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(54) Lubricating oil compositions and uses

(57) A non-aqueous lubricating oil composition comprises a major amount of a base oil and a minor amount of an additive which is present in solution in the base oil and is a non-halide, non-aromatic ionic liquid which is a salt of general formula C^+A^-, with the cation, C^+, being a quaternary phosphonium or quaternary ammonium ion having four hydrocarbyl groups, optionally containing heteroatoms, which hydrocarbyl groups do not all have the same number of carbon atoms, there being at least one long chain hydrocarbyl group having greater than 4 carbon atoms and at least one short chain hydrocarbyl group having fewer carbon atoms than each of the long chain hydrocarbyl groups, and the anion, A^-, comprising at least one oxygen atom and having an ionic head group attached to at least one alkyl or alicyclic hydrocarbyl group which has at least four carbon atoms and optionally at least one heteroatom. The ionic liquid may be used as an anti-wear component in a lubricating oil composition. The ionic liquid may be used as a friction modifier in the lubricating oil composition. The lubricating oil composition may be used in an ignition engine.

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Description

[0001] The present invention relates to a composition, in particular, to a non-aqueous lubricating oil composition and to an additive concentrate. The present invention also relates to the use of an additive to reduce wear and/or to modify friction properties.

[0002] Lubricating oil compositions, in general, comprise a major amount of a base oil and a minor amount of at least one additive. Additives frequently used in lubricating oil compositions include detergents, viscosity improvers, anti-oxidants, dispersants, anti-foam additives, friction modifiers and anti-wear additives.

[0003] Anti-wear additives are used in lubricating oil compositions to reduce the wear of components that are lubricated by the lubricating oil composition. The anti-wear additives most commonly used in lubricating oil compositions for engines are ZDDPs (zinc dialkyldithiophosphates). However, ZDDPs are a source of sulphated ash, sulfur and phosphorus which may poison catalysts in catalytic converters, which could result in a reduction in performance of the catalyst.

[0004] Ionic liquids have recently been shown to be potentially suitable for some lubricant applications.

[0005] An ionic liquid is an ionic material which, at atmospheric pressure, is in a liquid state at temperatures below 150˚C, particularly at temperatures below 100˚C. Since they are comprised entirely of ionic material, ionic liquids possess virtually no vapour pressure. Therefore, in use, they generally present a low risk of atmospheric contamination, have no odour, and are likely to have a low impact on human health. Further, ionic liquids are generally non-flammable, thermally stable and liquid over a wide range of temperatures. However, due to their ionic nature, miscibility of ionic liquids in non-polar organic solvents, for example non-aqueous lubricant base oils, tends to be limited.

[0006] Some ionic liquids have been shown to be capable of use as lubricant base oils, as neat lubricants and as solvents in the synthesis of polyalphaolefin base oils.

[0007] Jiménez et. al., in Wear 260 2006 766-782, and Wear 261 2006 347-359 have shown 1-*n*-alkyl-3-methylimidazolium ionic liquids to be potentially useful as neat lubricants and lubricant additives in the lubrication of steel-aluminium contacts. However, the Applicant has found that, at temperatures between room temperature and 100˚C, such ionic liquids are insoluble in Group I to IV base oils, as well as in some Group V base oils. Such insolubility is undesirable, for example for engine lubricants, which are desirably clear. Furthermore, the ionic liquids described in these two papers comprise fluorine-containing anions. The presence of fluorine in lubricants is undesirable, particularly for engine lubricants, since high temperatures may lead to the production of toxic compounds, for example, hydrofluoric acid. Fluorine compounds, such as salts of $[PF_6]^-$, are also expected to be corrosive.

[0008] Liu et al in Wear 261 (2006) 1174 - 1179 describe a series of asymmetrical tetraalkylphosphonium ionic liquids and their evaluation as lubricants for the contacts of steel/aluminium. The cations used is BF_4^-.

[0009] There remains a need for a lubricating oil composition which avoids or at least mitigates these disadvantages.

[0010] According to a first aspect of the present invention, there is provided a non-aqueous lubricating oil composition comprising a minor amount of an additive and a major amount of a base oil characterised in that the additive is present in solution in the base oil and is a non-halide, non-aromatic ionic liquid which is a salt of general formula C^+A^- having an atmospheric melting point in the range of -50˚C to 250˚C, with the cation, C^+, being a quaternary phosphonium or quaternary ammonium ion having four hydrocarbyl groups, optionally containing heteroatoms, which hydrocarbyl groups do not all have the same number of carbon atoms, there being at least one long chain hydrocarbyl group having greater than 4 carbon atoms and at least one short chain hydrocarbyl group having fewer carbon atoms than each of the long chain hydrocarbyl groups, and the anion, A^-, comprising at least one oxygen atom and having an ionic head group attached to at least one alkyl or alicyclic hydrocarbyl group which has at least four carbon atoms and optionally at least one heteroatom.

[0011] The cation and the anion of the ionic liquid according to the present invention do not contain any halide atoms. The ionic liquid is halide-free.

[0012] The ionic liquid defined herein may be used as an additive in a lubricating oil composition to reduce wear.

[0013] Thus, according to a further aspect of the present invention, there is provided the use of a base oil-soluble ionic liquid as an additive in a non-aqueous lubricating oil composition comprising a major amount of a base oil and a minor amount of the ionic liquid in solution in the base oil, to reduce wear of components lubricated by the lubricating oil composition, in which use, the ionic liquid is a non-halide, non-aromatic ionic liquid which is a salt of general formula C^+A^- having an atmospheric melting point in the range of -50˚C to 250˚C, with the cation, C^+, being a quaternary phosphonium or quaternary ammonium ion having four hydrocarbyl groups, optionally containing heteroatoms, which hydrocarbyl groups do not all have the same number of carbon atoms, there being at least one long chain hydrocarbyl group having greater than 4 carbon atoms and at least one short chain hydrocarbyl group having fewer carbon atoms than each of the long chain hydrocarbyl groups, and the anion, A^-, comprising at least one oxygen atom and having an ionic head group attached to at least one alkyl or alicyclic hydrocarbyl group which has at least four carbon atoms and optionally at least one heteroatom.

[0014] The ionic liquid defined herein may be used as an additive in a lubricating oil composition to modify friction properties.

[0015] Thus, according to yet a further aspect of the present invention, there is provided the use of a base oil-soluble ionic liquid as an additive in a non-aqueous lubricating oil composition comprising a major amount of a base oil and a minor amount of the ionic liquid in solution in the base oil, to modify the friction properties of the lubricating oil composition, in which use, the ionic liquid is a non-halide, non-aromatic ionic liquid which is a salt of general formula C^+A^- having an atmospheric melting point in the range of - 50°C to 250°C, with the cation, C^+, being a quaternary phosphonium or quaternary ammonium ion having four hydrocarbyl groups, optionally containing heteroatoms, which hydrocarbyl groups do not all have the same number of carbon atoms, there being at least one long chain hydrocarbyl group having greater than 4 carbon atoms and at least one short chain hydrocarbyl group having fewer carbon atoms than each of the long chain hydrocarbyl groups, and the anion, A^-, comprising at least one oxygen atom and having an ionic head group attached to at least one alkyl or alicyclic hydrocarbyl group which has at least four carbon atoms and optionally at least one heteroatom.

[0016] The present invention solves the technical problem defined above by providing an ionic liquid having a defined structure which imparts solubility in the base oil. The ionic liquid of the present invention may be used as an anti-wear additive and/or a friction modifier in a lubricating oil composition. It is believed that the ionic liquids of the present invention do not produce (or produce less) undesirable decomposition products, for example, like those produced by ZDDPs (e.g. sulphated ash). Also, it is believed that the ionic liquids of the present invention will not produce toxic or corrosive compounds, unlike halide-containing ionic liquids.

[0017] The cation, C^+, is a quaternary phosphonium or quaternary ammonium ion having four hydrocarbyl groups, optionally containing heteroatoms, which hydrocarbyl groups do not all have the same number of carbon atoms, there being at least one long chain hydrocarbyl group having greater than 4 carbon atoms and at least one short chain hydrocarbyl group having fewer carbon atoms than each of the long chain hydrocarbyl groups.

[0018] Preferably, the at least one short chain hydrocarbyl group of the cation has more than two fewer carbon atoms than each of the long chain hydrocarbyl groups. The hydrocarbyl groups of the cation are preferably straight chain hydrocarbyl groups. The hydrocarbyl groups of the cation may each have independently, up to and including 18 carbon atoms, more preferably, up to and including 16 carbon atoms. Suitable long chain hydrocarbyl groups of the cation may each have independently, 6 to 18 carbon atoms, preferably, 6 to 16 carbon atoms. Suitable short chain hydrocarbyl groups of the cation may each have independently, 1 to 8 carbon atoms.

[0019] The hydrocarbyl groups of the cation may each have independently, at least one heteroatom, for example oxygen and/or sulfur.

[0020] Examples of cations of ionic liquids according to the present invention are set out in Table 1 below.

Table 1

Long chain hydrocarbyl group(s)	Short chain hydrocarbyl group(s)
n-octyl, n-octyl, n-octyl	Methyl
n-tetradecyl	n-hexyl, n-hexyl, n-hexyl
n-dodecyl, n-dodecyl, n-dodecyl	n-butyl
n-dodecyl, n-dodecyl, n-dodecyl	2-n-butoxyethyl

[0021] These examples show that the cation may have three long chain hydrocarbyl groups and one short chain hydrocarbyl group, or may have one long chain hydrocarbyl group and three short chain hydrocarbyl groups. Alternatively, the cation may have two long chain hydrocarbyl groups and two short chain hydrocarbyl groups.

[0022] The cation may be selected from the group consisting of tri-n-octyl(methyl) phosphonium, tri-n-octyl(methyl) ammonium, tri-n-hexyl(n-tetradecyl) phosphonium, tri n-hexyl(n-tetradecyl) ammonium, tri-n-dodecyl(n-butyl) ammonium, tri-n-dodecyl(n-butyl) phosphonium, tri-n-dodecyl(n-butoxyethyl) phosphonium, tri-n-dodecyl(n-butoxyethyl) ammonium.

[0023] Examples of quaternary phosphonium cations include tri-n-hexyl(n-tetradecyl) phosphonium; tri-n-dodecyl(n-butyl) phosphonium; and tri-n-dodecyl(2-n-butoxyethyl) phosphonium cations. Examples of quaternary ammonium cations include tri-n-octyl(methyl)ammonium cation.

[0024] The anion may contain one or more heteroatoms, for example, sulfur and/or phosphorus. The anion has at least one alkyl or alicyclic hydrocarbyl group which has at least four carbon atoms, but no aromatic groups. The anion may have more than one alkyl or alicyclic hydrocarbyl group each independently having at least four carbon atoms. The alkyl and/or alicyclic hydrocarbyl group or groups of the anion may be independently, branched- or straight-chain.

[0025] Suitably, the anion, A^- is selected from the group consisting of anions (a) to (c) defined herein.

(a) Anions of the general formula: $[R^1R^2P(O)O]^-$

wherein R^1 and R^2 are independently, alkyl or alicyclic hydrocarbyl groups each having at least four carbon atoms and optionally containing at least one heteroatom. The hydrocarbyl groups may be branched or straight chain. Preferred alkyl hydrocarbyl groups include alkyl groups each independently, having 4 to 18 carbon atoms, preferably, 4 to 16 carbon atoms, more preferably 4 to 8 carbons atoms. Particularly preferred alkyl groups include 2,4,4-trimethylpentyl. Preferred alicyclic hydrocarbyl groups include alicyclic groups having 6 carbon atoms. Particularly preferred alicyclic groups include cyclohexyl. The hydrocarbyl groups may be branched or straight chain. Preferred hydrocarbyl groups include alkyl groups each having independently, 4 to 18 carbon atoms, preferably 4 to 16 carbon atoms, more preferably 4 to 8 carbons atoms. Examples of anions of this group include phosphinate anions, for example, bis(2,4,4-trimethylpentyl)phosphinate and dicyclohexylphosphinate.

The optional at least one heteroatom may be at least one heteroatom selected from the group consisting of oxygen, sulfur, phosphorus and combinations thereof. Thus, suitable anions can include those of general formula $[(R^3O)(R^4O)P(O)O]^-$ wherein R^3 and R^4 are independently, alkyl or alicyclic hydrocarbyl groups each independently, having at least four carbon atoms, preferably 4 to 18 carbon atoms, more preferably 4 to 16 carbon atoms, for example, 4 to 6 carbon atoms. R^3 and R^4 may each contain independently, at least one heteroatom, for example oxygen. Thus, R^3 and R^4 may each independently be ether groups having 4 to 18 carbon atoms, preferably 4 to 16 carbon atoms, for example, 4 to 6 carbon atoms. Specific examples of anions of this group include phosphate anions, for example di n-butylphosphate and bis(2-butoxyethyl)phosphate.

Preferred anions of group (a) are those of general formula $[(R^3O)(R^4O)P(O)O]^-$ wherein R^3 and R^4 are independently, alkyl hydrocarbyl groups each independently, having at least four carbon atoms, preferably 4 to 18 carbon atoms, more preferably 4 to 16 carbon atoms, for example, 4 to 6 carbon atoms and wherein R^3 and R^4 may each contain independently, at least one heteroatom, for example oxygen. Specific examples of anions of this group include phosphate anions, for example di n-butylphosphate and bis(2-butoxyethyl)phosphate.

(b) Sulfosuccinate esters of general formula: $R^1OOCCH_2CH(SO_3^-)COOR^2$

wherein R^1 and R^2 are straight chain or branched chain C_4 to C_8 alkyl groups. Examples of sulfosuccinate esters include dioctylsulfosuccinate and dihexylsulfosuccinate.

(c) Carboxylate anions of general formula: $RC(O)O^-$

wherein R is a straight chain or branched chain C_9 to C_{17} alkyl or alkenyl group. A suitable example of this group of anions is decanoate.

[0026] Aromatic hydrocarbyl groups are preferably not present in the anion.

[0027] Preferably, the minor amount of ionic liquid is present in the lubricating oil composition at a concentration in the range of 0.1 to 10% by weight.

[0028] The base oil may comprise one or more base stocks each of which is any one of Groups I to V according to API standard 1509, "ENGINE OIL LICENSING AND CERTIFICATION SYSTEM", November 2004 version 15th edition Appendix E, which defines base stocks for base oils as belonging to one of five Groups as set out in Table 2 below.

Table 2 - Base stocks

Group	Saturated hydrocarbon content (wt%)		Sulfur content (wt%)		Viscosity Index
I	< 90	and/or	> 0.03	and	≥ 80 and < 120
II	≥ 90	and	≤ 0.03	and	≥ 80 and < 120
III	≥ 90	and	≤ 0.03	and	≥ 120
IV	polyalpha olefins				
V	all base stocks not in Groups I, II, III or IV				

[0029] Preferably, phosphorus atoms are present in both the cation and the anion of the ionic liquid. Preferably, phosphorus atoms are present in the ionic liquid and the minor amount of the ionic liquid is present in the lubricating oil composition in an amount corresponding to no more than 0.05% by weight phosphorus based upon the lubricating oil composition.

[0030] Sulfur atoms may be present in the ionic liquid. If sulfur atoms are present in the ionic liquid, preferably the minor amount of the ionic liquid is present in the lubricating oil composition in an amount corresponding to no more than 0.2% by weight sulfur based upon the lubricating oil composition.

[0031] The lubricating oil composition may comprise at least one further additive component selected from the group consisting of detergents, viscosity improvers, anti-oxidants, dispersants, anti-foam and anti-wear additives.

[0032] The ionic liquid defined herein may be used as a friction modifier in a lubricating oil composition, in which case the lubricating oil composition will usually comprise one or more other friction modifiers. Such friction modifiers may be present in lesser amounts than might be required to achieve a predetermined performance of the lubricating oil composition and/or such friction modifiers may be present in conventional amounts such that the lubricating oil has improved friction properties. Suitable other friction modifiers may comprise oxygen-containing organic compounds, for example those selected from the group consisting of alcohols, esters and carboxylic acid derivatives. Other friction modifiers may comprise organic molybdenum compounds for example molybdenum dialkyldithiophosphates or molybdenum dialkyldithiocarbamates.

[0033] The other friction modifiers may be present in the lubricating oil composition at a concentration in the range from greater than 0 to 10% by weight, preferably in the range 0.1 to 10% by weight.

[0034] Preferably, the low shear rate kinematic viscosity of the lubricant composition is in the range 3.8 to 100 cSt at 100°C, preferably 3.8 to 41.0 cSt at 100°C, most preferably 3.8 to 26.1 cSt at 100°C.

[0035] The lubricating oil composition of the present invention may be prepared by mixing the ionic liquid into the base oil and heating the mixture to 70°C. The ionic liquid may be mixed with the base oil as an additive concentrate.

[0036] Thus, according to yet a further embodiment of the present invention, there is provided an additive concentrate comprising a base oil-soluble ionic liquid as herein defined and at least one further additive selected from the group consisting of detergents, viscosity improvers, anti-oxidants, dispersants, anti-foam and anti-wear additives and optionally a solvent. Preferably, the additive concentrate comprises a base oil-soluble ionic liquid as herein defined, at least one other friction modifier and at least one further additive selected from the group consisting of detergents, viscosity improvers, anti-oxidants, dispersants, anti-foam and anti-wear additives and optionally a solvent.

[0037] The lubricating oil composition of the present invention is suitable for use as a lubricant in an ignition engine. The lubricating oil composition of the present invention is suitable for use as a lubricant in transmissions and/or gears.

[0038] According to a further aspect of the present invention, there is provided a method of operating a spark ignition engine or a compression ignition engine which method comprises lubricating said engine with a lubricating oil composition according to any one of the embodiments described herein.

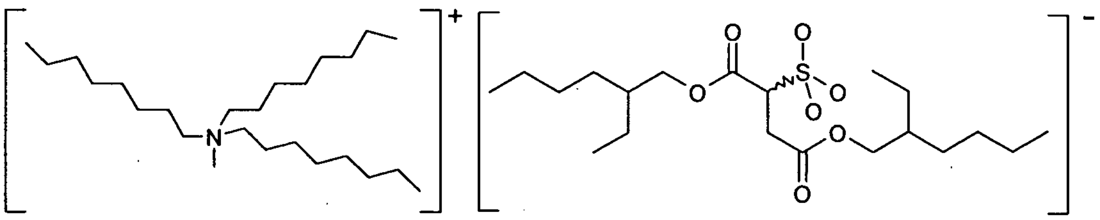
[0039] The present invention will now be illustrated with reference to the following nonlimiting examples and Figures 1 to 3. Figures 1 to 3 are graphs showing the friction properties of lubricating oil compositions according to the present invention, in particular, Figure 1 shows Stribeck curves, Figure 2 shows friction coefficients using a Cameron-Plint apparatus, and Figure 3 shows friction coefficients according to high frequency reciprocating rig (HFRR) and a high temperature high frequency reciprocating rig (HTHFRR) tests.

Ionic Liquid Preparation

[0040] The following ionic liquids (ILs) were prepared :

- Trioctyl(methyl)ammonium dioctylsulfosuccinate (IL 1)

[0041] This ionic liquid, also called trioctyl(methyl)ammonium docusate, may be represented by the general formula I.

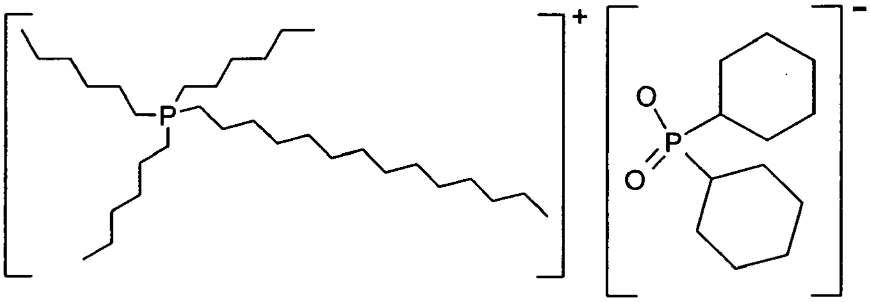


I

IL 1 was prepared by stirring a solution of trioctyl(methyl)ammonium chloride (404 g, 1.00 mol) and sodium dioctylsulfosuccinate salt (454 g, 1.02 mol) in deionised water (1.5 L) in a round-bottomed flask using an overhead stirrer set at 450 rpm for 16 hours at 60 °C. The product, a pale yellow liquid, formed an upper phase in the reaction mixture, which was separated and washed a number of times with water (7 x 750 mL). The product was dissolved in a minimum amount of dichloromethane and dried over anhydrous magnesium sulfate. It was then dried in a rotary evaporator and then further dried by heating at 80 °C, under vacuum at 1 mbar, to yield a pale yellow viscous liquid.

- Trihexyl(tetradecyl)phosphonium dicyclohexylphosphinate (IL 2)

[0042] This ionic liquid may be represented by the general formula II.



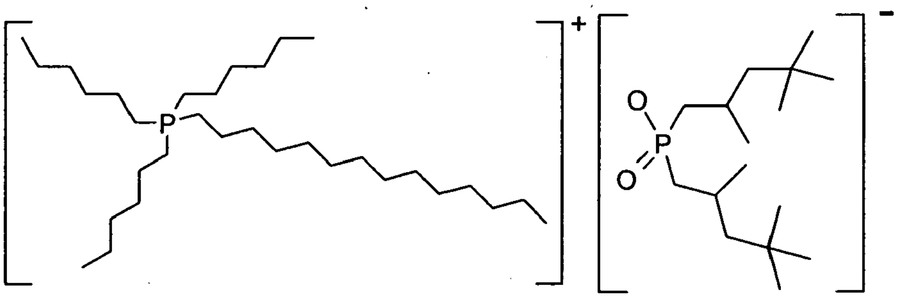
[0043] IL 2 was prepared by the following two step method adapted from that described in WO 02/079212 and Bradaric et al Green Chem. 2003, 5, 143.

[0044] Step 1: Dicyclohexylphosphinic acid (461 g, 2.0 mol) was dissolved in a minimum amount of methanol (100 mL) in a round-bottomed flask. An excess of sodium hydroxide (120 g, 3.0 mol) was dissolved in methanol (1.0 L) and was added slowly to the solution in small portions with stirring over a 30 minute period. After this time, a colour change of light yellow to dark yellow occurs. The product was then dried on a rotary evaporator giving a white solid of sodium salt of dicyclohexylphoshinic acid.

[0045] Step 2: Trihexyl(tetradecyl)phosphonium chloride (520 g, 1.0 mol) was dissolved in propanone (1 L) in a round-bottomed flask. The sodium salt of dicylcohexylphosphinic acid (2.0 mol) prepared in step 1 was dissolved in deionised water (1 L) and was added slowly,to the solution in small portions with stirring over a 10 minute period. The solution was stirred using an overhead stirrer set at 450 rpm, for 36 hours at 25 °C. The product, a pale yellow liquid, formed an upper phase in the reaction mixture, which was separated and washed a number of times with water (7 x 750 mL). The product was dissolved in a minimum amount of ethyl ethanoate and dried over anhydrous magnesium sulfate then dried on a rotary evaporator and then further dried by heating at 80 °C, under vacuum at 1 mbar, to yield a pale yellow viscous liquid.

- Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (IL 3)

[0046] This ionic liquid may be presented by the general formula III.



III

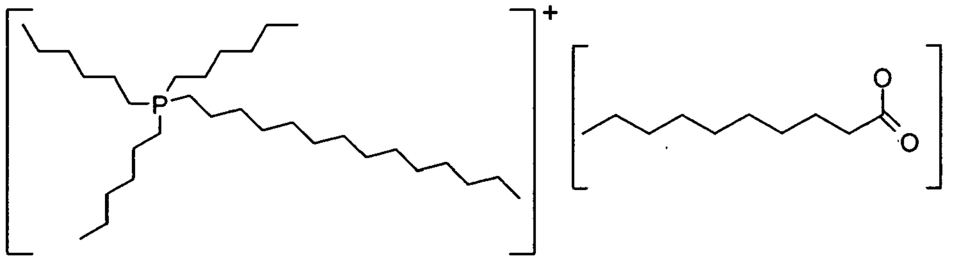
[0047] IL 3 was prepared by the following two step method adapted from that described in WO 02/079212 and Bradaric et al Green Chem. 2003, 5, 143.

[0048] Step 1: Bis(2,4,4-trimethylpentyl)phosphinic acid (290 g, 2.0 mol) was dissolved in a minimum amount of methanol (100 mL) in a round-bottomed flask. An excess amount of sodium hydroxide (120 g, 3.0 mol) was dissolved in methanol (1.0 L) and was added slowly to the solution in small portions with stirring over a 30 minute period. After this time a colour change of light yellow to dark yellow occurs. The product was then dried on a rotary evaporator giving a white solid of the sodium salt of bis (2,4,4-trimethylpentyl)phosphinic acid.

[0049] Step 2: Trihexyl(tetradecyl)phosphonium chloride (520 g, 1.0 mol) was dissolved in propanone (1 L) in a round-bottomed flask. The sodium salt of bis(2,4,4-trimethylpentyl)phosphinic acid (2.0 mol) prepared in step 1 was dissolved in deionised water (1 L) and was added slowly to the solution in small portions with stirring over a 10 minute period. The solution was stirred using an overhead stirrer set at 450 rpm, for 36 hours at 25 ˚C. The product, a pale yellow liquid, formed an upper phase in the reaction mixture, which was separated and washed a number of times with water (7 x 750 mL). The product was dissolved in a minimum amount of ethyl ethanoate and dried under anhydrous magnesium sulfate, then dried on a rotary evaporator and then further dried by heating at 80 ˚C, under vacuum at 1 mbar, to yield a pale yellow viscous liquid.

- Trihexyl(tetradecyl)phosphonium decanoate (IL 4)

[0050] This ionic liquid may be represented by the general formula IV.



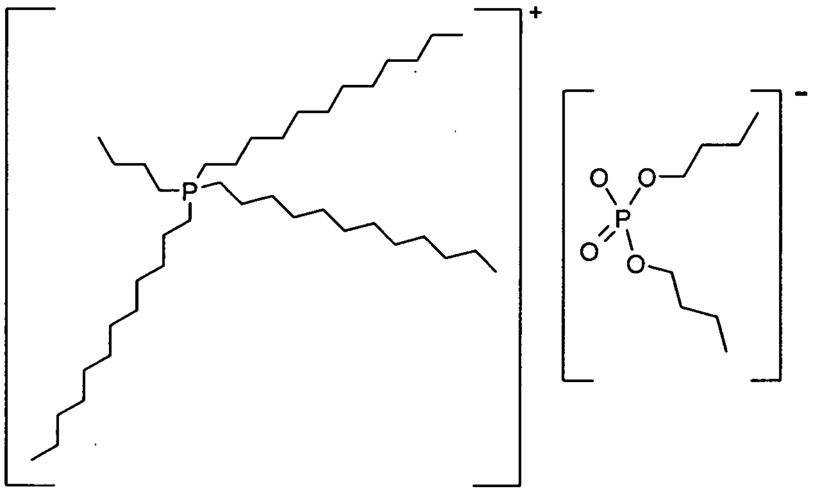
IV

IL 4 was prepared according to the following method.

[0051] Trihexyl(tetradecyl)phosphonium chloride (520 g, 1.0 mol) was dissolved in propanone (500 mL) in a round-bottomed flask. An excess of sodium decanoate (388 g, 2.0 mol) was dissolved in deionised water (500 mL) and was added slowly to the solution in small portions with stirring over a 20 minute period. The solution was stirred using an overhead stirrer set at 450 rpm, for 16 hours at 25 ˚C. The product, a pale yellow liquid, formed an upper phase in the reaction mixture, which was separated and washed a number of times with water (7 x 750 mL). The product was dissolved in a minimum amount of propanone and dried under anhydrous magnesium sulfate, then dried on a rotary evaporator and then further dried by heating at 80 ˚C, under vacuum at 1 mbar, to yield a pale yellow viscous liquid.

- Tridodecyl(butyl)phosphonium dibutylphosphate (IL 5)

[0052] This ionic liquid may be represented by the general formula V.



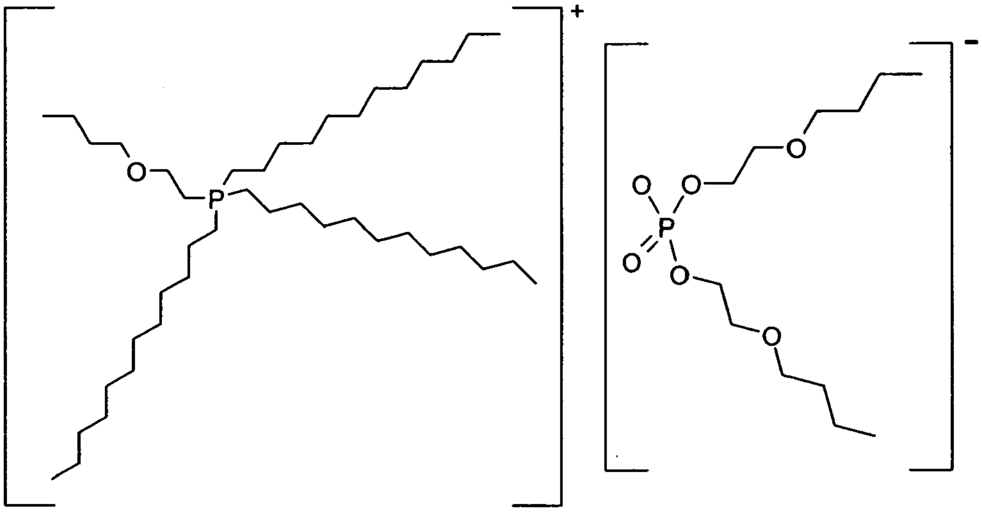
V

IL 5 was prepared according to the following method.

[0053] Tridodecylphosphine (270 g, 0.5 mol) was placed in a two-necked round-bottomed flask and was stirred under dinitrogen at 100˚C. Then, using a dropping funnel, an excess of tributylphosphate (160 g, 0.6 mol) was added slowly to the tridodecylphosphine over one hour. The reaction mixture was stirred for 20 hours under reflux conditions (210 ˚C). The product formed was a pale yellow liquid, which was dried on a rotary evaporator and heated at 80 ˚C under vacuum at 1 mbar, to yield a pale yellow viscous liquid.

- Tridodecyl(2-butoxyethyl)phosphonium bis(2-butoxyethyl)phosphate (IL 6)

[0054] This ionic liquid may be represented by the general formula VI.



VI

IL 6 was prepared according to the following method.

[0055] Tridodecylphosphine (270 g, 0.5 mol) was placed in a two-necked round-bottomed flask and stirred under dinitrogen at 100˚C. Then, using a dropping funnel, an excess of tris(2-butoxyethyl)phosphate (239 g, 0.6 mol) was added slowly to the tridodecylphosphine over one hour. The reaction mixture was stirred for 20 hours under reflux conditions (210˚C). The product formed was a pale yellow liquid, which was dried on a rotary evaporator and heated at 80 ˚C, under vacuum at 1 mbar, to yield a pale yellow viscous liquid.

Preparation of Lubricating Oil Compositions

[0056] Lubricating oil compositions according to the present invention were prepared by dissolving each of the above ionic liquids in Yubase 4 base oil, using ionic liquid concentrations of 5% by weight (for ILs 1 to 4) and 1% by weight (for ILs 1 to 6) based upon the lubricating oil composition. A lubricating oil formulation using ZDDP was prepared using a secondary zinc dialkyl dithiophosphate available from Lubrizol Corporation under the trade designation LZ 1371.

Wear testing

[0057] The wear properties of the lubricating oil compositions were tested using equipment designed to mimic the contact between engine components. The reciprocating component was held on the static wear surface and reciprocated at a frequency of 24 Hz. for 12 hours at 250˚C. The reciprocating component was able to articulate to a small degree around its centre point and carried a load of 300 N. There was a 15 mm sweep stroke. The lubricating oil composition under test was drip fed onto the wear surface at a rate of 3 ml/h. At the end of each test, the samples were cleaned with a nickel spatula and the wear volume loss determined to 2 significant figures using a Form Tallysurf apparatus.

[0058] The wear data obtained using lubricating oil compositions according to the present invention was compared with wear data obtained using the base oil alone, and a lubricating oil composition having a secondary ZDDP in place of ionic liquid. The compositions used and wear data obtained are shown in Table 3.

Table 3

Experiment	Additive	Amount of additive (wt. %)	Base oil	Base oil amount %	Wear test ref.	Wear (vol. loss) mm^3
Experiment A	No anti-wear additive	0	Yubase 4	100	006A	0.86
Experiment B	ZDDP	1	Yubase 4	99	005A	0.06
Example 1	IL 1	5	Yubase 4	95	001A	0.58
Example 2	IL 1	1	Yubase 4	99	001B	0.47
Example 3	IL 2	5	Yubase 4	95	002A	0.05
Example 4	IL 2	1	Yubase 4	99	002B	0.04
Example 5	IL 3	5	Yubase 4	95	003A	0.06
Example 6	IL 3	1	Yubase 4	99	003B	0.06
Example 7	IL 4	5	Yubase 4	95	004A	0.03
Example 8	IL 4	1	Yubase 4	99	004B	0.05
Example 9	IL 5	1	Yubase 4	99	008A	0.09
Example 10 IL 6		1	Yubase 4	99	009A	0.04

[0059] The wear data in Table 3 show that the lubricating oil compositions according to the present invention reduced wear of the components lubricated by the lubricating oil composition. In particular, the lubricating oils of the present invention reduced wear compared to the base oil alone and, in most cases; the wear rates are comparable to that obtained using 1% by weight ZDDP as the anti-wear additive in the lubricating oil composition.

Friction Properties.

[0060] The friction properties of lubricating oil compositions prepared above were tested using an MTM ball on disc test, operated at 150˚C, with a ball load of 71 N. The friction data obtained using lubricating oil compositions according to the present invention was compared with friction data obtained using conventional engine base oils alone and a lubricating oil composition having a secondary ZDDP in place of ionic liquid. The compositions tested are shown in Table 4 and the Stribeck curves obtained from the tests are shown in Figure 1.

Table 4

Experiment	Additive	Amount of additive (wt. %)	Base Oil	Amount of Base Oil (wt. %)
Experiment C	No additive	0	Yubase 6	100
Experiment D	No additive	0	PAO 4	100
Experiment E	ZDDP	1	Polyalpha olefin PAO4	99
Experiment F	Molybdenum dialkyl dithiocarbamate	1	Esso 150SN	99
Example 11	2	5	Yubase 4	95
Example 12	1	5	Yubase 4	95
Example 13	1	1	Yubase 4	99

[0061] The Stribeck curves shown in Figure 1 show that lubricating oil compositions according to the present invention have friction coefficients which are greater than the base oil, but lower than the formulation with ZDDP. Thus, not only are additives according to the present invention useful for wear, they also provide lower frictional properties than conventional ZDDP.

[0062] The friction properties of lubricating oil compositions prepared above were further tested using a Cameron-Plint apparatus at 250 ˚C, 300 N and 24 Hz. The friction data obtained using lubricant oil compositions according to the present invention were compared with friction data obtained using base oil alone and a lubricant oil composition having a secondary ZDDP in place of ionic liquid. The compositions tested are shown in Table 5 and the friction coefficients measured are shown in Figure 2.

Table 5

Experiment	Additive	Amount of Additive (wt. %)	Base Oil	Base Oil Amount (wt. %)
Experiment G	No additive	0	Yubase 4	100
Experiment H	ZDDP	1	Yubase 4	99
Example 14	IL 1	5	Yubase 4	95
Example 15	IL 1	1	Yubase 4	99
Example 16	IL 2	5	Yubase 4	95
Example 17	IL 2	1	Yubase 4	99
Example 18	IL 3	5	Yubase 4	95
Example 19	IL 3	1	Yubase 4	99
Example 20	IL 4	5	Yubase 4	95
Example 21 1	IL 4	1	Yubase 4	99
Example 22	IL 5	1	Yubase 4	99
Example 23	IL 6	1	Yubase 4	99

[0063] The friction coefficients shown in Figure 2 show that lubricating oil compositions according to the present invention generally exhibit a lower friction coefficient than secondary ZDDP. Thus, ILs 1 to 6 are suitable for use as additives to modify the friction properties of the lubricating oil composition. This will enable a lubricating oil composition according to the present invention to be formulated, using such ionic liquids, in which other friction modifiers may be present in lesser amounts than might be required to achieve a predetermined performance of the lubricating oil composition and/or such other friction modifiers may be present in conventional amounts such that the lubricating oil has improved friction properties.

[0064] The friction properties of lubricating oil compositions prepared above were further tested using a HFRR and HTHFRR apparatus. The friction data obtained using lubricant oil compositions according to the present invention were compared with friction data obtained using base oil alone and a lubricant oil composition having a secondary ZDDP in place of ionic liquid. The test conditions used are shown in Table 6, the compositions tested are shown in Table 7 and the friction coefficients measured are shown in Figure 3.

Table 6

	HFRR Test Conditions	HTHFRR Test Conditions
Stroke Length (mm)	1	1
Load (g)	400	400
Oil Temperatures (˚C)	40,60,80,100,120,140	150, 180, 210, 240, 270, 300
Oscillation Frequency (Hz)	40	40

Table 7

Experiment	Additive	Amount of Additive (wt. %)	Base Oil	Base Oil Amount (wt. %)
Experiment I	No additive	0	Yubase 4	100
Experiment J	ZDDP	1	Yubase 4	99

(continued)

Experiment	Additive	Amount of Additive (wt. %)	Base Oil	Base Oil Amount (wt. %)
Example 24	IL 1	5	Yubase 4	95
Example 25	IL 1	1	Yubase 4	99
Example 26	IL 2	5	Yubase 4	95
Example 27	IL 2	1	Yubase 4	99
Example 28	IL 3	5	Yubase 4	95
Example 29	IL 3	1	Yubase 4	99
Example 30	IL 4	5	Yubase 4	95
Example 31	IL 4	1	Yubase 4	99
Example 32	IL 5	1	Yubase 4	99
Example 33	IL 6	1	Yubase 4	99

[0065] The friction coefficients shown in Figure 3 demonstrate that as the test temperature is increased from 40˚C, the tested lubricant oil compositions of the present invention initially have a friction coefficient which is higher than that of the lubricant oil composition comprising ZDDP. However, at 80˚C ZDDP begins to decompose and the friction coefficient of the ZDDP-containing lubricant oil composition increases. Between 120 and 210˚C all of the lubricant oil compositions containing ionic liquids exhibit lower friction properties than the ZDDP-containing lubricant oil composition.

Engine testing.

[0066] Lubricating oils according to the present invention were used as lubricants in an ignition engine in engine tests. A base oil with additives was prepared by mixing a mixed Group I base oil with additive components to give a base oil with additives composition containing Group I base oil (93.37 wt.%), detergents (2.1 wt.%), dispersant (4 wt.%), anti-oxidant (0.5 wt.%) and anti-foam (0.003 wt.%).

[0067] Lubricating oil compositions were prepared by mixing ionic liquids or ZDDP into the base oil with additives as previously prepared and the resultant lubricating oil compositions were used to lubricate the ignition engine in engine tests. The engine was a Nissan KA24E four-cylinder, 2.4-litre engine with three valves per cylinder operated via a single overhead camshaft and rockers. The engine was operated in each engine test for 100 hours according to a two-stage cycle under low-speed, light-duty engine conditions. The results are shown in Table 8.

[0068] The data show that the phosphate ionic liquids performed well as additives in lubricating oil compositions to reduce wear. Thus, IL5 gave the best cam wear performance reducing the wear from about 45μm (no anti-wear additive) to 15.56μm. IL 6 also performed well reducing the wear to 18.55μm. The lubricating oil composition with IL 5 gave iron content of the oil at the end of the test which was less than that obtained for the lubricating oil composition with ZDDP. The lubricating oil composition with IL 6 gave iron content of the oil at the end of the test which was comparable with that obtained for the lubricating oil composition with ZDDP.

Table 8.

	Experiment K	Example 34	Example 35	Example 36	Example 37	Example 38	Experiment L
Lubricating oil composition							
Base oil with additives, % by weight	99.5	99	99	99	99	99	100
Additive % by weight	0.5	1	1	1	1	1	-
Additive	ZDDP (LZ1371)	IL1	IL3	IL6	IL5	IL4	none

(continued)

Used Oil data							
Kv40 decrease (cSt)	11.57	10.17	18.71	8.95	9.32	10.38	10.94
Kv100 decrease (cSt)	0.82	0.67	1.2	0.61	0.53	0.66	0.73
TBN depletion	1.64	2.66	2.18	6.29	1.65	3.31	2.24
End of test iron content in oil ppm	6	139	81	6	4	102	32
Camshaft Wear							
Average Cam Lobe Wear µm	24.60	149.37	129.81	15.56	18.55	148.23	45.03
Average Cam Nose wear µm	3.60	22.14	21.87	2.47	3.14	28.51	9.30
Camshaft Rating							
Average Follower Scuffing %	0.42	77.50	67.08	4.67	3.17	54.58	35.17

Claims

1. A non-aqueous lubricating oil composition comprising a minor amount of an additive and a major amount of a base oil **characterised in that** the additive is present in solution in the base oil and is a non-halide, non-aromatic ionic liquid which is a salt of general formula C^+A^- having an atmospheric melting point in the range of -50˚C to 250˚C, with the cation, C^+, being a quaternary phosphonium or quaternary ammonium ion having four hydrocarbyl groups, optionally containing heteroatoms, which hydrocarbyl groups do not all have the same number of carbon atoms, there being at least one long chain hydrocarbyl group having greater than 4 carbon atoms and at least one short chain hydrocarbyl group having fewer carbon atoms than each of the long chain hydrocarbyl groups, and the anion, A^-, comprising at least one oxygen atom and having an ionic head group attached to at least one alkyl or alicyclic hydrocarbyl group which has at least four carbon atoms and optionally at least one heteroatom.

2. A composition as claimed in claim 1 in which the cation has three long chain hydrocarbyl groups and one short chain hydrocarbyl group, or has one long chain hydrocarbyl groups and three short chain hydrocarbyl groups.

3. A composition as claimed in claim 1 or claim 2 in which the at least one short chain hydrocarbyl group of the cation has more than 2 fewer carbon atoms than each of the long chain hydrocarbyl groups.

4. A composition as claimed in any one of the preceding claims in which the hydrocarbyl groups of the cation are straight chain hydrocarbyl groups.

5. A composition as claimed in any one of the preceding claims in which the hydrocarbyl groups of the cation each have independently up to an including 18 carbon atoms.

6. A composition as claimed in claim 5 in which the long chain hydrocarbyl groups each have independently 6 to 18 carbon atoms.

7. A composition as claimed in any one of the preceding claims in which the short chain hydrocarbyl groups of the cation each have independently 1 to 8 carbon atoms.

8. A composition as claimed in any one of the preceding claims in which the hydrocarbyl groups of the cation each have independently, at least one heteroatom, for example oxygen and/or sulfur.

9. A composition as claimed in any one of the preceding claims in which the anion, A^- is selected from the group consisting of anions (a) to (c) wherein

(a) are anions of the general formula : $[R^1R^2P(O)O]^-$ wherein R^1 and R^2 are independently, alkyl or alicyclic hydrocarbyl groups having at least four carbon atoms and optionally containing at least one heteroatom;
(b) are sulfosuccinate esters of general formula: $R^1OOCCH_2CH(SO_3^-)COOR^2$ wherein R^1 and R^2 are straight chain or branched chain C_4 to C_8 alkyl groups; and
(c) are carboxylate anions of general formula : $RC(O)O^-$ wherein R is a straight chain or branched chain C_9 to C_{17} alkyl or alkenyl group.

10. A composition as claimed in claim 9 wherein the anion A^- is selected from the group of anions of general formula $[(R^3O)(R^4O)P(O)O]^-$ wherein R^3 and R^4 are independently, alkyl hydrocarbyl groups each independently, having at least four carbon atoms, preferably 4 to 18 carbon atoms, more preferably 4 to 16 carbon atoms, for example, 4 to 6 carbon atoms and wherein R^3 and R^4 may each contain independently, at least one heteroatom, for example oxygen.

11. A composition as claimed in claim 10 wherein the anions are selected from di n-butylphosphate and bis(2-butoxyethyl) phosphate.

12. A composition as claimed in any one of the preceding claims in which aromatic hydrocarbyl groups are not present in the anion.

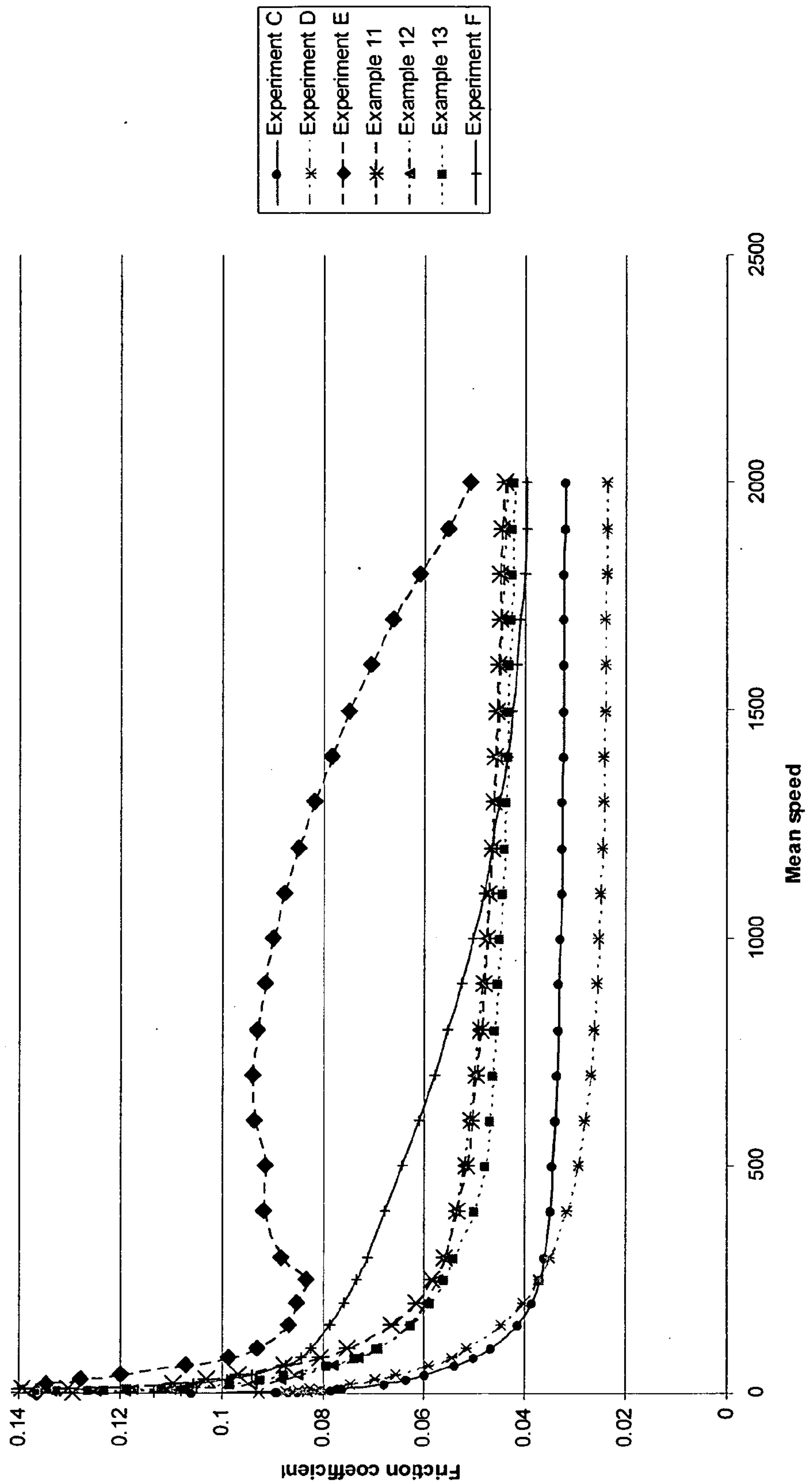
13. A composition as claimed in any one of the preceding claims in which the ionic liquid is present in the lubricating oil composition at a concentration in the range of 0.1 to 10 % by weight.

14. The use of a base oil-soluble ionic liquid in a non-aqueous lubricating oil composition comprising a major amount of a base oil and a minor amount of the ionic liquid in solution in the base oil, to reduce wear of components lubricated by the lubricating oil composition in which use, the ionic liquid is an ionic liquid as defined in any one of claims 1 to 12.

15. The use of a base oil-soluble ionic liquid in a non-aqueous lubricating oil composition comprising a major amount of a base oil and a minor amount of the ionic liquid in solution in the base oil, to modify the friction properties of the lubricating oil composition, in which use, the ionic liquid is an ionic liquid as defined in any one of claims 1 to 12.

16. An additive concentrate comprising a base oil-soluble ionic liquid as defined in any one of claims 1 to 12 and at least one further additive selected from the group consisting of detergents, viscosity improvers, anti-oxidants, dispersants, anti-foam and anti-wear additives and optionally a solvent.

Figure 1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0.12
0.1
0.08
0.06
0.04
0.02
0
Mean speed
0
500
1000
1500
2000
2500
Experiment C
Experiment D
Experiment E
Example 11
Example 12
Example 13
Experiment F

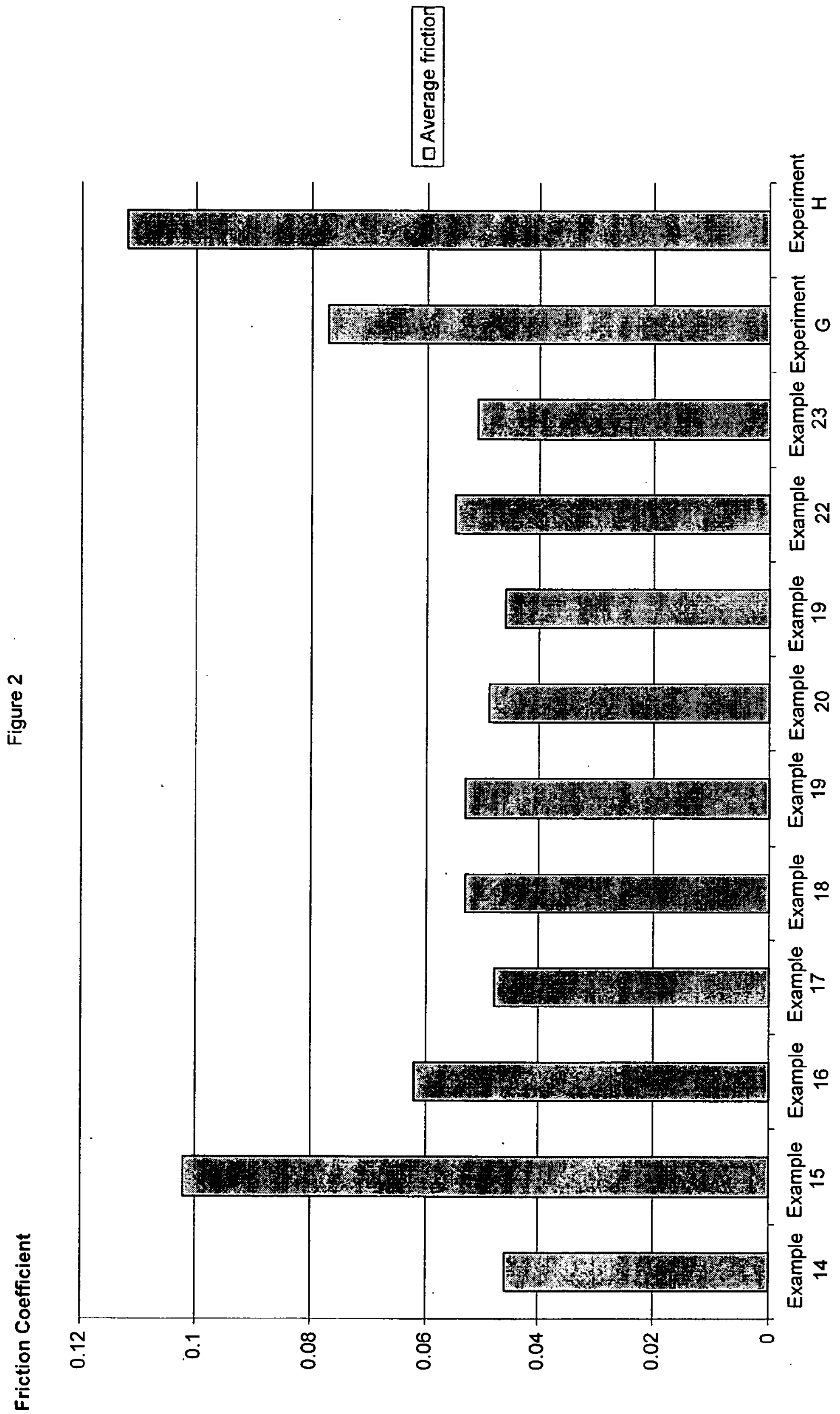
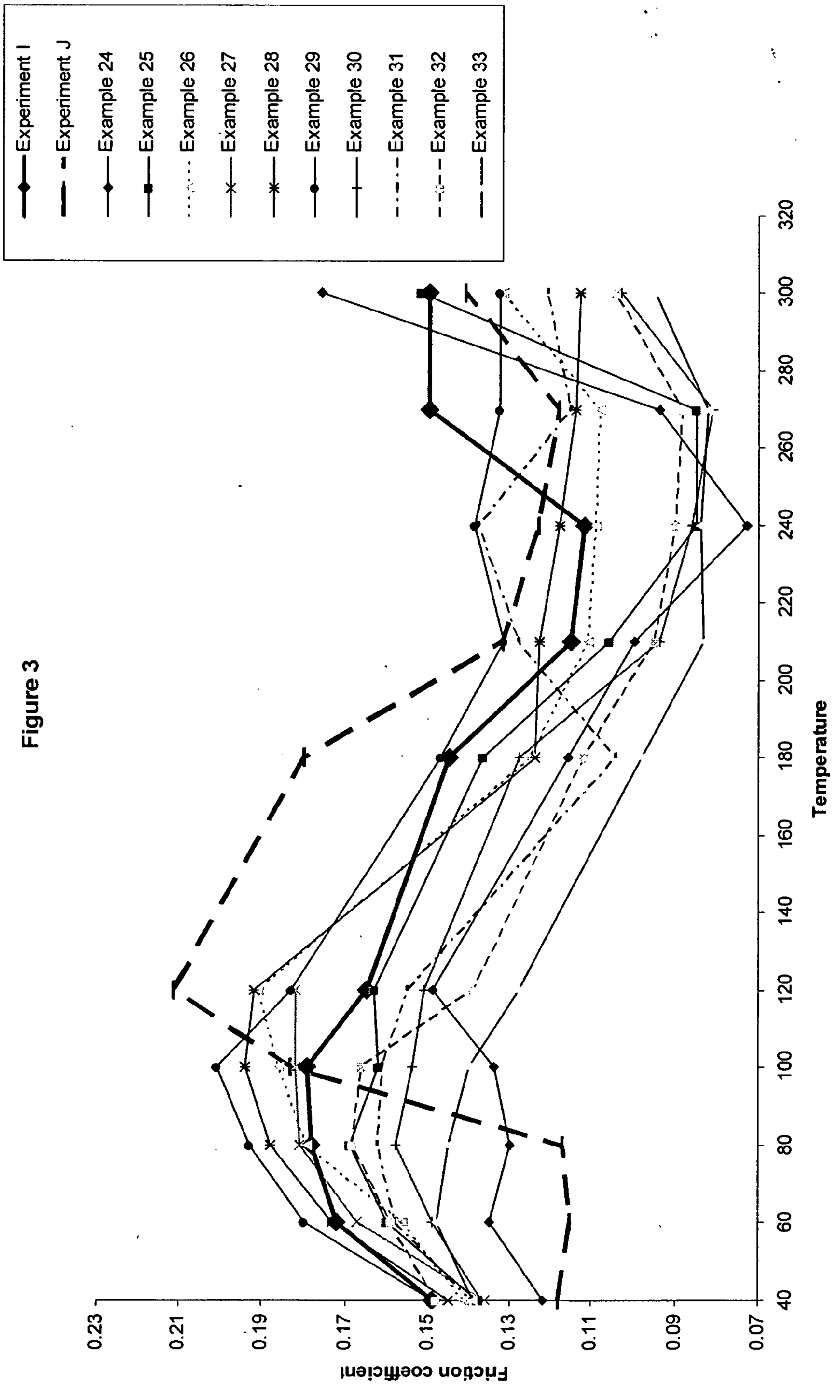

Friction Coefficient
0.12
0.1
0.08
0.06
0.04
0.02
0
Example 14
Example 15
Example 16
Example 17
Example 18
Example 19
Example 20
Example 19
Example 22
Example 23
Experiment G
Experiment H
□ Average frictio

Figure 2

Figure 3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0.19
0.17
0.15
0.13
0.11
0.09
0.07
Temperature
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60
80
100
120
140
160
180
200
220
240
260
280
300
320
Experiment I
Experiment J
Example 24
Example 25
Example 26
Example 27
Example 28
Example 29
Example 30
Example 31
Example 32
Example 33

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EUROPEAN SEARCH REPORT

Application Number
EP 06 25 6446

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CLASSIFICATION OF THE APPLICATION (IPC)

INV.
C10M129/40
C10M133/06
C10M135/10
C10M137/04
C10M137/12
C10M141/08
C10M141/10

ADD.
C10N30/06
C10N40/04
C10N40/25

TECHNICAL FIELDS SEARCHED (IPC)

C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	20 July 2007	Kazemi, Pirjo

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