°C in cSt (ASTM D445)	220	220	220	220	220	220	220	220	220
60 stroke penetration in mm/10 (ASTM D217-1/2 scale equipment)	240	265	261	245	229	263	263	259	263
softening in 60 stroke pen caused by the Rust Inhibitor	- 21	+ 4	0	- 16	- 32	+ 2	+ 2	- 2	+ 2
water washout in wt% (ASTM D1264)	2,0	0,9	2,1	1,4	1,7	2,5	2,4	2,0	
EMCOR rust test with 20% (v/v) synthetic sea water in distilled water (IP220)	2,2	2,2	4,4	2,3	3,3	0,0	1,2	2,2	0,1
See Table 2 for explanation of rating.									

TABLE 2

EMCOR Rust Test Rating Scale	
EMCOR Rust Test Result	Description
0	No rust
1	3 or fewer small corrosion spots, each sufficient to be visible to the naked eye
2	Small areas of corrosion covering less than 1% of the bearing area
3	Between 1% and 5% of bearing area corroded
4	Between 5% and 10% of bearing area corroded
5	More than 10% of bearing area corroded

[0056] The effect of alkoxyated amines on the corrosion prevention characteristics of greases containing synthetic lubricating oil was also investigated. Table 3 summarizes the formulation and performance characteristics of a polyalphaolefin and synthetic ester based complex lithium grease which contains Ethomeen T/15. The EMCOR results for this grease demonstrate that alkoxyated amines provide superior rust prevention/anti-corrosion characteristics in synthetic base oil greases.

[0057] As is seen, in all instances, the use of alkoxyated amine(s) in the grease enabled the grease to achieve a level of corrosion resistance at least equivalent to that achieved by using barium sulfonate, calcium sulfonate or basic calcium sulfonate, and at lower concentrations. Alkoxyated amines enhance corrosion resistance of mineral oil and polyalphaolefin/ester based greases.

[0058] Insofar as alkoxyated amines per se are not known from the literature as being corrosion inhibitors for greases, this performance is completely unexpected.

TABLE 3

SYNTHETIC GREASES CONTAINING ALKOXYLATED AMINES	
COMPONENT (in wt%)	Example 5
PAO 8 + PAO 100	66.79
Synthetic Ester Fluid	11.78
Lithium Complex thickener system	16.58
Glycerine	0.32
EP and antiwear additives	2.30
dialkyldiphenyl amine antioxidant	1.50
polymeric tackifier	0.23
RUST INHIBITOR	
ETHOMEEN T/15 (Structure A, R_1 =tallow, R_2 =CH ₂ CH ₂ , x+y=5)	0.50
TESTS	
Base oil viscosity @ 40°C in cSt (ASTM D445)	220
60 stroke penetration in mm/10 (ASTM D217-1/2 scale equipment)	253
EMCOR rust test with 20% (v/v) synthetic sea water in distilled water (IP220) See Table 2 for explanation of rating.	0,0

[0059] The effect of alkoxyated amines on the corrosion prevention characteristics of lubricating oil compositions which do not contain grease thickeners was investigated for comparison purposes. A synthetic turbine oil formulation was used to investigate the effect of the alkoxyated amines.

[0060] The rust prevention performance of circulating oils, such as turbine oils, is usually measured by the ASTM D665B rust test. In this test a cylindrical steel test rod is immersed in a stirred oil/water mixture comprising 300 mL of test oil and 30 mL of synthetic sea water. The oil/water mixture is held at a test temperature of 60°C for 24 hours. At the end of the test the rod is observed for any signs of visible rust. A "pass" indicates that no rust was observed.

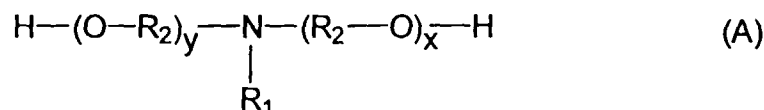
[0061] Table 4 contains a summary of the rust prevention characteristics of several synthetic turbine oil formulations. The first formulation listed in the table, the "base formulation", did not contain any alkoxyated amine corrosion inhibitor. This base formulation successfully inhibits the formation of rust on the steel test rod in the ASTM D665B rust test. Attempts were made to further improve the rust prevention characteristics of the base formulation by adding 0.1 wt% of various alkoxyated amines. The results from the standard ASTM D665B rust test are summarized in Table 4. These test results demonstrate that alkoxyated amines have a negative impact on the rust performance characteristics of turbine oils. The data in Table 4 show that alkoxyated amines per se do not contribute to improved corrosion prevention performance in oil formulations. Indeed, the presence of the alkoxyated amine per se in the oil appears to promote rust. The ability of alkoxyated amines per se to improve the corrosion prevention performance of greases is a characteristic unique to grease formulations.

TABLE 4 - RUST PERFORMANCE OF SYNTHETIC TURBINE OILS CONTAINING ALKOXYLATED AMINES

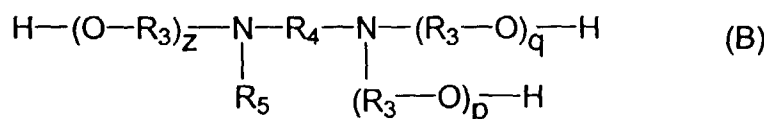
COMPONENT (in wt%)	Base Formulation - No Supplemental Rust Inhibitor Added	Oil Example 1	Oil Example 2	Oil Example 3	Oil Example 4
PAO 40 + PAO 100	88.1	88.0	88.0	88.0	88.0
Poly-isobutylene	5.0	5.0	5.0	5.0	5.0
Synthetic Ester Fluid	5.0	5.0	5.0	5.0	5.0
Antioxidant	1.0	1.0	1.0	1.0	1.0
Phosphate ester antiwear additive	0.8	0.8	0.8	0.8	0.8
Benzotriazole copper passivator	0.1	0.1	0.1	0.1	0.1
RUST INHIBITORS					
Ethomeen T/15 (R ₁ =soya, R ₂ =ethyl, x+y=5)		0.1			
Ethomeen T/25 (R ₁ =soya, R ₂ =ethyl, x+y=15)			0.1		
Ethomeen T/15 (R ₁ =tallow, R ₂ =ethyl, x+y=5)				0.1	
Ethomeen T/25 (R ₁ =tallow, R ₂ =ethyl, x+y=15)					0.1
TESTS					
ASTM D665B salt water rust test	pass	fail	fail	fail	fail

Claims

1. A lubricating grease composition having increased corrosion-inhibition, comprising (i) a major proportion of a base oil of lubricating viscosity, (ii) a thickener and (iii) a minor amount of at least one compound to impart corrosion-inhibiting properties, being at least one alkoxyated amine compound selected from those of the formula



and/or



wherein R_1 and R_5 are independently C_1 to C_{30} hydrocarbyl radicals, R_2 and R_3 are independently C_2 to C_6 hydrocarbyl radicals, R_4 is a C_1 to C_6 hydrocarbyl radical, x and y are integers from 0 to 50 provided that $0 < (x + y) \leq 50$, and p , q and z are integers from 0 to 50 provided $0 < (p + q + z) \leq 50$.

2. The grease composition claimed in claim 1, wherein R_1 and R_5 are independently C_{12} to C_{20} alkyl or alkenyl, R_2 and R_3 are independently C_2 to C_4 alkyl diradical, R_4 is a C_2 to C_4 alkyl diradical x and y are integers from 1 to 25 provided $1 \leq (x + y) \leq 25$ and p , q and z are integers from 1 to 25 provided $1 \leq (p + q + z) \leq 25$.
3. The grease composition of claim 1 or claim 2, containing at least one alkoxyated amine compound of each of structures A and B.
4. The grease composition of any preceding claim, wherein the corrosion-inhibiting additive is present in total amount in the range 0.01 to 10 wt%.
5. The grease composition of any preceding claim, wherein the thickener is a simple lithium or calcium soap, a complex lithium or calcium soap, a lithium and calcium soap or a polyurea thickener.
6. The grease composition of any preceding claim, further containing one or more conventional grease additives.
7. The grease composition of any preceding claim, wherein alkaline earth metal carbonates are absent.
8. A method of preparing the lubricating grease composition claimed in any preceding claim, comprising adding a corrosion-inhibiting amount of at least one said alkoxyated amine compound to a major proportion of said base oil and said thickener.
9. The use of at least one of the alkoxyated amine compounds defined in claim 1 or claim 2, as a corrosion-inhibiting additive in a lubricating grease composition.