Ionic liquid composition

Field of the Invention

[0001] The present invention concerns an ionic liquid composition, useful as an additive for hydrocarbonaceous liquids. The ionic liquid proves particularly advantageous for limiting the chemical degradation of hydrocarbonaceous liquids due to nitrogen dioxide contamination in service at elevated temperatures. The addition to the hydrocarbonaceous liquid of an additive quantity of the ionic liquid serves to inhibit the nitration of the hydrocarbonaceous liquid by nitrogen dioxide which initiates the degradation. The ionic liquid also shows the advantages of reducing friction or wear, or both, between contacting mechanical parts lubricated by the hydrocarbonaceous service liquid, and when deployed in an engine lubricating oil offers an advantageous balance of properties, including slower growth in acidification which also contributes to chemical degradation of the oil.

Background of the Invention

[0002] Hydrocarbonaceous liquids are used as service fluids in a variety of hardware applications, and in particular are used as lubricants, protective agents, hydraulic fluids, greases and heat transfer fluids for engineered parts and devices. The composition and properties of such liquids are selected for their intended application, and the ready availability of higher molecular weight hydrocarbonaceous species allows such fluids to be formulated for service at elevated temperatures, in particular above 100°C where aqueous fluids cease to be usable.

[0003] Such hydrocarbonaceous liquids may typically be derived from petroleum or synthetic sources, or from the processing of biomaterials. In particular, hydrocarbonaceous lubricants and hydraulic fluids have become the standard in a variety of applications, including automotive and power transmission fluids, such as engine lubricating oils.

[0004] An essential performance attribute of service liquids is their ability to retain beneficial properties over their service life. The rigours of service place physical and chemical strains on the liquid, and limiting the resulting degradation of the liquid is a major consideration in their selection and formulation. Service fluids typically have to meet a number of performance requirements in their development and certification relating to maintaining service life, which expose the candidate liquids to testing under relevant service conditions which promote degradation.

[0005] Elevated service temperatures and the presence of chemically reactive contaminants increase the demands on hydrocarbonaceous liquids. Higher bulk liquid temperatures and the build-up of reactive contaminants can promote degradation reactions and cause serious reductions in service life, leaving the surrounding hardware inadequately served or protected by the liquid.

[0006] There exists in the art a general need to improve the service life of hydrocarbonaceous liquids operating at elevated bulk temperatures, and particularly of lubricants, by providing improved resistance to chemical degradation in the bulk under service conditions. There also exists a general need for improving resistance to wear, and/or reducing friction, in mechanisms comprising moving parts under forceable contact which are immersed or coated with hydrocarbonaceous service liquids.

[0007] Degradation of hydrocarbonaceous liquids, especially at elevated bulk temperature, has typically been referred to in the art as 'oxidation', based on the conventional understanding that the chemical reactions responsible for degradation essentially involve the reaction of aging hydrocarbon species with oxygen, via a free-radical pathway involving peroxides formed in situ during service. The build-up of these species over time leads to increasing degradation of the liquid and deterioration in bulk liquid properties and service performance. A variety of additives conventionally designated 'anti-oxidants' have been proposed in the art to inhibit this oxidation pathway, including hydrocarbon-soluble hindered phenols and amines, slowing the resulting oxidative degradation that builds as the fluid ages in service.

[0008] However, work by the present applicant has characterised a different chemical degradation pathway that manifests itself in freshly prepared hydrocarbonaceous fluids lacking aged components. This degradation is initiated not by reaction with oxygen or peroxides, but from the direct chemical action at elevated temperatures of nitrogen dioxide which has become entrained in the liquid through contamination in service. It has been found that nitrogen dioxide initiates chemical degradation via nitration reactions with the hydrocarbonaceous liquid, and that these reactions result in substantial breakdown of the liquid in a process which commences when the liquid is still fresh. Nitrogen dioxide can also oxidise to nitric acid within the bulk liquid environment, and lead to acidic attack of the liquid and hardware it is designed to protect. Consequently, there is a specific need to limit the degradative effect of nitrogen dioxide contamination in hydrocarbonaceous liquids at elevated temperatures, which can cause deterioration at an early stage of service life and can also compound the issues caused by conventional oxygen-driven oxidation.

[0009] Such contamination by nitrogen dioxide occurs where the hydrocarbonaceous liquid is exposed to a source of nitrogen dioxide during service. Nitrogen dioxide (NO2) is formed through the reaction of naturally occurring nitrogen and oxygen in air when exposed to higher temperatures, often via the intermediate formation of nitrogen oxide (NO), for example during combustion reactions. Nitrogen dioxide is also a combustion product of fuels derived from petroleum or many bio-sources, both of which contain an amount of bound nitrogen, which is released as nitrogen dioxide upon complete combustion and can become entrained in-service liquids in contact therewith. Such exposure is particularly prevalent in combustion devices, for example internal combustion engines,

which generate nitrogen dioxide and are lubricated by hydrocarbonaceous liquids that become exposed to the exhaust gases; and in particular in crankcase lubricating oils, which experience direct contact with exhaust gases whilst resident on engine surfaces in the cylinder region, and also via blow-by exhaust gases which direct nitrogen dioxide past the piston rings into the crankcase oil reservoir, where it becomes entrained with the lubricant.

[0010] Modern engine and aftertreatment developments aimed at improving the fuel efficiency of engines and minimising carbonaceous particulate emissions have led to higher combustion temperatures, resulting in the production of higher nitrogen dioxide levels in engine-out exhaust gas by virtue of the effect known as the 'NOx – Particulate trade off'. The higher engine temperatures also result in higher bulk lubricant service temperatures, leading to conditions in which the chemical degradation initiated by nitrogen dioxide is increased.

[0011] In addition, the modern focus on increased fuel economy from internal combustion engines has resulted in designs in which internal friction is reduced by engineering greater clearances between the piston rings and cylinder liner surfaces, resulting in free-running engines in which more exhaust gas blows by the piston rings into the crankcase, where it becomes entrained in the bulk engine lubricant.

[0012] Accordingly, hydrocarbonaceous liquids exposed to contamination by nitrogen dioxide in service at elevated temperatures face a particular challenge, due to a chemical nitration pathway that takes effect early in the life of the liquid and is not initiated by the conventional oxidation of hydrocarbons. This challenge is especially severe in the case of engine lubricants, where a variety of engineering measures have increased the degree of nitrogen dioxide entrainment into the bulk lubricant at elevated operating temperatures. The applicant has determined that the resulting nitration pathway is particularly evident at bulk liquid temperatures of between 60 and 180°C, and particularly severe at bulk liquid temperatures of between 110 and 160°C, which temperatures are becoming more evident in crankcase lubricants used under severe operating conditions or in modern, hotter-running engine designs, thus exacerbating the impact of this chemical pathway on lubricant degradation.

[0013] The present invention provides a solution to this challenge through the deployment of a defined ionic liquid additive having the particular ability to deactivate nitrogen dioxide, and thus inhibit the nitration of the hydrocarbonaceous liquid. Through this action, the defined ionic liquid additive limits the chemical degradation initiated by nitration and improves the hydrocarbonaceous liquid's service life.

[0014] One physical consequence of chemical degradation in hydrocarbonaceous service liquids is an increase in liquid viscosity during service. This viscosity increase can lead to the liquid no longer satisfying specified viscosity criteria, prompting its premature replacement. Deployment of

the ionic liquid defined in this invention furthermore provides the advantage of limiting the viscosity growth in service, reducing this consequent limitation to service life.

[0015] Many hydrocarbonaceous liquids, most notably lubricants such as engine lubricants, are formulated to control the increase in acidity which oxidation processes cause, due to the formation of acid species in the liquid, and subsequent acidic corrosion or wear. Consequently, it is a further advantage for such liquids to control the build-up of acid species over service life. Deployment of the ionic liquid defined in this invention provides the further advantage of better control of acid build-up in the liquid, offering the formulator this additional benefit in the preparation of improved service liquids.

[0016] Reducing friction and wear between contact surfaces in mechanical devices remains a continual challenge for the engineer, especially under more severe physical conditions such as elevated temperature and pressure. Many such systems are lubricated or protected by hydrocarbonaceous liquids which serve to provide resistance to such wear and facilitate lower-friction movement. The present ionic liquid provides the further advantage of reducing friction and/or wear on mechanical contact surfaces and can be deployed as an additive for this purpose, separately or in addition to its use for deactivating nitrogen dioxide contamination. The ionic liquid defined in this invention thus provides a combination of advantages over conventional antioxidants and other ionic liquids previously contemplated in the art for use as additives in hydrocarbonaceous liquids, and offers an improved range of properties that enhance service liquid performance and service life.

[0017] US Patent No. 8,278,253 concerns enhancements in oxidation resistance of lubricating oils by the addition thereto of an additive amount of an ionic liquid. The description of the invention and Example 1 make clear that its method focusses on reducing hydroperoxide-induced oxidation, not the nitrogen-dioxide initiated degradation addressed by the present invention. A great variety of cations and anions are separately listed as possible constituents of the ionic liquid, of which the preferred anions and all anions in the examples are fluorine-containing, non-aromatic structures, the majority of which additionally comprise boron. This document does not disclose the defined cation - anion combination required for the ionic liquid of the present invention, and fails to teach its advantages for inhibiting nitration of fresh, un-aged oils by nitrogen dioxide and for improving other relevant properties.

[0018] WO-A-2008/075016 concerns an ionic liquid additive for non-aqueous lubricating oil compositions. The ionic liquid additive is directed towards reducing wear and/or modifying friction properties, and defined as a non-halide, non-aromatic ionic liquid, wherein the anion A- comprises at least one oxygen atom and has an ionic head group attached to at least one alkyl or alicyclic hydrocarbyl group. This document also fails to disclose the defined cation – aromatic anion

combination required for the ionic liquid of the present invention, and fails to teach its advantages for inhibiting nitration of fresh, un-aged oils by nitrogen dioxide and for improving other relevant properties.

[0019] WO-A-2013/158473 concerns lubricant compositions comprising ionic liquids and methods of using such compositions, targeted at minimising deposit and sludge formation in internal combustion engines. The worked examples target high temperature deposit formation that takes place after pre-test aging of the lubricating oil, in which fresh oil is blended with a substantial quantity of used lubricant, as well as being sparged with a dry air / nitrogen dioxide mixture, followed by a deposit-generating step on a metal surface heated to at least 200°C, and optimally to 320°C, whilst being exposed to simulated exhaust gases. The ionic liquid comprises a list of nitrogen-containing cations and an anion represented by the structure YCOO(-) wherein Y is alkyl or aromatic, preferably an alkyl or alkoxyl functional group having from 1 to 50 carbon atoms, or a benzene group, or an alkylated benzene group wherein said alkyl group(s) have 1 to 10 carbon atoms. This document fails to disclose the defined cation – anion combination of the ionic liquid deployed in the present invention, and fails to teach its advantage of inhibiting nitration of fresh, un-aged oils by nitrogen dioxide at bulk liquid temperatures below 200°C, and for improving other relevant properties.

[0020] US-A-2010/0187481 concerns the use of ionic liquids for improving the lubricating effect of synthetic, mineral or native oils. The invention discloses that the resulting lubricant composition is protected from thermal and oxidative attack. The ionic liquid is said to be superior to phenol-based or amine-based antioxidants as thermal and oxidative stabilisers, due to their solubility in organic systems or extremely low vapour pressure. The preferred anions of the ionic liquid are highly fluorinated for high thermal stability, such as bis(trifluoromethylsulfonyl)imide, and no mention or insight into the control of nitrogen-dioxide initiated degradation is provided.

[0021] The applicant has now found that deploying additive quantities of an ionic liquid composed of defined cations and boron- and halogen-free, multi-functional aromatic anions serves to inhibit the nitration of hydrocarbonaceous liquid due to nitrogen dioxide contamination at elevated temperature, and provides a method of limiting the chemical degradation of hydrocarbonaceous liquids even when fresh and un-aged by service. This method enables longer life from service liquids experiencing such contamination. The ionic liquid also serves to reduce friction and/or wear in mechanical systems serviced by the hydrocarbon liquid and provides additional advantages over the prior art as detailed herein.

Summary of the Invention

[0022] In a first aspect, the invention provides an ionic liquid composed of:

(i) one or more nitrogen-free organic cations each comprising a central atom or ring system bearing the cationic charge and multiple pendant hydrocarbyl substituents, and

(ii) one or more halogen- and boron-free organic anions each comprising an aromatic ring bearing a carboxylate functional group and a further heteroatom-containing functional group, these functional groups being conjugated with the aromatic ring and this conjugated system bearing the anionic charge, and the aromatic ring additionally bearing one or more hydrocarbyl substituents.

[0023] In a second aspect, the invention provides an additive concentrate for hydrocarbonaceous liquids, comprising the ionic liquid of the first aspect and a compatible carrier liquid therefor.

[0024] In a third aspect, the invention provides a hydrocarbonaceous liquid comprising the ionic liquid of the first aspect, or additive concentrate of the second aspect, in an amount of up to 5.0% by weight of ionic liquid, per weight of hydrocarbonaceous liquid.

[0025] In a fourth aspect, the invention provides the use of the ionic liquid of the first aspect, or of the additive concentrate of the second aspect, as an additive for a hydrocarbonaceous liquid to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous liquid.

[0026] In the use of the fourth aspect, the ionic liquid consequently inhibits the formation of hydrocarbonaceous nitrate esters and prolongs the service life of the hydrocarbonaceous liquid.

[0027] In a fifth aspect, the invention provides the use of the ionic liquid of the first aspect, or of the additive concentrate of the second aspect, as an additive for a hydrocarbonaceous liquid lubricant to reduce the friction coefficient of the lubricant, or improve its resistance to mechanical wear, or both. In the use of the fifth aspect, it is preferred that the ionic liquid is also used to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous lubricant, and more preferably to also inhibit the rise in total acid number, as measured according to test method ASTM D664, in the hydrocarbonaceous lubricant in service.

[0028] In a sixth aspect, the invention provides a method of prolonging the service life of a hydrocarbonaceous liquid lubricant exposed to nitrogen dioxide contamination in service, comprising the addition thereto prior to service of the ionic liquid of the first aspect, or the additive concentrate of the second aspect, in an amount effective to thereafter reduce the friction coefficient of the lubricant or improve its resistance to mechanical wear, or to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous liquid lubricant and consequently inhibit the formation of hydrocarbonaceous nitrate esters therein, or to both.

[0029] In the method of the sixth aspect, it is preferred that the ionic liquid or additive concentrate is effective both to chemically deactivate nitrogen dioxide entrained within the lubricant, and to reduce the friction coefficient of the lubricant and improve its resistance to mechanical wear.

[0030] Preferred embodiments of these various aspects of the invention are described hereafter.

Brief Description of the Drawings

[0031] This specification also makes reference to the following FIGURES, wherein:

FIGURE 1 reports the nitration peak heights in lubricating oil compositions containing ionic liquids during the T13 engine tests detailed in Worked Example 2 hereinafter;

FIGURE 2 reports the oxidation peak heights in lubricating oil compositions containing ionic liquids during the T13 engine tests detailed in Worked Example 2 hereinafter;

FIGURE 3 reports the kinematic viscosity increases in lubricating oil compositions containing ionic liquids during the T13 engine tests detailed in Worked Example 2 hereinafter.

FIGURE 4 reports the results of coefficient of friction tests by High Frequency Reciprocating Rig (HFRR) on lubricating oil compositions containing the ionic liquid of the invention, as detailed in Worked Example 3 hereinafter.

FIGURE 5 reports the results of coefficient of friction tests by the TE-77 test method on lubricating oil compositions containing the ionic liquid of the invention, as detailed in Worked Example 3 hereinafter.

FIGURE 6 reports the results of wear scar volume tests by the MTM-R test method on lubricating oil compositions containing the ionic liquid of the invention, as detailed in Worked Example 3 hereinafter.

FIGURE 7 reports the results of wear scar volume tests by High Frequency Reciprocating Rig (HFRR) on lubricating oil compositions containing the ionic liquid of the invention, as detailed in Worked Example 3 hereinafter.

Detailed Description of the Invention

[0032] It will be understood that various components used, essential as well as optional and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

[0033] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

[0034] Also, it will be understood that the preferred features of each aspect of the present invention are regarded as preferred features of every other aspect of the present invention. Accordingly, preferred and more preferred features of one aspect of the present invention may be independently combined with other preferred and/or more preferred features of the same aspect or different aspects of the present invention.

[0035] The importance of nitrogen dioxide-initiated degradation in fresh lubricant at elevated temperature has recently been reported by the applicant in the Paper cited as Coultas, D.R. "The Role of NOx in Engine Lubricant Oxidation" SAE Technical Paper 2020-0101427, 2020.

doi:10.4271/2020-01-1427. This paper notes in its introduction that "The principal mechanism by which NOx degrades the lubricant is through its involvement in free-radical nitro-oxidation reactions." The equations which follow show that nitrogen dioxide initiates the process via abstraction of a proton from liquid hydrocarbon species, setting in motion a sequence of reactions involving other species and leading to chemical degradation of the hydrocarbonaceous liquid. Nitrogen dioxide also features prominently further down this degradation pathway, by reacting with RO· radicals to form hydrocarbonaceous nitrate esters of the formula RONO2. These accumulate in the lubricant, forming a reservoir of nitrate esters. At higher operating temperatures, these nitrate esters increasingly dissociate to release the captured RO· radicals, leading to the characteristic nitrate ester "volcano curve" pictured in Figure 14 of this Paper. This rapid dissociation of nitrate esters into free radicals accelerates the chemical breakdown of the hydrocarbonaceous species in the liquid. This plurality of reactions involving nitrogen dioxide, including both initial proton abstraction and the dissociation of subsequently formed nitrate esters, is herein referred to as "nitration" of the hydrocarbonaceous liquid.

[0036] The initiation of this nitration reaction pathway through proton abstraction by nitrogen dioxide, and the formation and dissociation of a reservoir of nitrate esters in the further action of nitrogen dioxide, have been determined by the applicant to be a function of elevated bulk liquid temperature. The initiation of the nitration reaction sequence is underway at 60°C, and grows at higher temperatures of 80°C and above. The formation of nitrate ester builds significantly in the range of 110 to 180°C, and from 130°C the dissociation rate of nitrate esters increases. In the temperature range of 110 to 160°C, the production and dissociation of nitrate ester is most pronounced and leads to more chemical degradation of the hydrocarbonaceous liquid. The trend to higher bulk liquid (sump) temperatures in modern engine lubricants (to temperatures of 130°C and higher) thus increases the practical consequences of nitrogen dioxide contamination, and renders the lubricants of these engines more susceptible to this form of degradation.

[0037] Without being bound to a particular theory, the applicant believes from technical investigations that the ionic liquid deployed in this invention has a particularly advantageous affinity for nitrogen dioxide which leads to its deactivation when present as a contaminant in hydrocarbonaceous liquids. Consequently, the nitrogen dioxide is inhibited from reacting with hydrocarbonaceous liquid species and initiating degradation via proton abstraction to begin the nitration reaction pathway. The nitrogen dioxide is further inhibited from reacting to form the nitrate esters that produces the volcano curve at higher temperatures and its eruption of radicals that leads to further degradation.

[0038] In particular, as detailed herein, the applicant has demonstrated the affinity of the ionic liquid deployed in this invention for nitrogen dioxide and shown it to be superior to other ionic liquids

from the prior art. The applicant has also demonstrated the correspondingly improved ability of this invention to inhibit nitration of hydrocarbonaceous liquids under service conditions subject to elevated temperatures, and to inhibit the growth in bulk liquid acidity over time.

[0039] The applicant has also found the ionic liquid of the present invention to be particularly advantageous for reducing friction and/or wear of mechanical systems that are lubricated by hydrocarbonaceous liquids, as evidenced by its ability to reduce the friction coefficient of the lubricant, or improve its resistance to mechanical wear on the contact surfaces of the hardware it services. This benefit of the ionic liquid can be deployed independently, but is more advantageously employed in combination with the ionic liquid's ability to deactivate nitrogen dioxide contamination and so inhibit the nitration and consequent chemical degradation of the hydrocarbonaceous liquid.

[0040] The ionic liquid of the invention thus offers advantages over previous ionic liquid additives in providing control of nitration and consequent degradation in a hydrocarbonaceous liquid through the deactivation of nitrogen dioxide contamination, whilst also providing improved mechanical properties to the hydrocarbonaceous liquid in the form of reduced friction and/or wear on the contact surfaces of the hardware serviced by the liquid. This combination of features is believed to result from the selection of cation and anion comprising the ionic liquid of the present invention, which combine to provide an improved balance of properties to the ionic liquid.

[0041] The related benefits in service conditions for the ionic liquid deployed in the present invention are demonstrated in the worked examples later in this specification.

<u>The ionic liquid of the first aspect of the invention</u>

[0042] An ionic liquid is conventionally understood as an ionic compound, composed of one or more cation-anion pairs, which exists in liquid physical form at industrially useful temperatures. The present invention provides a defined ionic liquid composed of:

(i) one or more nitrogen-free organic cations each comprising a central atom or ring system bearing the cationic charge and multiple pendant hydrocarbyl substituents, and

(ii) one or more halogen- and boron-free organic anions each comprising an aromatic ring bearing a carboxylate functional group and a further heteroatom-containing functional group, these functional groups being conjugated with the aromatic ring and this conjugated system bearing the anionic charge, and the aromatic ring additionally bearing one or more hydrocarbyl substituents.

[0043] The one or more cations (i) carry the cationic (positive) charge and comprise multiple hydrocarbyl substituents providing organophilic character to the ionic liquid, enabling it to mix readily with hydrocarbonaceous bulk liquid.

[0044] In this specification the term "hydrocarbyl substituents" refer to groups which contain hydrogen and carbon atoms and are each bonded to the remainder of the compound directly via a

carbon atom. The group may contain one or more atoms other than carbon and hydrogen (i.e., heteroatoms) provided they do not affect the essentially hydrocarbyl nature of the group, namely oxygen, nitrogen and sulfur atoms; such groups include amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy. Preferably, however, the hydrocarbyl group consists essentially of, and more preferably consists of, hydrogen and carbon atoms unless specified otherwise. Preferably, the hydrocarbyl group is or comprises an aliphatic hydrocarbyl group. The term “hydrocarbyl” encompasses the term “alkyl” as conventionally used herein. Preferably, the term "alkyl" means a radical of carbon and hydrogen (such as a C1 to C30, such as a C4 to C20 group). Alkyl groups in a compound are typically bonded to the compound directly via a carbon atom. Unless otherwise specified, alkyl groups may be linear (i.e., unbranched) or branched, be cyclic, acyclic or part cyclic/acyclic. The alkyl group may comprise a linear or branched acyclic alkyl group. Representative examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and triacontyl. Substituted alkyl groups are alkyl groups where a hydrogen or carbon has been replaced with a heteroatom (i.e., not H or C) or heteroatom-containing group. The term "substituted' generally means that a hydrogen has been replaced with a carbon or heteroatom-containing group.

[0045] Each cation (i) of the ionic liquid is nitrogen-free. The ionic liquids of this composition have been found to be advantageous in the present invention.

[0046] It is preferred that each cation (i) of the ionic liquid consists of a tetra-hydrocarbyl substituted central atom or ring system bearing the cationic charge.

[0047] Most preferably, each cation (i) of the ionic liquid is a phosphorus-containing cation.

[0048] In this embodiment, it is preferred that each cation (i) is an alkyl substituted phosphonium cation, ideally a tetra-alkyl substituted phosphonium cation. The alkyl groups suitable as substituents for such phosphonium cations include those straight- or branched-chain alkyl groups containing 1 to 28 carbon atoms, such as 4 to 28 carbon atoms, preferably 6 to 28 carbon atoms, more preferably 6 to 14 carbon atoms. Particularly suitable alkyl substituents for such phosphonium cations include hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl groups, and especially where n-alkyl groups. Preferably at least one of the alkyl substituents contains at least 10 carbon atoms and is selected from the above examples.

[0049] Most preferably, each cation (i) is a trihexyltetradecyl phosphonium cation, i.e., a cation carrying three hexyl and one tetradecyl groups as substituents, these substituents preferably being linear alkyl groups. Such an anion is sometimes known in the industry by the shorthand term ‘P66614’

wherein the numbers relate the carbon numbers (6,6,6,14) of the three hexyl and one tetradecyl groups respectively.

[0050] The one or more anions (ii) comprise an aromatic ring bearing at least two substituent functional groups containing heteroatoms, these functional groups being conjugated with the aromatic ring and at least one of them being a carboxylate group, this conjugated system bearing the anionic (negative) charge. In this specification, the term "conjugated" is used in its conventional chemical sense to mean these substituent functional groups are bonded directly to the aromatic ring, wherein one or more p orbitals of one or more atoms comprised within each of these functional groups link to the p orbitals of the adjacent aromatic ring to participate in the delocalised electron cloud of the aromatic ring. It is believed that anions of this configuration have a particular affinity for nitrogen dioxide, and are able to bind to it in such a way that its reactivity towards hydrocarbonaceous compounds is significantly reduced.

[0051] The aromatic ring is composed of carbon and optionally one or more heteroatoms such as nitrogen or oxygen. However, it is preferred that each anion (ii) of the ionic liquid is nitrogen-free or sulfur-free or both. Such ionic liquids have been found to be more advantageous in the present invention, and cannot make a contribution to nitrogen and/or sulfur oxide(s) formation in environments where a proportion of the ionic liquid will be consumed by combustion, for example in engine lubricant environments.

[0052] The aromatic ring of each anion (ii) of the ionic liquid bears a carboxylate group and a further heteroatom-containing functional group bonded directly to the aromatic ring, this system bearing the anionic charge. It is preferred that the heteroatom(s) in both these functional groups consist of oxygen atoms. These functional groups are more preferably positioned on adjacent ring carbon atoms in 'ortho' configuration to each other on the aromatic ring.

[0053] In this respect, it is highly preferred that each anion (ii) is a disubstituted benzene ring bearing a carboxylate group and a second hetero-atom-containing functional group containing only oxygen as the heteroatom, these two groups preferably being positioned in 'ortho' configuration to each other on the aromatic ring. It is preferred that the second functional group is a hydroxyl group, giving rise to a hydroxybenzoate anion (ii). Most preferably the one or more anions (ii) of the ionic liquid are one or more salicylate anions, i.e., anions formed from the deprotonation of salicylic acid.

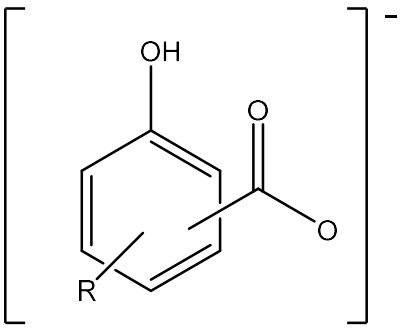
[0054] The aromatic ring of each anion (ii) of the ionic liquid additionally bears one or more hydrocarbyl substituents. These substituents provide additional organophilic character to the ionic liquid, enabling it to mix more readily with hydrocarbonaceous bulk liquid.

[0055] The hydrocarbyl substituent(s) of the anion are as previously defined. Preferably, these substituent(s) are alkyl substituents. Suitable alkyl groups include those straight- or branched-chain

alkyl groups containing 6 or more carbon atoms, preferably 6 to 28 carbon atoms, more preferably 6 to 14 carbon atoms. Particularly suitable alkyl substituents include hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl groups, and especially where n-alkyl groups.

[0056] The aromatic ring of anion (ii) may bear a single alkyl substituent or multiple alkyl substituents. The consequent ionic liquid may be composed of a mixture of anions (ii) differing in their number and/or position of alkyl substituents, which are preferably selected from the above-specified alkyl substituents. Preferably at least one of the alkyl substituents contains at least 10 carbon atoms and is selected from the above examples. More preferably, the aromatic ring of each anion (ii) of the ionic liquid bears one or more straight- or branched-chain alkyl substituents having more than 10 carbon atoms.

[0057] In the anion, it is particularly preferred that one or more, and preferably all, anions (ii) are hydrocarbyl-substituted hydroxybenzoates of the structure:



wherein R is a linear or branched hydrocarbyl group, and more preferably an alkyl group as defined above, including straight- or branched-chain alkyl groups. There may be more than one R group attached to the benzene ring. The carboxylate group and hydroxyl group are conjugated to the aromatic ring, and this system bears the negative (anionic) charge. The carboxylate group can be in the ortho, meta or para position with respect to the hydroxyl group; the ortho position is preferred. The R group can be in the ortho, meta or para position with respect to the hydroxyl group.

[0058] In this embodiment of the anion, one or more (and preferably all) anions (ii) of the ionic liquid are most preferably one or more alkyl-substituted salicylate anions, wherein the alkyl substituent(s) of each anion are independently selected from alkyl groups containing from 12 to 24 carbon atoms; and more preferably from dodecyl, tetradecyl, hexadecyl and octadecyl groups.

[0059] Such hydroxybenzoate and salicylate anions are typically prepared via the carboxylation, by the Kolbe-Schmitt process, of phenoxides, and in that case, will generally be obtained (normally in a diluent) in admixture with uncarboxylated phenol.

[0060] In particular, ionic liquids are preferred in which each cation (i) is nitrogen-free and consists of a tetra-hydrocarbyl substituted central atom or ring system bearing the cationic charge,

and each anion (ii) bears two substituent functional groups containing heteroatoms, being a carboxylate group and a further heteroatom-containing functional group as hereinbefore described. It is more preferred that the heteroatom(s) in both these functional groups consist of oxygen atoms. These functional groups are most preferably positioned on adjacent ring carbon atoms in 'ortho' configuration to each other on the aromatic ring. The preferred embodiments described hereinbefore for each such cation (i) and anion (ii) are particularly useful in combination.

[0061] In all the preferred ionic liquids, and especially the ionic liquids of the three preceding paragraphs, each cation (i) is most preferably an alkyl substituted phosphonium cation, ideally a tetra-alkyl substituted phosphonium cation as hereinbefore described. The trihexyltetradecyl-phosphonium cation (P66614 cation) is most preferred. Each anion is most preferably an alkyl-substituted salicylate anion, wherein the alkyl substituent(s) of each anion are independently selected from alkyl groups containing from 12 to 24 carbon atoms; and more preferably from dodecyl, tetradecyl, hexadecyl and octadecyl groups.

[0062] The ionic liquid of all aspects of the invention may be prepared by synthetic routes known in the art, chosen by the skilled person according to conventional synthesis criteria with regard to suitability for the desired cation-anion combination.

[0063] Thus, the cation (i) can can be formed from the cation – halide complex of the desire cation (ii), such as the preferred phosphonium cation, which is then subjected to anion exchange in a suitable solvent with the precursor of the desired anion. An anion exchange resin may be employed to promote the exchange. The solvent is then stripped and the ionic liquid recovered.

[0064] Examples of synthetic methods for ionic liquids are provided in US-A-2008/0251759 and in the worked examples detailed later in this specification. In addition, the individual cations and anions or precursors thereto are available as items of chemical commerce.

[0065] Without being bound to a particular theory, the applicant believes that the particular advantages of the ionic liquid of this invention in deactivating the degradative effects of nitrogen dioxide arises from the ionic liquid's composition and elucidated mechanism of action, with both anion and cation combining to play advantageous roles.

[0066] Firstly, the functionalised aromatic anion (ii) in the ionic liquid ion-pair is particularly highly capable of interacting with nitrogen dioxide molecules, effectively removing them from reactive circulation within the hydrocarbonaceous liquid. Consequently, the initial deprotonation of hydrocarbonaceous components in the bulk liquid is inhibited, and the nitration reaction sequence and formation of nitrate esters is likewise inhibited, resulting in a slower degradation of the bulk liquid over time.

[0067] Secondly, it is postulated that nitric acid formed in situ from the oxidation of some bound nitrogen dioxide is captured by the associated cation of the ionic liquid. This nitric acid loses its acidic proton to the negatively-charged anion – nitrogen dioxide complex, resulting in the formation of an ion-pair comprising the ionic liquid cation and nitrate anion, and a further complex between the protonated anion and remaining bound nitrogen dioxide. This sequence effectively also locks away the nitric acid from reactive circulation within the hydrocarbonaceous liquid. As a result, the build-up of acid over time in the hydrocarbonaceous liquid is also slower, and the ionic liquid helps to contain acid-mediated oxidation and acidic attack of the hydrocarbonaceous liquid and the underlying hardware.

[0068] In this way, the cation and anion of the ionic liquid act in combination to inhibit the degradative consequences of nitrogen dioxide contamination of the hydrocarbonaceous liquid and prolong service life.

[0069] The applicant further believes that the reduction in friction and/or wear attributable to the ionic liquid of the invention arises from its particular composition, which imparts advantageous protection to the contact surfaces of the mechanism concerned.

The additive composition of the second aspect of the invention

[0070] The second aspect of the invention is an additive composition for a hydrocarbonaceous liquid, comprising the ionic liquid of the first aspect, a carrier liquid and, optionally, further additives. This additive composition is preferably in the form of a concentrate, allowing the ionic liquid to be added to the hydrocarbonaceous liquid without the need to introduce large quantities of excess carrier liquid.

[0071] It is desirable to prepare one or more additive concentrates according to the second aspect, comprising the ionic liquid in a carrier liquid (being a diluent or solvent mutually compatible with both the ionic liquid and the hydrocarbonaceous liquid), to enable easier mixing or blending, whereby other additives can also be added simultaneously or sequentially to the concentrate (such concentrates sometimes being referred to as additive packages).

[0072] Where an additive concentrate is used in the second aspect, it may contain from 5 to 25 mass %, preferably 5 to 22 mass %, typically 10 to 20 mass % of the ionic liquid, the remainder of the concentrate being solvent or diluent.

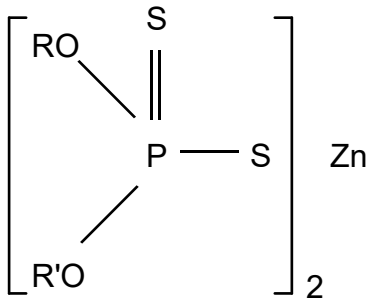
[0073] The additive composition (and preferably the additive concentrate composition) may comprise further additives as a convenient way of incorporating multiple additives simultaneously into the hydrocarbonaceous liquid. Such further additives can have various properties and purposes depending on the needs of the service liquid in question.

[0074] Where an additive concentrate of the second aspect is used, it may contain from 5 to 25 mass %, preferably 5 to 22 mass %, typically 10 to 20 mass % of the ionic liquid, the remainder of the concentrate being solvent or diluent.

[0075] In particular, where the hydrocarbonaceous liquid is a lubricating oil or power transmission oil, particularly an engine lubricating oil, a variety of further additives may be incorporated to enhance other characteristics of the oil, which may comprise one or more phosphorus-containing compounds; dispersants; metal detergents; anti-wear agents; friction modifiers, viscosity modifiers; anti-oxidants; and other co-additives, provided they are different from essential ionic liquids hereinbefore described. These are discussed in more detail below.

[0076] Suitable phosphorus-containing compounds include dihydrocarbyl dithiophosphate metal salts, which are frequently used as antiwear agents. The metal is preferably zinc, but may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 mass %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P2S5, and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

[0077] The preferred zinc dihydrocarbyl dithiophosphates are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups in this context are alkyl groups

of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e., R and R') in the dithiophosphoric acid will generally be 5 or greater. The zinc dihydrocarbyl dithiophosphate (ZDDP) can therefore comprise zinc dialkyl dithiophosphates. Additive concentrates of the present invention for lubricants may have a phosphorus content of no greater than about 0.08 mass % (800 ppm).

[0078] Preferably, in the practice of the present invention, ZDDP is used in an amount close or equal to the maximum amount allowed, preferably in an amount that provides a phosphorus content within 100 ppm of the maximum allowable amount of phosphorus. Thus, resulting lubricating oil compositions preferably contain ZDDP or other zinc-phosphorus compounds, in an amount introducing from 0.01 to 0.08 mass % of phosphorus, such as from 0.04 to 0.08 mass % of phosphorus, preferably, from 0.05 to 0.08 mass % of phosphorus, based on the total mass of the lubricating oil composition.

[0079] A dispersant is an additive whose primary function is to hold oil-insoluble contaminations in suspension, thereby passivating them and reducing deposition on surfaces. For example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use, thus preventing solids flocculation and precipitation or deposition on hardware parts.

[0080] Dispersants in this invention are preferably "ashless", being non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing and hence ash-forming materials. They comprise a long hydrocarbon chain with a polar head, the polarity being derived from inclusion of preferably an oxygen, phosphorus or nitrogen atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms, such as 60 to 250 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric backbone. The hydrocarbon portion of the dispersant may have a number average molecular weight (Mn) of from 800 to 5,000 g/mol, such as from 900 to 3000 g/mol.

[0081] A preferred class of olefin polymers is constituted by polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C4 refinery stream.

[0082] Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. Typically, a hydrocarbon polymeric material, such as polyisobutylene, is reacted with an acylating group (such as maleic acid or anhydride) to form a hydrocarbon-substituted succinic acid (succinate). A noteworthy group of dispersants is constituted by hydrocarbon-substituted

succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine. Particularly preferred are the reaction products of polyalkylene polyamines with alkenyl succinic anhydrides, such as described in US-A-3,202,678; -3,154,560; -3,172,892; -3,024,195; -3,024,237, -3,219,666; and -3,216,936, that may be post-treated to improve their properties, such as borated (as described in US-A-3,087,936 and -3,254,025), fluorinated or oxylated. For example, boration may be accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from boron oxide, boron halides, boron acids and esters of boron acids.

[0083] Preferably, the dispersant, if present, is a succinimide-dispersant derived from a polyisobutene of number average molecular weight in the range of 800 to 5000 g/mol, such as 1000 to 3000 g/mol, preferably 1500 to 2500 g/mol, and of moderate functionality. The succinimide is preferably derived from highly reactive polyisobutene.

[0084] Another example of dispersant type that may be used is a linked aromatic compound such as described in EP-A-2 090 642.

[0085] Combinations of borated and non-borated succinimide are useful herein.

[0086] Combinations of one or more (such as two or more) higher Mn succinimides (Mn of 1500 g/mol or more, such as 2000 g/mol or more) and one or more (such as two or more) lower Mn (Mn less than 1500 g/mol, such as less than 1200 g/mol) succinimides are useful herein, where the combinations may optionally contain one, two, three or more borated succinimides.

[0087] A detergent is an additive that reduces formation of deposits, for example high-temperature varnish and lacquer deposits; it normally has acid-neutralising properties and is capable of keeping finely divided solids in suspension. Most detergents are based on metal “soaps”, that is metal salts of acidic organic compounds.

[0088] Detergents generally comprise a polar head with a long hydrophobic tail, the polar head comprising the metal salt of the acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal when they are usually described as normal or neutral salts and would typically have a total base number or "TBN" at 100 % active mass (as may be measured by ASTM D2896) of from 0 to 150 mg KOH/g, such as 10 to 80 mg KOH/g. Large amounts of a metal base can be included by reaction of an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide.

[0089] The resulting overbased detergent comprises neutralised detergent as an outer layer of a metal base (e.g., carbonate) micelle. Such overbased detergents may have a total base number (TBN) at 100 % active mass of more than 150 mg KOH/g, such as 200 mg KOH/g or greater, such as such as 250 mg KOH/g or greater and typically of from 200 to 800 mg KOH/g, 225 to 700 mg KOH/g,

such as 250 to 650 mg KOH/g, or 300 to 600 mg KOH/g, such as 150 to 650 mg KOH/g, preferably from 200 to 500 or more.

[0090] Suitably, detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurised phenates, thiophosphonates, salicylates and naphthenates and other oil-soluble carboxylates of a metal, particularly alkali metal or alkaline earth metals, e.g., Na, K, Li, Ca and Mg. The most commonly used metals are Ca and Mg, which may both be present in detergents used particularly in lubricating compositions, and mixtures of Ca and/or Mg with Na. Detergents may be used in various combinations.

[0091] Preferably, the detergent additive(s) useful in the present invention comprises calcium and/or magnesium metal salts. The detergent may a calcium and or magensium carboxylate (e.g., salicylates), sulfonate, or phenate detergent. More preferably, the detergents additives are selected from magnesium salicylate, calcium salicylate, magnesium sulfonate, calcium sulfonate, magnesium phenate, calcium phenate, and hybrid detergents comprising two, three, four or more of more of these detergents and/or combinations thereof.

[0092] The magnesium detergent provides the lubricating composition thereof with from 200-4000 ppm of magnesium atoms, suitably from 200-2000 ppm, from 300 to 1500 or from 450-1200 ppm of magnesium atoms (ASTM D5185).

[0093] Calcium detergent is typically present in amount sufficient to provide at least 500 ppm, preferably at least 750 more preferably at least 900 ppm atomic calcium to the lubricating oil composition (ASTM D5185). If present, any calcium detergent is suitably present in amount sufficient to provide no more than 4000 ppm, preferably no more than 3000, more preferably no more than 2000 ppm atomic calcium to the lubricating oil composition (ASTM D5185). If present, any calcium detergent is suitably present in amount sufficient to provide at from 500-4000 ppm, preferably from 750-3000ppm more preferably from 900-2000 ppm atomic calcium to the lubricating oil composition (ASTM D5185).

[0094] The detergent composition may comprise (or consist of) a combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents.

[0095] The combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents provides the lubricating composition thereof with: 1) from 200-4000 ppm of magnesium atoms, suitably from 200-2000 ppm, from 300 to 1500 or from 450-1200 ppm of magnesium atoms (ASTM D5185), and 2) at least 500 ppm, preferably at least 750 more preferably at least 900 ppm of atomic calcium, such as from 500-4000 ppm, preferably from 750-3000ppm, more preferably from 900-2000 ppm atomic calcium (ASTM D5185).

[0096] Additional additives may be incorporated into the additive concentrates of the invention to enable particular performance requirements to be met. Examples of such additives which may be included in lubricating oil compositions of the present invention are friction modifiers, viscosity modifiers, metal rust inhibitors, viscosity index improvers, corrosion inhibitors, oxidation inhibitors, anti-foaming agents, anti-wear agents and pour point depressants.

[0097] Friction modifiers (and, also in engine lubricants, fuel economy agents) that are compatible with the other ingredients of hydrocarbonaceous liquid may be included in the lubricating oil composition. Examples of such materials include glyceryl monoesters of higher fatty acids, for example, glyceryl mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; and alkoxylated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

[0098] Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. Examples of such oil-soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0099] Additionally, the molybdenum compound may be an acidic molybdenum compound. These compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkali metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOCl4, MoO2Br2, Mo2O3Cl6, molybdenum trioxide or similar acidic molybdenum compounds.

[0100] Among the molybdenum compounds useful in the compositions of this invention are organo-molybdenum compounds of the formulae:

$$Mo(R"OCS_2)_4 \text{ and}$$

$$Mo(R"SCS_2)_4$$

wherein R" is an organo group selected from the group consisting of alkyl, aryl, aralkyl and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. Especially preferred are the dialkyldithiocarbamates of molybdenum.

[0101] Another group of organo-molybdenum compounds useful as further additives in this invention are trinuclear molybdenum compounds, especially those of the formula Mo3SkAnDz and mixtures thereof wherein the A are independently selected ligands having organo groups with a

sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 to 7, D is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 carbon atoms should be present among all the ligand organo groups, such as at least 25, at least 30, or at least 35, carbon atoms.

[0102] Where the hydrocarbonaceous liquid is a lubricating oil, it preferably contains at least 10 ppm, at least 30 ppm, at least 40 ppm and more preferably at least 50 ppm molybdenum. Suitably, such lubricating oil compositions contain no more than 1000 ppm, no more than 750 ppm or no more than 500 ppm of molybdenum. Lubricating oil compositions useful in the present invention preferably contain from 10 to 1000, such as 30 to 750 or 40 to 500, ppm of molybdenum (measured as atoms of molybdenum).

[0103] The viscosity index of the hydrocarbonaceous liquid, and especially lubricating oils, may be increased or improved by incorporating therein certain polymeric materials that function as viscosity modifiers (VM) or viscosity index improvers (VII). Generally, polymeric materials useful as viscosity modifiers are those having number average molecular weights (Mn) of from 5,000 to 250,000, preferably from 15,000 to 200,000, more preferably from 20,000 to 150,000. These viscosity modifiers can be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional viscosity modifiers (dispersant-viscosity modifiers).

[0104] Polymers prepared with diolefins will contain ethylenic unsaturation, and such polymers are preferably hydrogenated. When the polymer is hydrogenated, the hydrogenation may be accomplished using any of the techniques known in the prior art. For example, the hydrogenation may be accomplished such that both ethylenic and aromatic unsaturation is converted (saturated) using methods such as those taught, for example, in U.S. Pat. Nos. 3,113,986 and 3,700,633 or the hydrogenation may be accomplished selectively such that a significant portion of the ethylenic unsaturation is converted while little or no aromatic unsaturation is converted as taught, for example, in U.S. Pat. Nos. 3,634,595; 3,670,054; 3,700,633 and Re 27,145. Any of these methods can also be used to hydrogenate polymers containing only ethylenic unsaturation and which are free of aromatic unsaturation.

[0105] Pour point depressants (PPDs) lower the lowest temperature at which the bulk liquid flows and may also be present, especially in lubricating oils. PPDs can be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example,

amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional additives.

[0106] In the present invention it may be advantageous to include a co-additive which maintains the stability of the viscosity of the blend. Thus, although polar group-containing additives achieve a suitably low viscosity in the pre-blending stage, it has been observed that some compositions increase in viscosity when stored for prolonged periods. Additives which are effective in controlling this viscosity increase include the long chain hydrocarbons functionalized by reaction with mono- or dicarboxylic acids or anhydrides which are used in the preparation of the ashless dispersants as hereinbefore disclosed.

The hydrocarbonaceous liquid composition of the third aspect of the invention

[0107] In a third aspect, the invention provides a hydrocarbonaceous liquid comprising the ionic liquid of the first aspect, or additive concentrate of the second aspect, in an amount of up to 5.0% by weight of ionic liquid, per weight of hydrocarbonaceous liquid.

[0108] The hydrocarbonaceous liquid deployed in this aspect of the invention is a liquid suitable for service at bulk liquid temperatures of between 60 and 180°C and being free of aged components and nitrogen dioxide contamination prior to service. Such service liquids are used in a variety of applications, including industrial and automotive oils and power transmission fluids, such as engine lubricating oils.

[0109] The hydrocarbonaceous liquid is preferably a lubricating oil for a mechanical device. More preferably, the hydrocarbonaceous liquid is a crankcase lubricating oil for an internal combustion engine, and is subjected in service to nitrogen dioxide contamination originating from exhaust gas, which gas becomes entrained in the lubricant via the effects of blow-by gas into the crankcase and direct contact on the engine cylinder walls. Most preferably, this crankcase lubricating oil is one periodically or continuously to bulk liquid temperatures in the crankcase of between 110 and 160°C.

[0110] It is important to obtaining the benefits of the invention that, prior to service, the hydrocarbonaceous liquid be initially free of nitrogen dioxide contamination and also of the aged liquid components that arise during service from oxidative or other chemical breakdown, in order not to seed the liquid with significant quantities of reactive chemical species that can offer an alternative or complementary degradative pathway to nitrogen-dioxide initiated nitration. Thus, the hydrocarbonaceous liquid should be freshly prepared and not have been in prior service; and prior to being placed into the service environment should not be pre-mixed or diluted with a proportion of aged liquid that has been in prior use or exposed to nitrogen dioxide contamination.

[0111] It is also important that the ionic liquid is added prior to service and the resulting onset of elevated temperatures and nitrogen dioxide contamination, to maximise its nitration-inhibiting effect and not allow nitrogen dioxide concentration in the bulk liquid to build unhindered.

[0112] The hydrocarbonaceous liquid used as the bulk service liquid may be derived from petroleum or synthetic sources, or from the processing of renewable materials, such as biomaterials.

[0113] Where the hydrocarbonaceous liquid is a petroleum oil, and especially a lubricating oil, such oils range in viscosity from light distillate mineral oils to heavy lubricating oils such as gasoline engine oils, mineral lubricating oils and heavy-duty diesel oils. Generally, the kinematic viscosity of the oil ranges from about 2 mm2/sec (centistokes) to about 40 mm2/sec, especially from about 3 mm2/sec to about 20 mm2/sec, most preferably from about 9 mm2/sec to about 17 mm2/sec, measured at 100°C (ASTM D445-19a).

[0114] Suitable oils, especially as lubricating oils, include natural oils such as animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful bulk oils.

[0115] Synthetic oils, and especially synthetic lubricating oils, include hydrocarbon oils and halo-substituted hydrocarbon oils retaining hydrocarbonaceous character, such as polymerized and copolymerized olefins (e.g., ethylene-propylene copolymers, polybutylene homo- and copolymers, polypropylene homo and copolymers, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly-n-decenes (such as decene homopolymers or copolymers of decene and one or more of C8 to C20 alkenes, other than decene, such as octene, nonene, undecene, dodecene, tetradecene and the like); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivative, analogs and homologs thereof. Also useful are synthetic oils derived from a gas to liquid process from Fischer-Tropsch synthesized hydrocarbons, which are commonly referred to as gas to liquid, or “GTL” base oils.

[0116] Esters are useful as synthetic oils having hydrocarbonaceous character, and include those made from C5 to C12 monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0117] Where the hydrocarbonaceous liquid is a lubricating oil, it may comprise a Group I, Group II, Group III, Group IV or Group V base stock or blend of the aforementioned base stocks. Preferably, the lubricating oil is a Group II, Group III, Group IV or Group V base stock, or a mixture thereof, such as a mixture of a Group I base stock and one or more a Group II, Group III, Group IV or Group

V base stock. Definitions for these base stocks and base oils are found in the American Petroleum Institute (API) publication Engine Oil Licensing and Certification System, ("ELOCS") Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998.

[0118] The base stock, or base stock blend preferably has a saturate content of at least 65%, more preferably at least 75%, such as at least 85%. Preferably, the base stock or base stock blend is a Group III or higher base stock or mixture thereof, or a mixture of a Group II base stock and a Group III or higher base stock or mixture thereof. Most preferably, the base stock, or base stock blend, has a saturate content of greater than 90%. Preferably, the oil or oil blend will have a sulfur content of less than 1 mass %, preferably less than 0.6 mass %, most preferably less than 0.4 mass %, such as less than 0.3 mass % (as determined as indicated in API EOLCS). Group III base stock has been found to provide a wear credit relative to Group I base stock and therefore, in one preferred embodiment, at least 30 mass %, preferably at least 50 mass %, more preferably at least 80 mass % of the lubricating oil is Group III base stock.

[0119] Preferably the volatility of the lubricating oil or oil blend, as measured by the Noack test (ASTM D5800), is less than or equal to 30 mass %, such as less than about 25 mass%, preferably less than or equal to 20 mass %, more preferably less than or equal to 15 mass %, most preferably less than or equal 13 mass %. Preferably, the viscosity index (VI) of the oil or oil blend is at least 85, preferably at least 100, most preferably from about 105 to 140 (ASTM D 2270).

[0120] In this aspect of the invention, the ionic liquid can be added to the hydrocarbonaceous liquid by physical mixing or blending techniques known in the art. It may be desirable, although not essential, to prepare one or more additive concentrates according to the second aspect, comprising the ionic liquid in a carrier liquid (being a diluent or solvent mutually compatible with both the ionic liquid and the hydrocarbonaceous liquid), to enable easier mixing or blending, whereby other additives can also be added simultaneously to the concentrate, and hence to the oil, to form the lubricating oil composition (such concentrates sometimes being referred to as additive packages). The ionic liquid may be added to an additive concentrate prior to the concentrate being combined with a hydrocarbonaceous liquid or may be added to a combination of additive concentrate and hydrocarbonaceous liquid. The ionic liquid may be added to an additive package prior to the package being combined with a hydrocarbonaceous liquid or may be added to a combination of additive package and hydrocarbonaceous liquid.

[0121] Where an additive concentrate of the second aspect is used, it may contain from 5 to 25 mass %, preferably 5 to 22 mass %, typically 10 to 20 mass %, based upon the weight of the concentrate of the ionic liquid, the remainder of the concentrate being solvent or diluent.

[0122] Where an additive package is used, it may contain from 5 to 25 mass %, preferably 5 to 22 mass %, typically 10 to 20 mass %, based upon the weight of the concentrate of the ionic liquid, the remainder of the package being other additives (such as dispersant, detergent, etc.), solvent or diluent.

[0123] When hydrocarbonaceous liquids contain one or more of the above-mentioned further additives in addition to the ionic liquid, each further additive is typically blended into the bulk liquid in an amount that enables the additive to provide its desired function. Representative effective amounts of such further additives, when used in hydrocarbonaceous liquids which are crankcase lubricants, are listed below. All the values listed (with the exception of detergent values since the detergents are used in the form of colloidal dispersants in an oil) are stated as mass percent active ingredient (A.I.). These amounts of further additives are used in combination with the amount of ionic liquid hereinbefore described.

ADDITIVE	MASS % (Broad)	MASS % (Preferred)
Dispersant	0.1 - 20	1 - 8
Metal Detergents	0.1 - 15	0.2 - 9
Corrosion Inhibitor	0 - 5	0 - 1.5
Metal dihydrocarbyl dithiophosphate	0.1 - 6	0.1 - 4
Antioxidant	0 - 5	0.01 - 2.5
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Antifoaming Agent	0 - 5	0.001 - 0.15
Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier	0.01 - 10	0.25 - 3
Ionic Liquid	0.1 to 5.0	0.1 to 3
Hydrocarbonaceous liquid (basestock)	Balance	Balance

The use of the fourth aspect of the invention

[0124] In a fourth aspect, the invention provides the use of the ionic liquid of the first aspect, or of the additive concentrate of the second aspect, as an additive for a hydrocarbonaceous liquid to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous liquid. In the use of the fourth aspect, the ionic liquid consequently inhibits the formation of hydrocarbonaceous nitrate esters and prolongs the service life of the hydrocarbonaceous liquid.

[0125] In this use, the effectiveness of the ionic liquid in inhibiting the nitration reactions initiated by the nitrogen dioxide on hydrocarbonaceous compounds at elevated temperatures leads to the slower onset of degradation in the bulk liquid by this chemical pathway, prolonging its service life. The ionic liquid firstly acts through inhibiting the proton abstraction by nitrogen dioxide which initiates nitration of the bulk liquid, slowing the initial formation of free radicals which feeds other chemical reactions further along the pathway and delaying the onset of significant degradation. The ionic liquid further acts later in the pathway by inhibiting the formation of hydrocarbonaceous nitrate esters from the reaction of nitrogen dioxide with subsequent RO·radicals, resulting in a smaller

accumulation of these reactive compounds within the bulk liquid. As a result, the bulk liquid is exposed to lower concentrations of released RO·radicals at elevated temperatures, especially those service temperatures rising (continuously or periodically) above 110°C, where the rate of dissociation of these nitrate esters greatly increases and results in escalating, more severe degradation of the bulk liquid.

[0126] The amount of ionic liquid effective to inhibit nitration in the use can be arrived at by routine testing under conditions reproducing or simulating nitrogen dioxide contamination at the elevated service temperatures experienced in the system in question.

[0127] In a preferred aspect of the use, the chemical degradation inhibited by the ionic liquid is that resulting from the decomposition of hydrocarbonaceous nitrate esters formed in service by the nitration of the hydrocarbonaceous liquid by nitrogen dioxide at bulk liquid temperatures of between 60 and 180°C, wherein the ionic liquid is used to inhibit the formation of hydrocarbonaceous nitrate esters in that service. In this way, the accumulation of a reservoir of reactive hydrocarbonaceous nitrate esters at elevated service temperatures is directly inhibited, and degradation is better limited.

[0128] In a more preferred aspect of the use, the chemical degradation inhibited by the ionic liquid is that resulting from the decomposition of the hydrocarbonaceous nitrate esters due to the hydrocarbonaceous liquid being periodically or continuously subjected in service to bulk liquid temperatures of between 110 and 160°C, wherein the ionic liquid is used to inhibit the formation of hydrocarbonaceous nitrate esters in that service. In this way, the more rapid, severe degradation that occurs in service at higher elevated temperatures is directly inhibited.

[0129] In these embodiments of the invention, the level of nitrate ester formation in the bulk liquid can be determined spectroscopically by observing the growth in the infra-red peak height associated with nitrate ester over time in the bulk liquid under suitable test conditions. This spectroscopic approach allows the determination of the amount of ionic liquid required to inhibit the formation of nitrate esters in the bulk liquid. The inhibition of hydrocarbonaceous nitrate ester formation in service is determined by the observance of a lower nitrate ester peak height in the bulk liquid in the presence of the ionic liquid, as measured by infrared spectroscopy according to DIN 51 453 or ASTM D8048-20 (in the event of conflict between DIN 51 453 and ASTM D8048-20, DIN 51 453 shall control), under like conditions of service and nitrogen dioxide contamination. According to the DIN method, the height of a single infrared absorption frequency at 1630 cm-1 is measured above a straight-line baseline defined by the absorption at 1615 and 1645 cm-1. The higher the peak height, the more nitrate ester is present in the bulk liquid. Measurement of a series of samples taken over time also allows the change in peak height to be followed as the level of nitrate ester in the service liquid changes over time. According to the ASTM D8048-20 Standard test method, oxidation and nitration

peak heights are measured by first subtracting the fresh oil infrared spectrum. The baseline is defined by absorption between 1950 cm-1 and 1850 cm-1 with highest peak in the range 1740 cm-1 to 1700 cm-1 used for oxidation and 1640 cm-1 to 1620 cm-1 for nitration.

[0130] Determining the amount of reduction or limitation of nitrate ester formation in a lubricating oil composition is determined by the observance of a lower (by at least 10 %, such by at least 20%, such as by at least 30%, such as by at least 40%, such as by at least 50%, such as by 100%) nitrate ester peak height in the presence of the lubricating oil composition containing ionic liquid (as compared to the nitrate ester peak of the same lubricating oil composition where the ionic liquid is replaced with an ionic liquid having the same cation, but hexanoate as the anion in the same proportions), as measured by infrared spectroscopy according to DIN 51 453 or ASTM D8048-20, under like conditions of service and nitrogen dioxide contamination, provided that in the event of conflicting results between DIN 51 453 and ASTM D8048-20, DIN 51 453 shall control.

[0131] In normal circumstances, however, the amount of ionic liquid added to thereafter inhibit the nitration of the hydrocarbonaceous liquid in service at bulk liquid temperatures of 60 °C or more, such as 110 °C or more, such as between 60 and 180°C (such as from 60 to 180°C, such as 60 to 160 °C, such as 110 to 160°C, such as 130 to 160°C), in the presence of nitrogen dioxide contamination, is in the range of 0.1 to 5.0 % by weight, per weight of hydrocarbonaceous liquid; and preferably 0.5 to 4.0 % by weight, per weight of hydrocarbonaceous liquid. More preferably, the ionic liquid is added in an amount in the range of 1.0 to 3.5 % by weight, per weight of hydrocarbonaceous liquid; and most preferably in the range of 1.0 to 3.0 % by weight, per weight of hydrocarbonaceous liquid.

[0132] The hydrocarbonaceous liquid deployed in the method of the invention is a liquid suitable for service at bulk liquid temperatures of 60 °C or more, such as 110 °C or more, such as between 60 and 180 °C (such as from 60 to 180°C, such as 60 to 160 °C, such as 110 to 160°C, such as 130 to 160°C) and being free of aged components and nitrogen dioxide contamination prior to service (or substantially free, e.g., less than 5 ppm, of aged components and less than 10 ppm, of nitrogen dioxide contamination). Such service liquids are used in a variety of applications, including industrial and automotive oils and power transmission fluids, such as engine lubricating oils.

[0133] In the use the hydrocarbonaceous liquid is preferably a lubricating oil for a mechanical device. More preferably in the use, the hydrocarbonaceous liquid is a crankcase lubricating oil for an internal combustion engine, and is subjected in service to nitrogen dioxide contamination originating from exhaust gas, which gas becomes entrained in the lubricant via the effects of blow-by gas into the crankcase and direct contact on the engine cylinder walls. Most preferably, this

crankcase lubricating oil is one periodically or continuously subjected to bulk liquid temperatures in the crankcase of between 110 and 160°C.

[0134] It is important to obtaining the benefits of the use that, prior to service, the hydrocarbonaceous liquid be initially free of nitrogen dioxide contamination and also be initially free of the aged liquid components that arise during service from oxidative or other chemical breakdown, in order not to seed the liquid with significant quantities of reactive chemical species that can offer an alternative or complementary degradative pathway to nitrogen-dioxide initiated nitration. Thus, preferably the hydrocarbonaceous liquid should be freshly prepared and not have been in prior service; and prior to being placed into the service environment should not be pre-mixed or diluted with a proportion of aged liquid that has been in prior use or exposed to nitrogen dioxide contamination.

[0135] Alternately, prior to service, the hydrocarbonaceous liquid may be initially substantially free of nitrogen dioxide contamination (10 ppm or less, such as 5 ppm or less, such as 0 ppm) and also substantially free of the aged liquid components (10 ppm or less, such as 5 ppm or less, such as 0 ppm) that arise during service from oxidative or other chemical breakdown (or substantially free, e.g., less than 0.0001-mass % of aged components and less than 10 ppm, of nitrogen dioxide contamination).

[0136] It is also important that the ionic liquid is added prior to service and the resulting onset of elevated temperatures and nitrogen dioxide contamination, to maximise its nitration-inhibiting effect and not allow nitrogen dioxide concentration in the bulk liquid to build unhindered.

[0137] In this use aspect, the ionic liquid can be added to the hydrocarbonaceous liquid by physical mixing or blending techniques known in the art. It may be desirable, although not essential, to prepare one or more additive concentrates under the second aspect comprising the ionic liquid in a carrier liquid (being a diluent or solvent mutually compatible with both the ionic liquid and the hydrocarbonaceous liquid), to enable easier mixing or blending, whereby other additives can also be added simultaneously to the concentrate, and hence to the oil, to form the lubricating oil composition (such concentrates sometimes being referred to as additive packages).

[0138] Where an additive concentrate is used, it may contain from 5 to 25 mass %, preferably 5 to 22 mass %, typically 10 to 20 mass % of the ionic liquid, the remainder of the concentrate being solvent or diluent.

[0139] The advantageous nature of the use in chemically deactivating nitrogen dioxide entrained in the hydrocarbonaceous liquid, thereby limiting its chemical degradation due to nitration, is demonstrated hereinafter in the worked examples of the invention.

<u>The use of the fifth aspect of the invention</u>

[0140] In a fifth aspect, the invention provides the use of the ionic liquid of the first aspect, or of the additive concentrate of the second aspect, as an additive for a hydrocarbonaceous liquid lubricant to reduce the friction coefficient of the lubricant, or improve its resistance to mechanical wear, or both.

[0141] In the use of the fifth aspect, it is preferred that the ionic liquid is also used to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous lubricant, and more preferably to also inhibit the rise in total acid number, as measured according to ASTM D664, in the hydrocarbonaceous lubricant in service, as described under the fourth aspect of the invention.

[0142] The ionic liquids and hydrocarbonaceous liquids that are suitable and preferred in the fifth aspect of the invention are those already described in this specification.

[0143] The amount of ionic liquid effective to reduce the friction coefficient, or improve its resistance to mechanical wear, or both can be determined through the use of industry-recognised friction and wear tests, by comparing the effect of ionic liquid addition on the baseline performance of the hydrocarbonaceous liquid lubricant in question.

[0144] In normal circumstances, however, the amount of ionic liquid used to friction or wear or both of the hydrocarbonaceous liquid lubricant in service is in the range of 0.1 – 5.0 % by weight, per weight of hydrocarbonaceous liquid; and preferably 0.5 to 4.0 % by weight, per weight of hydrocarbonaceous liquid. More preferably, the ionic liquid is used in an amount in the range of 1.0 to 3.5 % by weight, per weight of hydrocarbonaceous liquid; and most preferably in the range of 1.0 to 3.0 % by weight, per weight of hydrocarbonaceous liquid.

[0145] The amount of ionic liquid effective to inhibit nitration in the preferred embodiment of this use of the invention can be arrived at by routine testing under conditions reproducing or simulating nitrogen dioxide contamination at the elevated service temperatures experienced in the system in question.

[0146] In a preferred aspect of this use, the chemical degradation inhibited by the ionic liquid is that resulting from the decomposition of hydrocarbonaceous nitrate esters formed in service by the nitration of the hydrocarbonaceous liquid by nitrogen dioxide at bulk liquid temperatures of between 60 and 180°C, and the ionic liquid inhibits the formation of hydrocarbonaceous nitrate esters in that service. In this way, the accumulation of a reservoir of reactive hydrocarbonaceous nitrate esters at elevated service temperatures is directly inhibited, and degradation is better limited.

[0147] In a more preferred aspect of this use, the chemical degradation inhibited by the ionic liquid is that resulting from the decomposition of the hydrocarbonaceous nitrate esters due to the hydrocarbonaceous liquid being periodically or continuously subjected in service to bulk liquid temperatures of between 110 and 160°C, and the ionic liquid inhibits the formation of

hydrocarbonaceous nitrate esters in that service. In this way, the more rapid, severe degradation that occurs in service at higher elevated temperatures is directly inhibited.

[0148] In these use embodiments of the invention, the level of nitrate ester formation in the bulk liquid can be determined spectroscopically by observing the growth in the infra-red peak height associated with nitrate ester over time in the bulk liquid under suitable test conditions. This spectroscopic approach allows the observation of the effect of ionic liquid to inhibit the formation of nitrate esters in the bulk liquid. The inhibition of hydrocarbonaceous nitrate ester formation in service is determined by the observance of a lower nitrate ester peak height in the bulk liquid in the presence of the ionic liquid, as measured by infrared spectroscopy according to DIN 51 453, under like conditions of service and nitrogen dioxide contamination. According to this DIN method, the height of a single infrared absorption frequency at 1630 cm-1 is measured above a straight-line baseline defined by the absorption at 1615 and 1645 cm-1. The higher the peak height, the more nitrate ester is present in the bulk liquid. Measurement of a series of samples taken over time also allows the change in peak height to be followed as the level of nitrate ester in the service liquid changes over time.

[0149] In normal circumstances, however, the amount of ionic liquid used to inhibit the nitration of the hydrocarbonaceous liquid in service at bulk liquid temperatures of between 60 and 180°C, in the presence of nitrogen dioxide contamination, is in the range of 0.1 – 5.0 % by weight, per weight of hydrocarbonaceous liquid; and preferably 0.5 to 4.0 % by weight, per weight of hydrocarbonaceous liquid. More preferably, the ionic liquid is used in an amount in the range of 1.0 to 3.5 % by weight, per weight of hydrocarbonaceous liquid; and most preferably in the range of 1.0 to 3.0 % by weight, per weight of hydrocarbonaceous liquid.

The method of the sixth aspect of the invention

[0150] In a sixth aspect, the invention provides a method of prolonging the service life of a hydrocarbonaceous liquid lubricant exposed to nitrogen dioxide contamination in service, comprising the addition thereto prior to service of the ionic liquid of the first aspect, or the additive concentrate of the second aspect, in an amount effective to thereafter reduce the friction coefficient of the lubricant or improve its resistance to mechanical wear, or to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous liquid lubricant and consequently inhibit the formation of hydrocarbonaceous nitrate esters therein, or to both.

[0151] In the method of the sixth aspect, it is preferred that the ionic liquid or additive concentrate is effective both to chemically deactivate nitrogen dioxide entrained within the lubricant, and to reduce the friction coefficient of the lubricant and improve its resistance to mechanical wear.

[0152] Most preferably, the uses of the fourth and fifth aspects of the invention and the method of the sixth aspect, are directed to limiting the chemical degradation, and friction and/or wear, of hydrocarbonaceous liquids that are engine lubricating oils. These oils are exposed to nitrogen dioxide contamination in service, due to the presence of exhaust gas blow-by from the combustion chamber past the piston rings into the crankcase. Such oils, also termed crankcase oils, operate at bulk liquid temperatures wherein the nitration pathway to oil degradation is significant, especially when the oil is fresh and aged oil components have not appreciably formed by other mechanisms. Hotter-running engines are particularly susceptible to such degradation, especially those experiencing temperature regimes or cycles in the bulk crankcase oil of between 110 and 160°C, and in particular between 130 and 160°C.

Definitions

[0153] For purposes of this specification and all claims to this invention, the following words and expressions, if and when used, have the meanings ascribed below.

[0154] For purposes herein, the new numbering scheme for the Periodic Table of the Elements is referred to as set out in CHEMICAL AND ENGINEERING NEWS, 63(5), 27 (1985). Alkali metals are Group 1 metals (e.g., Li, Na, K, etc.). Alkaline earth metals are Group 2 metals (e.g., Mg, Ca, Ba, etc.)

[0155] The term "comprising" or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof. The expressions "consists of" or "consists essentially of" or cognates may be embraced within “comprises” or cognates, wherein "consists essentially of" permits inclusion of substances not materially affecting the characteristics of the composition to which it applies.

[0156] The term "mass%" means mass percent of a component, based upon the mass of the composition as measured in grams, unless otherwise indicated, and is alternately referred to as weight percent ("weight %", "wt%" or "%w/w").

[0157] The term "absent" or "free" as it relates to components included within the lubricating oil compositions described herein and the claims thereto means that the particular component is present at 0 wt %, based upon the weight of the lubricating oil composition, or if present in the lubricating oil composition the component is present at levels that do not impact the lubricating oil composition properties, such as less than 10 ppm, or less than 1 ppm or less than 0.001 ppm. The term "absent" or "free" as it relates to amounts of aged components and nitrogen dioxide contamination means levels that do not impact the lubricating oil composition properties, such as less than 10 ppm, or less than 1 ppm or less than 0.001 ppm.

[0158] Unless otherwise indicated, all percentages reported are mass % on an active ingredient basis, i.e., without regard to carrier or diluent oil, unless otherwise stated.

[0159] This invention further relates to:

1. An ionic liquid composed of:

(i) one or more nitrogen-free organic cations each comprising a central atom or ring system bearing the cationic charge and multiple pendant hydrocarbyl substituents, and

(ii) one or more halogen- and boron-free organic anions each comprising an aromatic ring bearing a carboxylate functional group and a further heteroatom-containing functional group, these functional groups being conjugated with the aromatic ring and this conjugated system bearing the anionic charge, and the aromatic ring additionally bearing one or more hydrocarbyl substituents.

2. The ionic liquid of paragraph 1 wherein each cation (i) of the ionic liquid consists of a tetra-hydrocarbyl substituted central atom or ring system bearing the cationic charge.

3. The ionic liquid of paragraph 1 or paragraph 2, wherein each cation (i) of the ionic liquid is a tetra-alkyl substituted phosphonium cation.

4. The ionic liquid of paragraph 3, wherein each cation (i) is a trihexyltetradecyl phosphonium cation.

5. The ionic liquid of any preceding paragraph 1 to 4, wherein each anion (ii) of the ionic liquid is nitrogen-free.

6. The ionic liquid of any preceding paragraph 1 to 5, wherein the one or more hydrocarbyl substituents on the aromatic ring of each anion (ii) of the ionic liquid are one or more straight- or branched-chain alkyl substituents.

7. The ionic liquid of paragraph 5, or of paragraph 6 when read with paragraph 5, wherein the one or more anions (ii) of the ionic liquid are one or more alkyl-substituted salicylate anions, wherein the alkyl substituent(s) of each anion are independently selected from alkyl groups containing from 12 to 24 carbon atoms.

8. An additive concentrate for hydrocarbonaceous liquids, comprising the ionic liquid of any preceding paragraph and a compatible carrier liquid therefor.

9. A hydrocarbonaceous liquid comprising the ionic liquid or additive concentrate of any preceding paragraph in an amount of up to 5.0% by weight of ionic liquid, per weight of hydrocarbonaceous liquid.

10. The additive concentrate of paragraph 8, or hydrocarbonaceous liquid of paragraph 9, further comprising one or more performance-enhancing additives, preferably which comprise one or more of: phosphorus-containing compounds; dispersants; metal detergents; anti-wear agents; friction

modifiers, viscosity modifiers, anti-oxidants; metal rust inhibitors, viscosity index improvers, corrosion inhibitors, anti-foaming agents, and pour point depressants.

11. The use of the ionic liquid of any of paragraphs 1 to 7, or of the additive concentrate of paragraph 8 or paragraph 10, as an additive for a hydrocarbonaceous liquid to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous liquid.

12. The use of paragraph 11, wherein the ionic liquid consequently inhibits the formation of hydrocarbonaceous nitrate esters and prolongs the service life of the hydrocarbonaceous liquid.

13. The use of the ionic liquid of any of paragraphs 1 to 7, or of the additive concentrate of paragraph 8 or paragraph 10, as an additive for a hydrocarbonaceous liquid lubricant to reduce the friction coefficient of the lubricant, or improve its resistance to mechanical wear, or both.

14. The use of paragraph 13, wherein the ionic liquid also chemically deactivates nitrogen dioxide entrained within the hydrocarbonaceous lubricant.

15. The use of paragraph 14, wherein the ionic liquid inhibits the rise in total acid number, as measured according to ASTM D664, in the hydrocarbonaceous lubricant in service.

16. A method of prolonging the service life of a hydrocarbonaceous liquid lubricant exposed to nitrogen dioxide contamination in service, comprising the addition thereto prior to service of the ionic liquid of any of paragraphs 1 to 8, or the additive concentrate of paragraphs 8 or 10, in an amount effective to thereafter reduce the friction coefficient of the lubricant or improve its resistance to mechanical wear, or to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous liquid lubricant and consequently inhibit the formation of hydrocarbonaceous nitrate esters therein, or to both.

17. The method of paragraph 16, wherein the ionic liquid or additive concentrate is effective both to chemically deactivate nitrogen dioxide entrained within the lubricant, and to reduce the friction coefficient of the lubricant and improve its resistance to mechanical wear.

18. A method of prolonging the service life of a hydrocarbonaceous liquid lubricant exposed to nitrogen dioxide contamination in service, comprising the addition thereto prior to service of the ionic liquid of any of paragraphs 1 to 7 or the concentrate of paragraph 8 or 10, in an amount effective to thereafter to have 1, 2, or 3 of the following effects:

1) to reduce the friction coefficient of the lubricant,
2) to improve its resistance to mechanical wear, and
3) to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous liquid lubricant and consequently inhibit the formation of hydrocarbonaceous nitrate esters therein.

19. The method of paragraph 18, wherein the ionic liquid is effective:

to chemically deactivate nitrogen dioxide entrained within the lubricant,

to reduce the friction coefficient of the lubricant, and

to improve its resistance to mechanical wear.

Examples

[0160] The practice and advantages of the present invention are now illustrated by way of examples.

[0161] For purposes of this invention and the claims thereto, determining the amount of reduction or limitation of nitrate ester formation in a lubricating oil composition is determined by the observance of a lower (such as by at least 10 %, such by at least 20%, such as by at least 30%, such as by at least 40%, such as by at least 50%, such as by 100%) nitrate ester peak height in the presence of the lubricating oil composition containing ionic liquid (as compared to the nitrate ester peak of the same lubricating oil composition where the ionic liquid is replaced with an ionic liquid having the same cation, but hexanoate as the anion in the same proportions), as measured by infrared spectroscopy according to DIN 51 453 or ASTM D8048-20, under like conditions of service and nitrogen dioxide contamination, provided that in the event of conflicting results between DIN 51 453 and ASTM D8048-20, DIN 51 453 shall control.

Preparatory Examples - Preparation of ionic liquids

[0162] Ionic liquids were synthesised using the following method deploying an ion-exchange resin.

Example 1 : [P66614][Alkyl-Salicylate] (Example of the Invention)

[0163] [P66614][Alkyl-Salicylate] was produced using a two-step synthesis method starting from commercially available trihexyltetradecylphosphonium chloride, [P66614]Cl (CYPHOS IL-101, >95 %, CAS: 258864-54-9).

[0164] In the first step, [P66614][OH] was synthesized from [P66614]Cl using a commercially available basic anion exchange resin (Amberlite IRN-78, OH-form resin, CAS: 11128-95-3). [P66614]Cl (100 g, 0.193 mol) was added to a 2 L round-bottom flask and diluted with absolute ethanol (900 mL, 19.5 mol, CAS: 64-17-5). To this, 100 g of the ion exchange resin was added, and the mixture was stirred for 5 hours at 22 °C. The resin was then filtered off, and 100 g of fresh resin was added. This step was repeated three times, or until a negative silver halide test was observed, indicating complete ion exchange.

[0165] The silver halide test was carried out as follows: a small aliquot (0.2 mL) of the reaction mixture was transferred to a 2 mL vial, and diluted with 1 mL absolute ethanol. 2-3 drops of HNO_3 were added to acidify the solution, and 2-3 drops of a saturated aqueous solution of $AgNO_3$ (≥99 wt.%, Sigma-Aldrich, CAS: 7761-88-8) was subsequently added. Complete ion exchange was indicated when a transparent solution with no precipitate was observed.

[0166] In the second step, the concentration of [P66614][OH] in ethanol was determined using 1H NMR. This was followed by the dropwise equimolar addition, dissolved in 100 mL ethanol, of commercially available alkyl-salicylic acid from Infineum UK Ltd, being a mono-alkyl salicylic acid mixture bearing alkyl substituents of 14 and 16 carbon atoms. The acid number of the alkyl-salicylic acid (0.00261 g H+/mol) was used to calculate the amount of acid required (equimolar – equating to 73.96g of alkyl salicylic acid) for the neutralisation reaction with [P66614][OH], and this mixture was subsequently stirred overnight at 22 °C. The solution was then dried under rotary evaporation and subsequently in vacuo (10-3 Pa) at 50 °C for a minimum of 96 h, to obtain the dry pure ionic liquid.

[0167] Following drying the ionic liquid material was characterised via NMR:

[0168] [P66614][Alkyl-Salicylate]: 1H NMR (500 MHz, DMSO–d6): δ (ppm) = 0.69-0.88 (s), 1.04-1.29 (m), 1.37 (m), 1.46 (m), 2.15 (m), 2.29 (s), 3.34 (s), 3.43 (m), 4.36 (s), 6.49 (m), 6.72 (m), 6.93 (m), 7.18 (m), 7.25 (m), 7.41 (s), 7.47 (m), 7.65 (s), 7.70 (s), 8.16 (s), 9.07 (s), 9.11 (s), 9.15 (s).

[0169] A further sample of [P66614][Alkyl-Salicylate] was prepared by the following scaled up procedure.

[0170] [P66614]Cl (808 g, 1.56 mol) was charged into a 5 L glass reactor and diluted with absolute ethanol (770 mL, 13.2 mol). To this solution was dosed a pre-prepared solution of KOH (87.3 g, 1.56 mol) in absolute ethanol (770 mL, 13.2 mol) over 28 minutes using a water bath to limit the exotherm to 23 °C. The mixture was aged for between 90 and 250 min and then blended with celite filter aid (164 g, 20 mass%) and filtered to remove KCl, rinsing the filter cake with absolute ethanol (160 mL, 2.74 mol). The filtrate was transferred to a clean 5 L glass reactor and treated with Amberlite ion exchange resin IRN-78 (400 g, 50 mass%) for 30–70 min and then separated by filtration, rinsing the resin with absolute ethanol (2 × 160 mL, 2 × 2.74 mol). The filtrate was transferred to a clean 5 L glass reactor, into which was dosed an equimolar amount of the same alkyl-salicylic acid as a xylene solution over 33 min using a water bath to limit the exotherm to 28 °C. The mixture was aged for 16 hours and then the volatile components were removed via rotary evaporation at 60–80 °C at 10 mbar for min. 3 h.

Example 2 : [P66614][Hexanoate] (Comparative example)

[0171] [P66614][Hexanoate] was synthesised via the procedure used for [P66614][Alkyl-Salicylate] in Example 1.1. [P66614][OH] was firstly prepared from [P66614]Cl (100 g, 0.193 mol). Equimolar addition of hexanoic acid (≥99 wt.%, CAS: 142-62-1) in place of salicylic acid in the second step (22.4 g, 0.193 mol) was used to produce the desired ionic liquid, followed by drying.

Example 3 : [P66614][NTf_2] (Comparative Example)

[0172] Trihexyltetradecylphosphonium chloride, [P66614]Cl (100 g, 0.193 mol) was dissolved in a minimum amount of dichloromethane (>99 %, CAS: 75-09-2), in a 1 L round-bottom flask. To this, an aqueous solution of commercially available LiNTf2 (55.3 g, 0.193 mol; 99 wt.%, CAS: 90076-65-6) was added dropwise. The reaction mixture was stirred for 12 h at 22 °C, forming a biphasic solution. The organic layer was extracted and washed with ultrapure water five times to remove the LiCl by-product, and until a negative halide test was observed. The solution was then dried under rotary evaporation and subsequently in vacuo (10-3 Pa) at 50 °C for a minimum of 96 hours, to obtain dry pure trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)imide, [P66614][NTf2], determined by NMR as follows:

[0173] [P66614][NTf2]: 1H NMR (500 MHz, CDCl3): δ (ppm) = 0.88 (m, 12H, CH3--(P)) 1.23-1.29 (m, 32H, -CH2-(P)), 1.46 (m, 16H, -CH2-(P)), 2.08 (m, 8H, -CH2-(P)); 13C NMR (126 MHz, CDCl3): δ (ppm) = 13.85, 14.12, 18.56, 18.94, 21.55, 22.28, 22.69, 28.80, 29.25, 29.36, 29.49, 29.65, 30.17, 30.52, 30.89, 31.92, 118.62, 121.17.

[0174] The ionic liquids prepared by these syntheses were used in the further examples below.

Worked Example 1: Mechanistic evaluation of the ionic liquid of the invention

[0175] To evaluate the effectiveness and mechanism of the ionic liquid of the invention, the onset and progress of nitration in a hydrocarbonaceous liquid subject to nitrogen dioxide contamination can be observed and measured using infrared spectroscopy.

[0176] Monitoring the progressing nitration of the hydrocarbonaceous liquid involves taking periodic samples of the liquid in use under real or simulated service conditions, and following the evolution of the fingerprint nitration peak height on the infrared spectrum. The rate of increase of the nitration peak height provides information on the rate of chemical degradation due to nitration and build-up of the nitrate ester reservoir in the bulk liquid.

[0177] According to the DIN 51453 peak height method [Standard DIN 51453 (2004-10): Testing of lubricants - Determination of the oxidation and nitration of used motor oils - Infrared spectrometric method], the height of a single infrared absorption frequency at 1630 cm-1 attributable to forming hydrocarbonaceous nitrate ester is measured above a straight-line baseline defined by the absorptions at 1615 and 1645 cm-1. The higher the peak height, the more hydrocarbonaceous nitrate ester is present in the bulk liquid. The above DIN method also provides for monitoring of the progress of conventional oxidation of the bulk liquid via the measurement of peak height at 1710 cm-1 attributable to carbonyl moieties (ketones, aldehydes, esters and carboxylic acids) formed as a result of oxidation. This peak height is measured relative to a straight-line baseline defined by absorptions at 1970 and 1650 cm-1. Again the rate of increase of peak height provides information on the rate of chemical oxidation in the bulk liquid.

[0178] According to ASTM D8048-20 Standard test method for evaluation of diesel engine oils in Volvo (Mack) T-13 diesel engines, oxidation and nitration peak heights are measured by first subtracting the fresh oil infrared spectrum. The baseline is defined by absorption between 1950 cm-1 and 1850 cm-1 with highest peak in the range 1740 cm-1 to 1700 cm-1 used for oxidation and 1640 cm-1 to 1620 cm-1 for nitration.

[0179] Samples of hydrocarbonaceous liquid being tested under service conditions can be measured via the above methods, and allow the reporting of the effect of different ionic liquids present in the hydrocarbonaceous liquid on the progress, and/or level of inhibition, of degradation due to nitration and due to oxidation.

Anion contribution towards inhibiting degradation caused by nitration

[0180] The DIN 51453 method was used to illustrate the contribution of the anion of the ionic liquid in the performance of the present invention. Testing was conducted on a freshly prepared lubricating oil as bulk hydrocarbonaceous liquid, this composition containing a conventional package of commercial additives. To this starting composition was added 2% by mass, per mass of the oil, of the ionic liquid Example 1 of this invention, being composed of the tetraalkylphosphonium cation "P66614" and an alkyl salicylate anion. A comparative test sample was prepared from the same starting oil composition by adding 2% by mass, per mass of oil, of an ionic liquid composed of Example 3, having the same P66614 cation but an NTf2 anion [Trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)imide]. This comparative ionic liquid thus contains an anion of the type favoured in US-A-2010/0187481 for conventional antioxidancy. The starting oil composition was also used as a control run to set the baseline offered by a commercial formulated oil.

[0181] The test samples were subjected to a laboratory simulation of service conditions as an engine lubricant, in which the oil was exposed to sump operating temperatures and exposed to a source of nitrogen dioxide to mimic contamination in service. This simulation comprises a three-necked 250 mL conical flask fitted with a glycol condenser and heated on an electrical hot-plate. Gas containing 766ppm NO2 in air is bubbled through 250 g of the test lubricant at a rate of 10 litres per minute. A sintered glass frit is used to disperse the gas in the oil. The gas flow rate is regulated using a mass flow controller. The third neck is used to introduce a thermocouple which feeds-back to the hotplate to maintain constant temperature. The test samples were each run for 96 hours at 130°C, and the nitration and oxidation peak heights determined at the end of the test by the above DIN 51453 method. The results for the two samples containing ionic liquid were then compared with the control oil formulation, and the impact of their respective ionic liquids reported as percentage reductions in nitration and oxidation peak height against the control.

Results

2% treat rate by mass of ionic liquid	peak height % reduction vs control	
	Oxidation	Nitration
Example 3 - [P66614][Ntf2]	59	43
Example 1 - [P66614][Alkyl-Salicylate]	70	70

[0182] The presence of the P66614 alkyl-salicylate ionic liquid of the invention resulted in substantially greater reduction in nitration peak height than the comparative ionic liquid with identical cation, but anion not according to the present invention. These results support the differential effect of anion composition in the ionic liquid, and demonstrate the significant advantage provided by the anion defined in the present invention for deactivating nitrogen dioxide entrained in the bulk liquid.

[0183] Whilst the present invention also showed a substantial reduction in oxidation peak height, the oxidation results showed less differentiation between the two ionic liquid samples, supporting the existence of different chemical pathways to nitration and classical oxidation of the lubricant. The differential benefit for the present invention towards nitration indicates its higher selectivity for inhibiting the nitration pathway and greater suitability for controlling the effect of nitrogen dioxide contamination under service.

Cation contribution towards inhibiting degradation caused by nitration

[0184] The DIN 51453 method and laboratory test method of the above anion comparison was also used to illustrate the contribution of the cation of the ionic liquid in the performance of the present invention. Testing was again conducted on the freshly prepared formulated lubricating oil as bulk hydrocarbonaceous liquid containing a conventional package of commercial additives. To this starting composition was added 2% by mass, per mass of the oil, of ionic liquid Example 1 of this invention, being composed of the tetraalkylphosphonium cation "P66614" and an alkyl salicylate anion. However, the comparative test sample was prepared from the same starting oil composition by adding the alkyl salicylic acid from which the ionic liquid had been prepared, in an amount equivalent to the amount of anion in the ionic liquid sample. Thus, in this case, the same aromatic ring structure was added to the oil, in the same amount, but the cation was omitted. The starting oil composition was again used as a control.

[0185] The test samples were subjected to the same laboratory simulation of service conditions as an engine lubricant, in which the oil was exposed to sump operating temperatures and exposed to a source of nitrogen dioxide to mimic contamination in service. The test samples were each run for 96 hours at 130°C, and the nitration and oxidation peak heights determined at the end of the test by the above DIN method. The results for the two samples were then compared with the control oil, and their impact reported as percentage reductions in nitration and oxidation peak height against the control:

2% treat rate by mass of ionic liquid	peak height % reduction vs control	
	Oxidation	Nitration
Example 1.2 - [P66614][Alkyl-Salicylate]	70	70
0.84 % Alkyl-Salicylic acid	34	27

[0186] The results demonstrate that whilst alkyl-salicylic acid itself brought about some reduction in nitration, the ionic liquid was a more potent inhibitor of nitration. This performance advantage was much more apparent for nitration than for oxidation. The full nitration-inhibiting effect of the ionic liquid of the present invention is therefore attributable to the ion-pair combination in the ionic liquid, which co-operate to deactivate nitrogen dioxide present in the bulk liquid.

[0187] Further investigation of the mechanism of this combination effect was carried out in the same laboratory simulation test using the same freshly prepared lubricating oil composition, this time treated with the ionic liquid P66614 Cl. This comparative ionic liquid did not give as much reduction in nitration peak height as the alkyl salicylate example of the invention, but nevertheless still reduced the nitration level by over 60% as compared to the control lacking this ionic liquid.

[0188] Compositional analysis of the bulk oil composition at the end of the test showed a decrease in chloride concentration in the oil over the course of the test; and a gas purge through the end-of-test bulk oil and into silver nitrate solution confirmed the formation of hydrochloric acid during the test. Thus, the P66614 cation is considered too complex with nitric acid formed in situ from a proportion of the nitrogen dioxide, this complex rearranging to the P66614-nitrate ion pair and releasing HCl. In this way, the cation of the ionic liquid also serves to lock away some nitrogen dioxide in a deactivated form, reducing the effective contaminant level and slowing the resulting degradation.

[0189] In the practice of the present invention, the advantages of the defined ionic liquid thus result from the co-operative effect of the defined anion's particularly high affinity for sequestering away nitrogen dioxide, coupled with the ability of the associated cation to form a stable complex with nitrate ions formed in situ from a proportion of the nitrogen dioxide, which further reduces the available nitrogen dioxide concentration within the bulk liquid. This combined effect produces particularly good inhibition of the nitration, and hence degradation, caused by nitrogen dioxide in the bulk liquid. This effect likewise provides for slower increases in total acid number in the bulk liquid, and reduces the potential for the consequences of nitration and acidification, such as bulk liquid viscosity growth.

Worked Example 2 : Performance of the invention in controlling degradation under service conditions

[0190] The advantageous nature of the present invention is illustrated by testing under real service conditions.

[0191] For these purposes, an engine lubricating oil was used as the hydrocarbonaceous liquid and the service environment chosen was the ASTM D8048-20 Standard test method for evaluation of diesel engine oils in Volvo (Mack) T-13 diesel engines. The test uses a 2010 Volvo/Mack D13/MP8, 505BHP, 13L in-line six cylinder diesel engine with electronically controlled fuel injection, with six electronic unit injectors, VGT (variable geometry turbocharger), and cooled EGR (exhaust gas recirculation). It is a 360 hour test run at at 1500 RPM steady state conditions producing approximately 2200 Nm torque and 130°C oil temperature with 19-20% EGR. The principal aim is to evaluate the oxidation stability performance of engine oils at an elevated oil temperature using ULSD (ultra-low sulfur diesel) fuel. The test appears in the following industry specification for oil quality: Mack EOS-4.5, Volvo EOS-4.5, Renault RLD-4, API CK-4 and FA-4The T13 engine test was chosen in view of its known-in-the-art characteristics of high operating temperatures and representative engine-out NOx emissions. The engine (crankcase) lubricating oil of the T13 test is thus exposed in service to higher bulk temperatures in the sump and to nitrogen dioxide contamination via direct entrainment in the lubricant draining down from the cylinder walls, and exhaust gas blowby past the piston rings into the crankcase.

[0192] The T13 test provides an endurance test for the lubricant under conditions that promote chemical degradation due to nitration initiated by nitrogen dioxide contamination. To increase the endurance element of the test further, its normal duration of 360 hours was extended to 400 hours in some cases below. Periodically during the test, the oil is sampled and nitration and oxidation peak heights measured by infrared spectroscopy using the ASTM D8048-20 Mack (Volvo) T13 oxidation method described in application 3 above. The rise in total acid number (TAN ASTM D445) during the test and the increase in viscosity (ASTM D445) of the oil at 40°C and 100°C during the test were also measured.

[0193] Three T13 tests were conducted to compare the effects of different additives to controlling chemical degradation due to nitration and ultimately oxidation. In each case, the same freshly prepared starting lubricating oil composition was used, being a conventional lubricant base oil base-stock containing a standard commercial package of additives. To this starting composition was added one further material in each test, and the effects of these materials compared.

[0194] In Oil 1 (comparative), the further material was a comparative ionic liquid from the prior art, being composed of the tetra-alkylphosphonium cation “P66614” and a hexanoate anion, i.e., having an anion of the structure YCOO(-) wherein Y is C6 alkyl. This ionic liquid was used at the treat rate of 2% by mass, per mass of lubricating oil composition, and was produced in preparative Example 2 as hereinbefore described.

[0195] In Oil 2 (comparative), the further material was a commercial antioxidant additive composed of a hindered phenolic compound. This material is known to be an effective control on conventional free-radical based oxidation processes.

[0196] In Oil 3 (invention), the further material was an ionic liquid from the present invention, being composed of the tetraalkylphosphonium cation "P66614" and an alkyl salicylate anion. This ionic liquid was used in the lubricating oil composition at equimolar concentration to the P66614-hexanoate ionic liquid used in the first case, approximating to a treat rate of 2.8% by mass, per mass of lubricating oil composition. This ionic liquid was produced by the scaled-up process in preparative Example 1 as hereinbefore described.

[0197] The results over the course of the T13 tests are shown graphically in Figures 1, 2 and 3 for nitration, oxidation and increase in kinematic viscosity at 100°C respectively.

[0198] In Figure 1, all three test compositions showed an increase in nitration peak height as the test progressed, with some nitration occurring due to the contamination by nitrogen dioxide. However, Oil 2 containing the conventional antioxidant generally showed the fastest growth in nitration peak height, which accelerated from the 300 hour point of its test. This test run was accordingly stopped at the normal 360 hour point, with the nitration peak height at over 40.

[0199] The progress of nitration was generally slower with the ionic liquid-treated Oils 1 and 3, however the nitration rate with hexanoate-based ionic liquid (Oil 1) also increased after the 200 hour mark, and by 360 hours had exceeded 30 on nitration peak height. In contrast, the alkyl salicylate-based ionic liquid (Oil 3) retained a slow and steady gradient throughout the 360 hours normal duration, and by that point had only just exceeded 20 on nitration peak height, less than half the nitration of the conventional anti-oxidant Oil 2, and substantially less than Oil 1. By 400 hours the nitration level of Oil 3 was still significantly less than that of Oil 1.

[0200] Thus, in the real service conditions of the engine, under hot sump temperatures and in the presence of nitrogen dioxide contamination, the present invention showed substantially improved ability to inhibit nitration over the conventional antioxidant additive solution. It also showed significantly better performance than an analogous alkyl-carboxylate ionic liquid, demonstrating the benefit arising from its different composition.

[0201] Likewise Figure 2 shows that both the conventional antioxidant solution (Oil 2) and the hexanoate-based ionic liquid (Oil 1) showed rapid increase in oxidation towards the end of the test, as the oils lost their oxidation control and oxidation peak height rose sharply. In contrast, Oil 3 retained excellent oxidation control right through to the 360 hour mark, and by 400 hours was still showing significantly lower oxidation than either comparative oil.

[0202] The slower growth in nitration peak height and consequently oxidation peak height exhibited by Oil 3 likewise demonstrates the greater efficacy of the present invention to inhibit the chemical degradation of the bulk liquid (lubricating oil) caused by nitrogen dioxide contamination during service. The slower growth in nitration peak height over time records a slower build-up of nitrate esters in the bulk liquid and, consequently, a slower onset of chemical degradation due to nitration, allowing the liquid to remain in service for longer.

[0203] The rise in kinematic viscosity (as measured by ASTM D445) over the course of the tests shown in Figure 3 also diverged between the two ionic liquids. The kinematic viscosity of Oil 1 rose steeply towards the end of the test, as this oil lost its control of the degradative processes. In contrast, Oil 3 of the invention maintained an essentially flat viscosity for the whole duration of the test. The higher initial viscosity of the ionic-liquid treated oils in these tests results from the direct viscosity effect of the addition of the ionic liquid without adjustment to the underlying oil composition, in order to avoid introducing other variables, and would be formulated out in practice of the invention by viscometric adjustments to the underlying oil composition.

[0204] The invention also showed improved TAN control over the analogous hexanoate-based ionic liquid. At the end of the test, Oil 3 had a TAN of only 2.8 at the normal end of test point of 360 hours, and a TAN of 4.2 at the end of the 400 hours extended test; whereas by 360 hours the TAN of Oil 1 had already risen to 8.32, so this test was not extended further.

[0205] Thus, the present invention (Oil 3) also provided advantages in terms of both viscosity control and total acid number control, providing formulating benefits to the user.

Worked Example 3 : Performance of the ionic liquid in reducing friction and wear

[0206] The ability of the ionic liquid of the invention to lower the coefficient of friction and to reduce wear on contact surfaces lubricated by hydrocarbonaceous liquids was demonstrated using the following industrial tests.

[0207] Coefficient of friction and wear scar volume were both measured using the High Frequency Reciprocating Rig (HFRR) test, in which a steel plate is reciprocated against a steel ball under standard conditions whilst immersed in the liquid lubricant.

[0208] In this test, a commercially available HFRR machine was used with test disc plates of 10mm SAEAMS 6440 steel (AISO 52100/535A99) with a surface finish of <0.2 μm Ra and a hardness of 190-210 Hv30, and 6.00 mm test balls (grade 28 per ISO 3290) of SAE-AMS 6440 steel with a roughness of <0.5 μm and a hardness of 58-66 on the Rockwell “C” scale.

[0209] The test was run according to the following profile: the test specimen was subjected to a series of increasing temperature steps of 40, 60, 80, 100, 120 and 140°C. At each step, the specimen was held constant at that temperature for 1 minute, and a reciprocating cycle then run at that stabilised

temperature for 5 minutes using a 400g load, frequency of 40 Hz and stroke length of 1000um, and 5 seconds output interval. The sample temperature was then raised to the next step, and the reciprocating cycle repeated, until all temperature steps were completed. Coefficient of friction was measured during the test, and the wear scar volume determined at end of test.

[0210] Coefficient of friction was also measured using the TE-77 test method, for which the test specimens were cut from an uncoated steel top-ring and steel liner used in the DD13 engine test. Temperature was fixed at 150 °C throughout the test, and the frequency of reciprocation was fixed at 10 Hz throughout the test.

[0211] The test profile involved running in for 5 minutes at 20 N load, followed by progressive load increase from 20 N to 200N at a rate of 1.5 N/min (a step time approximately 2 hours), followed by a constant load of 200 N for a further 1 hour.

[0212] The wear scar volume is also measured using the MTM-R test. In this test, commercially available MTM equipment was used with test discs of 46mm AISI 52100 steel with a surface finish of <0.02 μm Ra and a hardness of 720-780 Hv, and test balls of 19.05 mm AISI 52100 steel with a surface finish of <0.02 μm Ra and a hardness of 800-920 Hv.

[0213] The test profile involved a stroke length of 4mm and maximum force (Fmax) of 20N at position 5. In the ball on disc reciprocating step, the ball speed was 350m/s at a frequency of 10Hz and test temperature stabilised at 100 °C. The step duration was 45 min and log interval 10 s.

[0214] Tests according to the above methods were conducted on a hydrocarbonaceous lubricating engine oil containing a typical package of commercial oil additives (the "baseline" oil formulation), with and without the presence of Example 1 of the present invention in the amount of 2% by weight, per weight of the baseline oil formulation. These comparisons allowed the effect of the ionic liquid to be seen directly. The results are shown in Figures 5 to 8 inclusive.

[0215] In Figures 4 and 5, the results show how the introduction of ionic liquid Example 1 resulted in a lower coefficient of friction over the HFRR and TE-77 tests. In the TE-77, the friction coefficient achieved in the presence of Example 1 ran lower than the baseline oil formulation throughout the test sequence. In the HFRR test, the coefficients of friction in the presence and absence of Example 1 diverged over the course of the test, with the ionic liquid enabling a constant friction level to be maintained over time.

[0216] In Figures 6 and 7, the presence of Example 1 resulted in lower wear scar volumes in both the MTM-R and HFRR tests respectively, showing the ionic liquid of the invention also to be effective in reducing wear on the contact surfaces lubricated by the oil.

[0217] A follow-up fuel economy test conducted in an M276 motored engine rig, using the ionic liquid of Example 1 in the amount of 1% by weight, per weight of the lubricating oil demonstrated a

reduction in torque of 0.5 and 0.7% at medium, high and extra-high temperatures, confirming the ability of the ionic liquid to provide a frictional advantage that translates into a measurable benefit in engine performance.

[0218] In the above examples, the ionic liquid of the invention is thus shown to have a combination of performance benefits when employed as an additive for hydrocarbonaceous liquids, reducing the chemical degradation of the hydrocarbonaceous liquid by inhibiting the formation of hydrocarbonaceous nitrate esters arising from nitrogen dioxide contamination, and serving to reduce friction and/or wear between contact surfaces lubricated by the hydrocarbonaceous liquid. Consequent benefits are also seen, such as inhibiting the viscosity or acid number increase in service and improved fuel economy.

[0219] All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures, to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby. The term "comprising" specifies the presence of stated features, steps, integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof. Likewise, the term "comprising" is considered synonymous with the term "including." Likewise, whenever a composition, an element, or a group of elements is preceded with the transitional phrase "comprising," it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa. Further, when a range is stated as between A and B, the range includes endpoints A and B, thus "between A and B" is synonymous with "from A to B."

Claims:

What is Claimed is:

1. An ionic liquid comprising:

(i) one or more nitrogen-free organic cations each comprising a central atom or ring system bearing the cationic charge and multiple pendant hydrocarbyl substituents, and

(ii) one or more halogen- and boron-free organic anions each comprising an aromatic ring bearing a carboxylate functional group and a further heteroatom-containing functional group, these functional groups being conjugated with the aromatic ring and this conjugated system bearing the anionic charge, and the aromatic ring additionally bearing one or more hydrocarbyl substituents.

2. The ionic liquid of claim 1, wherein each cation (i) of the ionic liquid consists of a tetra-hydrocarbyl substituted central atom or ring system bearing the cationic charge.

3. The ionic liquid of claim 1, wherein each cation (i) of the ionic liquid is a tetra-alkyl substituted phosphonium cation.

4. The ionic liquid of claim 1, wherein each cation (i) is a trihexyltetradecyl phosphonium cation.

5. The ionic liquid of claim 1, wherein each anion (ii) of the ionic liquid is nitrogen-free.

6. The ionic liquid of claim 1, wherein the one or more hydrocarbyl substituents on the aromatic ring of each anion (ii) of the ionic liquid are one or more straight- or branched-chain alkyl substituents.

7. The ionic liquid of claim 5, wherein the one or more anions (ii) of the ionic liquid are one or more alkyl-substituted salicylate anions, wherein the alkyl substituent(s) of each anion are independently selected from alkyl groups containing from 12 to 24 carbon atoms.

8. The ionic liquid of claim 6, wherein each anion (ii) of the ionic liquid is nitrogen-free, wherein the one or more anions (ii) of the ionic liquid are one or more alkyl-substituted salicylate anions, and wherein the alkyl substituent(s) of each anion are independently selected from alkyl groups containing from 12 to 24 carbon atoms.

9. A hydrocarbonaceous liquid comprising the ionic liquid of any of claims 1 to 8 in an amount of up to 5.0% by weight of ionic liquid, per weight of hydrocarbonaceous liquid.

10. An additive concentrate for hydrocarbonaceous liquids, comprising the ionic liquid of any of claims 1 to 8 and a compatible carrier liquid therefor.

11. The additive concentrate of claim 10, further comprising one or more performance-enhancing additives which comprise one or more of: phosphorus-containing compounds; dispersants; metal detergents; anti-wear agents; friction modifiers, viscosity modifiers, antioxidants; metal rust inhibitors, viscosity index improvers, corrosion inhibitors, anti-foaming agents, and pour point depressants.

12. The use of the ionic liquid of any of claims 1 to 8, or of the additive concentrate of claims 10 to 11, as an additive for a hydrocarbonaceous liquid to chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous liquid.

13. The use of the ionic liquid of claim 12, wherein the ionic liquid consequently inhibits the formation of hydrocarbonaceous nitrate esters and prolongs the service life of the hydrocarbonaceous liquid.

14. The use of the ionic liquid of any of claims 1 to 8, or of the additive concentrate of claim 10 or 11, as an additive for a hydrocarbonaceous liquid lubricant to reduce the friction coefficient of the lubricant, or improve its resistance to mechanical wear, or both.

15. The use of claim 14, wherein the ionic liquid also chemically deactivates nitrogen dioxide entrained within the hydrocarbonaceous lubricant.

16. The use of claim 14, wherein the ionic liquid inhibits the rise in total acid number, as measured according to ASTM D664, in the hydrocarbonaceous lubricant in service.

17. A method of prolonging the service life of a hydrocarbonaceous liquid lubricant exposed to nitrogen dioxide contamination in service, comprising the addition thereto prior to service of the ionic liquid of any of claims 1 to 8, or the additive concentrate of claims 10 or 11, in an amount effective to thereafter obtain one, two or three of the following effects:

a) reduce the friction coefficient of the lubricant,

b) improve the lubricant's resistance to mechanical wear, and

c) chemically deactivate nitrogen dioxide entrained within the hydrocarbonaceous liquid lubricant and consequently inhibit the formation of hydrocarbonaceous nitrate esters therein.

18. The method of claim 17, wherein the ionic liquid or additive concentrate is effective both to chemically deactivate nitrogen dioxide entrained within the lubricant, and to reduce the friction coefficient of the lubricant and improve its resistance to mechanical wear.