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(54) **LUBRICATING COMPOSITIONS**

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(57) **ABSTRACT**

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A lubricating composition comprising: (i) from 50% to 99% by weight of base oil; (ii) from 0.01% to 5% by weight of ionic liquid; and (iii) from 0.01% to 10% by weight of additive; wherein the lubricating composition has a pour point of at most -54° C., a flashpoint of at least 246° C. and a kinematic viscosity at 100° C. in the range of from 4.9 to 5.4 mm²/s. The lubricating compositions according to the present invention are suitable for use in turbine engine oils and are useful for reducing the build up of sludge and for reducing coking in the lubricating composition.

(30) **Foreign Application Priority Data**

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LUBRICATING COMPOSITIONS

FIELD OF THE INVENTION

[0001] The present invention relates to lubricating compositions, particularly to lubricating compositions which are useful as aviation turbine engine oils.

BACKGROUND OF THE INVENTION

[0002] Aviation turbine engine oils (TEOs) are required to exhibit excellent performance over a wide temperature range in order to meet military and civilian product specifications for these products, namely MIL-PRF-23699 and SAE-AS-5780, respectively. In particular, both specifications state that approved products must meet certain viscosity, pour point and flash point requirements.

[0003] As modern turbine engines evolve aviation turbine engines oils are exposed to increasingly aggressive environments including high thermal and oxidative stress. This can lead to undesirable consequences for the turbine engine oil, in particular, unacceptable build up of sludge and unacceptable levels of coking in the oil system. Coke can generically be described as carbonaceous deposits that form on the engine surface as the oil ages. If these deposits form in an aircraft engine they have the potential to block oil-ways and filters and cause heat transfer reduction. The Hot Liquid Process Simulator (HLPS) test (SAE ARP 5996) has been developed by the aviation industry to assess the propensity of aviation turbine engine oils to form coke and is a key requirement in both the civil and military specifications. It would therefore be desirable to formulate a turbine engine oil wherein the build-up of sludge is reduced and wherein the level of coking is reduced.

[0004] Ionic liquids are known for use in certain lubricating compositions. WO2008/154998 discloses the use of ionic liquids for improving the properties of lubricating compositions. However, there is no mention in this document of the use of ionic liquids in turbine engine oils. There is also no mention in this document of a reduction in build-up of sludge or of a reduction in coking of the lubricating composition.

[0005] WO2008/075016 discloses a non-aqueous lubricating oil composition comprising a major amount of a base oil and a minor amount of an additive which is present in solution in the base oil and is a non-halide, non-aromatic ionic liquid which is a salt of general formula C^+A^- , with the cation C^+ being a quaternary phosphonium or quaternary ammonium ion having four hydrocarbyl groups, optionally containing heteroatoms, which hydrocarbyl groups do not all have the same number of carbon atoms, there being at least one long chain hydrocarbyl group having greater than 4 carbon atoms and at least one short chain hydrocarbyl group having fewer carbon atoms than each of the long chain hydrocarbyl groups, and the anion A^- , comprising at least one oxygen atom and having an ionic head group attached to at least one alkyl or alicyclic hydrocarbyl group which has at least four carbon atoms and optionally one heteroatom. The ionic liquid may be used as an anti-wear component and as a friction modifier in a lubricating oil composition. The lubricating oil composition may be used in an ignition engine. However, there is no mention in this document of the use of ionic liquids in turbine engine oils. There is also no mention in this document of a reduction in sludge build-up or of a reduction of coking of the lubricating composition.

[0006] It has now surprisingly been found by the present inventors that when ionic liquids are incorporated into turbine engine oils there is a reduction in the build-up of sludge in the engine oil and a reduction in coking. Advantageously, these benefits are achieved while maintaining the physical properties of the lubricating composition as required by military and civilian specifications.

SUMMARY OF THE INVENTION

[0007] According to the present invention there is provided a lubricating composition comprising:

- (i) from 50% to 99% by weight of base oil;
- (ii) from 0.01% to 5% by weight of ionic liquid; and
- (iii) from 0.01% to 10% by weight of additive;

wherein the lubricating composition has a pour point of at most -54°C ., a flashpoint of at least 246°C . and a kinematic viscosity at 100°C . in the range of from 4.9 to $5.4\text{ mm}^2/\text{s}$.

[0008] It has surprisingly been found that by substituting a portion of the base oils used in a turbine engine oil with an ionic liquid, the observed sludge content according to Test Method FTD-STD-791-5308.7 is significantly reduced.

[0009] Hence according to the present invention there is further provided the use of an ionic liquid to reduce the build-up of sludge in a lubricating composition comprising (i) a base oil, (ii) an ionic liquid and (iii) one or more additives.

[0010] It has also surprisingly been found that by substituting a portion of the base oils used in a turbine engine oil with an ionic liquid, the level of coking is significantly reduced.

[0011] Hence according to another aspect of the present invention there is provided the use of an ionic liquid to reduce the coking in a lubricating composition comprising (i) a base oil, (ii) an ionic liquid and (iii) one or more additives.

[0012] It has also been found that the lubricating composition of the present invention provides a reduction in viscosity increase, a reduction in TAN increase and a reduction in evaporation loss observed during the test method FTD-STD-791-5308.7.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The lubricating composition of the present invention has particular use as a turbine engine oil. Turbine engine oils are required to meet certain physical properties as set out in military and civilian product specifications, MIL-PRF-23699 and SAE-AS-5780, respectively.

[0014] The lubricating composition of the present invention has a kinematic viscosity at 100°C . (as measured by ASTM DIN455) in the range of from 4.9 to $5.4\text{ mm}^2/\text{s}$, preferably in the range of from 4.9 to $5.1\text{ mm}^2/\text{s}$.

[0015] The lubricating composition of the present invention has a pour point (as measured by ASTM D97) of at most -54°C ., preferably at most -57°C .

[0016] The lubricating composition of the present invention has a flashpoint (as measured by ASTM D92) of at least 246°C ., preferably at least 250°C .

[0017] The lubricating composition of the present invention preferably has a kinematic viscosity at -40°C . (as measured by ASTM DIN455) of at most $13,000\text{ mm}^2/\text{s}$, more preferably at most $11,500\text{ mm}^2/\text{s}$.

[0018] The lubricating composition of the present invention preferably has a kinematic viscosity at 40°C . (as measured by ASTM DIN455) of at least $23\text{ mm}^2/\text{s}$, preferably at least $25\text{ mm}^2/\text{s}$.

[0019] The lubricating composition comprises, as an essential component, a base oil.

[0020] The base oil is present at a level in the range of from 50% to 99%, preferably in the range of from 70% to 99%, more preferably in the range of from 80% to 97%, by weight of the lubricating composition.

[0021] Any base oil suitable for use in a turbine engine oil may be used herein.

[0022] Preferably, the base oil has a kinematic viscosity at 40° C. in the range of from 20 to 30 mm²/s, more preferably in the range of from 22 to 25 mm²/s, a kinematic viscosity at 100° C. in the range of from 4 to 6 mm²/s, more preferably in the range of from 4.85 to 5.15 mm²/s, a kinematic viscosity at -40° C. in the range of from 7,000 to 13,000 mm²/s, more preferably in the range of from 8,000 to 10,000 mm²/s, a pour point in the range of -50 to -65° C., more preferably in the range of from -55 to -60° C., and a flash point in the range of 230 to 260° C., more preferably in the range of 250 to 260° C.

[0023] Preferably the base oil comprises a synthetic ester based base stock, in particular polyol ester-based base oils. Synthetic ester based base oils are well known in the art and are for example described in GB-A-2384245. Ester-based base oils (together with a selected additive package) are functional over a wide temperature range and exhibit good thermal and oxidative stability.

[0024] The preparation of esters from alcohols and carboxylic acids can be accomplished using conventional methods and techniques known and familiar to those skilled in the art, and form no part, per se, of the present invention. In general, an alcohol, e.g. technical pentaerythritol, is heated with the desired carboxylic acid mixture, optionally in the presence of a catalyst. Generally, a slight excess of acid is employed to force the reaction to completion. Water is removed during the reaction and any excess acid is then stripped from the reaction mixture. The esters, for example of technical pentaerythritol, may be used without further purification or may be further purified using conventional techniques such as distillation.

[0025] For further information with respect to the synthetic ester based base oil, reference is made to GB-A-2384245, EP-A-0695797, EP-A-1323815, U.S. Pat. No. 4,826,633 and U.S. Pat. No. 5,503,761, the teaching of which is hereby incorporated by reference.

[0026] Suitable synthetic polyol ester based base oils may be formed by the esterification of an aliphatic polyol with carboxylic acid. Preferably the aliphatic polyol contains from 4 to 15 carbon atoms and has from 2 to 8 esterifiable hydroxyl groups. Preferred examples are trimethylol propane, pentaerythritol, dipentaerythritol, neopentyl glycol, tripenaerythritol and mixtures thereof.

[0027] The carboxylic acid reactant used to produce the synthetic polyol ester base oil may suitably be selected from aliphatic monocarboxylic acid or a mixture of aliphatic monocarboxylic acid and aliphatic dicarboxylic acid. The carboxylic acid may contain from 2 to 20 carbon atoms, preferably from 4 to 12 carbon atoms, more preferably from 5 to 10 carbon atoms and includes straight and branched chain aliphatic acids. Mixtures of monocarboxylic acids may also be used.

[0028] Suitable polyol esters are those commercially available under the tradenames Hatcol 2954, Hatcol 1754, Hatcol 1764, Hatcol 1765 and Hatcol 1760 from Chemtura, Middle-

bury, Conn., USA, Priolube 3939 from Croda, Snaith, UK and Synative ES 2939 and Synative ES 2931 from Cognis, Monheim, Germany.

[0029] In addition, all base stocks described in EP-A-0518567 and EP-A-0695797 are suitable for use in the lubricating compositions of the present invention.

[0030] According to a preferred embodiment the polyol ester base oil comprises at least 80 wt. % monopentaerythritol.

[0031] Suitably, the polyol ester base oil may be a mixture of about 80 to 95 wt. % monopentaerythritol and 5 to 20 wt. % dipentaerythritol. This mixture is typically known as 'technical' pentaerythritol and may also contain some tri and tetra pentaerythritol, which are typically formed as by-products during the production of technical pentaerythritol.

[0032] It is even more preferred that the polyol ester base oil comprises more than 90 wt. % monopentaerythritol, more preferably more than 95 wt. % monopentaerythritol. It is even more preferred that the polyol ester base oil comprises about 100 wt. % monopentaerythritol.

[0033] Another essential component of the lubricating composition of the present invention is an ionic liquid.

[0034] The ionic liquid is present at a level in the range of from 0.01% to 5%, preferably in the range of from 0.01% to 2%, more preferably in the range of from 0.05% to 0.5%, especially in the range of from 0.1% to 0.3%, by weight of the lubricating composition.

[0035] Ionic liquids are molten salts which are liquid at room temperature or by definition have a melting point of less than 100° C. They have virtually no vapour pressure and can exhibit high thermal stability.

[0036] An ionic liquid can be presented by the formula C⁺A⁻ wherein C⁺ is a suitable cation and A⁻ is a suitable anion.

[0037] Suitable cations C⁺ are selected from a quaternary ammonium cation, a phosphonium cation, an imidazolium cation, a pyridinium cation, a pyrazolium cation, an oxazolium cation, a pyrrolidinium cation, a piperidinium cation, a trialkylsulfonium cation, a thiazolium cation, a guanidinium cation, a morpholinium cation, a sulfonium cation and a triazolium cation. Preferred cations are selected from quaternary ammonium cations and phosphonium cations.

[0038] Suitable anions A⁻ are selected from [PF₆]⁻, [BF₄]⁻, [CF₃CO₂]⁻, [CF₃SO₃]⁻, as well as its higher homologues, [C₄F₉SO₃]⁻ or [C₈F₁₇SO₃]⁻ and higher perfluoroalkylsulfonates, [(CF₃SO₂)₂N]⁻, [(CF₃SO₂)(CF₃COO)N]⁻, Cl⁻, Br⁻, I⁻, [C(CN)₃]⁻, SCN⁻, [B(C₂O₄)₂]⁻, [N(SO₂CF₃)₂]⁻, [R⁴SO₃]⁻, [R⁴OSO₃]⁻, [R⁴COO]⁻, [NO₃]⁻, [N(CN)₂]⁻, [HSO₄]⁻, PF_{6-x}R^x or [R⁴R⁵PO₄]⁻, wherein R⁴ and R⁵ are independently selected from hydrogen, linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms; heteroaryl, heteroaryl-C₁-C₆-alkyl groups with 3 to 8 carbon atoms in the hetero aryl residue and at least one heteroatom selected from N, O and S, which can be substituted with at least one group selected from C₁-C₆ alkyl groups and/or halogen atoms; aryl-aryl-C₁-C₆-alkyl groups with 5 to 12 carbon atoms in the aryl residue, which can be substituted with at least one C₁-C₆-alkyl group, R⁶ can be a perfluoroethyl or a higher perfluoroalkyl group, and x is an integer of from 1 to 4.

[0039] Particularly preferred are ionic liquids with highly fluoridated anions, since these are generally highly thermally stable. Also, the ability for water uptake by these anions can

be significantly reduced, for example, with bis(trifluoromethylsulfonyl)imide anion. Another preferred anion is trifluoroacetate.

[0040] Examples of suitable ionic liquids include, but are not limited to, butyl methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide (MBPimid), methylpropylpyrrolidinium-bis(trifluoromethylsulfonyl)imide (MPPimid), tris-hexylmethylimidazolium (perfluoroethylene)-trifluorophosphate (HMIMPFET), hexylmethylimidazolium-bis(trifluoromethylsulfonyl)imide (HMIMimid), hexylmethylpyrrolidinium-bis(trifluoromethylsulfonyl)imide (HMP), tris-tetrabutylphosphonium (perfluoroethylene)trifluorophosphate (BuPPFET), octylmethylimidazolium-hexafluorophosphate (OMIM PF6), hexylpyridinium-bis(trifluoromethylsulfonyl)imide (Hpyimid), methyltrioctylammonium-trifluoroacetate (MOAac), butylmethylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate (MBPPFET), trihexyl(tetradecyl)phosphonium-bis(trifluoromethylsulfonyl)imide (HPDimid), hexylmethylimidazolium tetrafluoroborate (HMI BF4), hexylmethylimidazolium hexafluorophosphate (HMI PF6), 1-ethyl-3-methylimidazolium diethylphosphate (EMIM DEP), 1-ethyl-3-methylimidazolium methyl sulphate (EMIM DSU), 1-ethyl-3-methylimidazolium bis[oxalate(2-)-O,O+]borate (EMIM BOB) and mixtures thereof.

[0041] Ionic liquids such as those listed above are commercially available from Merck, Darmstadt, Germany and Sigma Aldrich, St Louis, Mo., USA. Ionic Liquids commercially available under the tradename Bacionics from BASF, Ludwigshafen, Germany, are also suitable for use herein.

[0042] Preferred ionic liquids for use in the compositions of the present invention are selected from methyltrioctylammonium-trifluoroacetate (MOAac), trihexyl(tetradecyl)phosphonium-bis (trifluoromethylsulfonyl)imide (HDPimid), hexylmethylimidazolium tetrafluoroborate (HMI BF4), hexylmethylimidazolium hexafluorophosphate (HMI PF6), 1-ethyl-3-methylimidazolium diethylphosphate (EMIM DEP), 1-ethyl-3-methylimidazolium methyl sulphate (EMIM DSU) and mixtures thereof.

[0043] Especially preferred ionic liquids for use herein are trihexyl(tetradecyl)phosphonium-bis(trifluoromethylsulfonyl)imide (HDPimid), hexylmethylimidazolium hexafluorophosphate (HMI PF6), and mixtures thereof.

[0044] The lubricating composition further comprises one or more additives, in effective amounts, typically at a level of from 0.01% to 10% by weight of the lubricating composition, such as for example, but not limited to, metallic and ashless oxidation inhibitors, metallic and ashless dispersants, metallic and ashless detergents, corrosion and rust inhibitors, metal deactivators, metallic and non-metallic, low-ash, phosphorus-containing and non-phosphorus, sulphur-containing and non-sulphur-containing anti-wear agents, metallic and non-metallic, phosphorus-containing and non-phosphorus, sulphur-containing and non-sulphurous extreme pressure additives, anti-seizure agents, pour point depressants, wax modifiers, viscosity modifiers, seal compatibility agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, anti foaming agents, demulsifiers, and other usually employed additive packages. For a review of many commonly used additives, reference is made to D. Klamann in *Lubricants and Related Products*, Verlag Chemie, Deerfield Beach, Fla.; ISBN 0-89573-177-0, and to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, N.J. (1973).

[0045] Viscosity index improvers (also known as VI improvers, viscosity modifiers, or viscosity improvers) provide lubricants with high- and low-temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures.

[0046] Preferable antiwear additives to be used with the composition according to the invention include triaryl phosphates, such as those available from Chemtura under the tradenames Reolube OMTI, Durad 310M, Durad 110, Durad 125, Durad 150B, Reolube TXP, Durad 220B, Durad 620B, Durad 110B, Fryquel 150 and Fryquel 220, those available from Rhein Chemie under the tradenames Additin RC 3661, Additin RC 3760 and Additin RC 3680 and those commercially available from Supresta under the tradenames SynOAd 8475, SynOAd 8484, SynOAd 8485, SynOAd 8478, SynOAd 8477, SynOAd 8499 and SynOAd 9578. Included within the term triaryl phosphates are tricresyl phosphates, such as those approved to the specification TT-T-656.

[0047] Other preferred antiwear additives include metal alkylthiophosphates, more particularly zinc dialkyldithiophosphates. Other preferred antiwear additives include phosphorus-free antiwear additives such as sulphur-containing aliphatic, arylaliphatic or alicyclic olefinic hydrocarbons. Other preferred antiwear additives include polysulfides of thiophosphorus acids and thiophosphorus acid esters, and phosphorothionyl disulfides.

[0048] Esters of glycerol may be used as antiwear agents. For example, mono-, di-, and tri-oleates, mono-palmitates and mono-myristates may preferably be used. Generally, antiwear additives may be used in an amount of about 0.01 to 6% by weight, preferably about 0.01 to 4% by weight, based on the total weight of the lubricating composition.

[0049] Suitable antioxidants retard the oxidative degradation of the lubricating composition during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the fluid. A wide variety of suitable oxidation inhibitors are known, as for instance those described in Klamann in *Lubricants*, and for example U.S. Pat. No. 4,798,684 and U.S. Pat. No. 5,084,197.

[0050] Preferred antioxidants for the lubricating composition of this invention include aminic antioxidants. These include alkylated and non-alkylated aromatic amines such as aromatic monoamines with aliphatic, aromatic or substituted aromatic group substituents at the nitrogen atom. Typical aromatic amines antioxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines may also be used, such as for example a mixture of phenyl-alpha-naphthylamine (PANA)-type antioxidant(s) and diphenylamine (DPA)-type antioxidant(s). Polymeric amine antioxidants may also be used, such as Vanlube 9317 commercially available from RT Vanderbilt. Particular examples of aromatic amine antioxidants useful in the present invention include: p,p'-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0051] Commercially available phenyl-alpha-naphthylamine (PANA)-type antioxidants include, for example, Irganox L06 commercially available from Ciba, Additin 7130

commercially available from Rhein Chemie, Naugalube APAN and Naugard PAN commercially available from Chemtura.

[0052] Commercially available diphenylamine (DPA)-type antioxidants include, for example, Vanlube 81 commercially available from RT Vanderbilt, Naugalube AMS, Naugalube 438, Naugalube 635, Naugalube 640, Naugalube 680 Commercially available from Chemtura, Germany, Additin 7001, Addition 7005A, Additin 7135, Additin 10314A, commercially available from Rhein Chemie, Hitec 4720, Hitec 4721, Hitec 4777 commercially available from Afton, Irganox L57, Irganox L67 commercially available from Ciba.

[0053] Other useful antioxidants include hindered phenols. Phenolic antioxidants may be used either as such or in combination with aminics. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics which are the ones which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Examples of phenolic materials of this type include 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic propionic ester derivatives.

[0054] Bis-phenolic antioxidants may also be advantageously used in the lubricating composition. Sulphurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants. Low sulfur peroxide decomposers are useful as antioxidants. Another class of suitable antioxidants is oil soluble copper compounds. Examples of suitable copper antioxidants include copper dihydrocarbyl-thio or dithio-phosphates and copper salts of carboxylic acids. Other suitable copper salts include copper dithiocarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are known to be particularly useful. These antioxidants may be used individually by type or in combination with one another. Such additives may be used in an amount of about 0.01 to 5% by weight, preferably about 0.01 to 2% by weight.

[0055] Detergents useful as additives may be simple detergents or hybrid or complex detergents. Suitable detergents include anionic compounds that contain a long chain oleophilic portion of the molecule and a smaller anionic or oleophobic portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid such as a sulphuric acid, carboxylic acid, phosphorus acid, phenol, or mixtures thereof. The counter ion is typically an alkaline earth or alkali metal. Preferred detergents include the alkali or alkaline earth metal salts of sulfates, sulfonates, phenates, carboxylates, phosphates, and salicylates. Suitable alkaryl sulfonates typically contain about 9 to about 80 or more carbon atoms, more typically from about 16 to 60 carbon atoms. Preferred are those disclosed in Klamann in Lubricants and Related Products, and in "Lubricant Additives" cited above, and C. V. Smallheer and R. K. Smith, published by the Lezius-Hiles Co. of Cleveland, Ohio (1967). Alkaline earth phenolates represent another useful class of detergents. These detergents are the products of reacting alkaline earth

metal hydroxides or oxides with an alkyl phenol or sulphurized alkylphenol. Useful alkyl groups include straight chain or branched C₁-C₃₀ alkyl groups, preferably, C₄-C₂₀. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, 1-ethyldecylphenol, and the like. Metal salts of carboxylic acids are also useful as detergents. Another preferred class of detergents is alkaline earth metal salicylates, including monoalkyl to tetraalkyl salicylates, wherein the alkyl groups have from 1 to 30 carbon atoms. Preferably, the alkaline earth metal is calcium, magnesium, or barium; calcium being the most preferred. Another useful class of detergents encompasses alkaline earth metal phosphates. Typically, the total detergent concentration is about 0.01 to about 6% by weight, preferably, about 0.1 to 4% by weight, calculated on the total lubricating composition. In addition, non-ionic detergents may be preferably used in lubricating compositions. Such non-ionic detergents may be ashless or low-ash compounds, and may include discrete molecular compounds, as well as oligomeric and/or polymeric compounds.

[0056] The additives may further comprise dispersants. Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorous. Typical hydrocarbon chains contain about 50 to 400 carbon atoms. Suitable dispersants include phenolates, sulfonates, sulphurized phenolates, salicylates, naphthenates, stearates, carbamates and thiocarbamates. A particularly useful class of dispersants is alkenylsuccinic derivatives, in which the alkenyl chain constitutes the oleophilic portion of the molecule which confers solubility in the oil. The alkenyl chain may be a polyisobutylene group, such as those described in U.S. Pat. No. 3,172,892; U.S. Pat. No. 3,2145,707; U.S. Pat. No. 3,219,666; U.S. Pat. No. 3,316,177; U.S. Pat. No. 3,341,542; U.S. Pat. No. 3,454,607; U.S. Pat. No. 3,541,012; U.S. Pat. No. 3,630,904; U.S. Pat. No. 3,632,511; U.S. Pat. No. 3,787,374 and U.S. Pat. No. 4,234,435.

[0057] Other types of suitable dispersants are described in U.S. Pat. No. 3,036,003; U.S. Pat. No. 3,200,107; U.S. Pat. No. 3,254,025; U.S. Pat. No. 3,275,554; U.S. Pat. No. 3,438,757; U.S. Pat. No. 3,454,555; U.S. Pat. No. 3,565,804; U.S. Pat. No. 3,413,347; U.S. Pat. No. 3,697,574; U.S. Pat. No. 3,725,277; U.S. Pat. No. 3,725,480; U.S. Pat. No. 3,726,882; U.S. Pat. No. 4,454,059; U.S. Pat. No. 3,329,658; U.S. Pat. No. 3,449,250; U.S. Pat. No. 3,519,565; U.S. Pat. No. 3,666,730; U.S. Pat. No. 3,687,849; U.S. Pat. No. 3,702,300; U.S. Pat. No. 4,100,082; U.S. Pat. No. 5,705,458; and EP-A-471071.

[0058] Other suitable dispersants include hydrocarbyl-substituted succinic acid compounds, such as succinimides, succinate esters, or succinate ester amides prepared by the reaction of hydrocarbon-substituted succinic acid preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine, are particularly useful.

[0059] Friction modifiers i.e. a material or compound that can alter the coefficient of friction of the fluid may be effectively used in combination with the base oil components. Suitable friction modifiers may include metal salts or metal-ligand complexes where the metals may include alkali, alkaline earth, or transition group metals, as those described in WO2004/053030.

[0060] Other useful additives include pour point depressants to lower the minimum temperature at which the lubricating composition will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers, such as those referred to in WO2004/053030.

[0061] Suitable seal compatibility agents include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride.

[0062] Such additives may be used in an amount of about 0.01 to 3% by weight.

[0063] Anti-foaming agents may advantageously be added to the lubricating compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents, such as for example polysiloxanes. Anti-foam agents are commercially available, such as, for example, DCF 200/12500, DCF 200/500, DCF 200/30000, DCF 200/1000 from Dow Corning, and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1% by weight.

[0064] Suitable corrosion inhibitors are those referred to in Klamann, as cited above. Examples of suitable corrosion inhibitors include thiadiazoles, benzotriazoles, tolutriazoles, zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids, carboxylic acids and amines. Such additives may be used in an amount of from about 0.01 to 5% by weight, preferably from about 0.01 to 1.5% by weight, more preferably from about 0.01 to 1% by weight. Examples of suitable corrosion inhibitors can be found in, for example, U.S. Pat. No. 2,719,125; U.S. Pat. No. 2,719,126; and U.S. Pat. No. 3,087,932. Examples of suitable corrosion inhibitors are those commercially available under the tradenames Irgamet 39, Irgamet TTA and Irgamet 42 from Ciba, and those commercially available under the tradenames Vanlube 887 and Vanlube 887E from Vanderbilt. A further example of suitable corrosion inhibitors are dicarboxylic acids such as those commercially available from Cognis under the tradenames Emerox 1144 and Emerox 1110.

[0065] Additional types of additives may be further incorporated into the lubricating compositions of this invention may include one or more additives such as, for example, demulsifiers, solubilizers, fluidity agents, colouring agents, chromophoric agents, and the like. Each additive may include individual additives or mixtures thereof.

[0066] The present invention will now be described by reference to the following Examples:

Examples 1-18 and Comparative Example A

[0067] The turbine engine oils of Examples 1-18 and Comparative Example A were prepared by blending together the base oil and additives shown in Tables 1 to 3 below.

[0068] The amounts in Tables 1 to 3 are in wt. %, based on the total weight of the fully formulated formulations.

[0069] The base oil as used in the formulations of Tables 1 to 3 was a 5 cSt pentaerythritol ester further containing tricresyl phosphate antiwear additive, tolutriazole corrosion

inhibitor, dicarboxylic acid corrosion inhibitor, dioctyldiphenyl amine (DODPA) and diaryldiphenylamine as diphenylamine (DPA)-type anti-oxidant components, p-tert-octylphenyl-alpha-naphthylamine as phenyl-alpha-naphthalene (PANA)-type anti-oxidant component, and a polysiloxane anti-foam agent. The pentaerythritol ester had a viscosity of 5 mm²/s at 100° C. and a maximum viscosity of 13,000 mm²/s at -40° C. In addition, the pentaerythritol ester has a maximum pour point of -54° C. and a minimum flash point of 246° C.

TABLE 1

	Comparative						
	Ex. A	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Base Oil + Additive Package	100	99.8	99.5	99.0	99.8	99.5	99.0
MOAc ¹	0	0.2	0.5	1.0	0	0	0
HDPimid ²	0	0	0	0	0.2	0.5	1.0

¹Methyltriocetylammmonium Trifluoroacetate

²Trihexyl(tetradecyl)phosphonium Bis(trifluoromethylsulfonyl)imide

TABLE 2

	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Base Oil + Additive Package	99.8	99.5	99.0	99.8	99.5	99.0
HMI BF4 ³	0.2	0.5	1.0	0	0	0
HMI PF6 ⁴	0	0	0	0.2	0.5	1.0

³Hexylmethylimidazolium tetrafluoroborate

⁴Hexylmethylimidazolium hexafluorophosphate

TABLE 3

	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18
Base Oil + Additive Package	99.8	99.5	99.0	99.8	99.5	99.0
EMIM DEP ⁵	0.2	0.5	1.0	0	0	0
EMIM DSU ⁶	0	0	0	0.2	0.5	1.0

⁵1-Ethyl-3-methylimidazolium diethylphosphate

⁶1-Ethyl-3-methylimidazolium methyl sulphate

Measurement of Physical Properties

[0070] Various physical properties of the lubricating compositions of Examples 1 to 18 and Comparative Example A were determined by subjecting the lubricating compositions to various standard test methods (as indicated in Table 4). The measured properties are shown in Table 4.

TABLE 4

Example	Kinematic Viscosity at 40° C. (mm ² /s) (as measured by Test Method ASTM D445)	Kinematic Viscosity at 100° C. (mm ² /s) (as measured by Test Method ASTM D445)	Pour Point ° C. (as measured by Test Method ASTM D5950)	Flash Point ° C. (as measured by Test Method ASTM D92)	TAN (mm ² /s) (as measured by Test Method ARP5088)
A	25.47	5.02	-57	>246	0.3
1 (0.2% MOAac)	25.62	4.99	-57	>246	0.23
2 (0.5% MOAac)	25.71	5.02	-57	>246	0.25
3 (1% MOAac)	26.08	5.05	-57	>246	0.26
4 (0.2% HDPimid)	25.54	5.01	-57	>246	0.23
5 (0.5% HDPimid)	25.61	5.01	-57	>246	0.24
6 (1% HDPimid)	25.89	5.05	-57	>246	0.25
7 (0.2% HMI BF4)	25.44	4.99	-57	268	0.22
8 (0.5% HMI BF4)	25.45	4.99	-57	274	0.22
9 (1% HMI BF4)	25.46	4.99	-57	256	0.20
10 (0.2% HMI PF6)	25.5	5.00	-57	269	0.21
11 (0.5% HMI PF6)	25.47	5.00	-57	273	0.23
12 (1% HMI PF6)	25.5	5.00	-57	264	0.23
13 (0.2% EMIM DEP)	25.62	5.005	-57	266	0.06
14 (0.5% EMIM DEP)	25.68	5.000	-57	262	0.04
15 (1% EMIM DEP)	25.69	5.013	-57	267	0.04
16 (0.2% EMIM MSU)	25.56	5.011	-57	263	0.19
17 (0.5% EMIM MSU)	25.62	5.010	-57	265	0.18
18 (1% EMIM MSU)	25.7	5.010	-57	263	0.17

Measurement of Viscosity Increase, TAN Increase and Evaporation Loss

[0071] To demonstrate the various benefits of the turbine engine oils of the present invention, Examples 1, 4 and 16 (containing 0.2% MOAac, 0.2% HDPimid and 0.2% EMIM MSU respectively) and Comparative Example A were subjected to the test methods as set out in FED-STD-791-5308.7 in order to measure viscosity increase, TAN increase and evaporation loss during the test. The test was run at 218° C. for 72 hours. The results are shown in Table 5 below.

TABLE 5

Example	Viscosity Change %	TAN Change mg KOH/l	Evaporation Loss %	Sludge Content mg
A [#]	60.44	9.71	4.56	1.0
1 (0.2% MOAac) ^{##}	39.10	5.61	3.72	0.1
4 (0.2% HDPimid) ^{##}	46.85	6.62	3.72	<0.1
16 (0.2% EMIM MSU)	48.87	7.53	3.91	0.4

[#]results are the average of 8 measurements

^{##}results are the average of 2 measurements

Measurement of Coking Behaviour

[0072] To measure the coking behaviour of the lubricating compositions according to the present invention, Examples 1 and 4 (containing 0.2 wt % MOAac and 0.2 wt % HDPimid, respectively) and Comparative Example A were subjected to the HPLS standard test method SAE ARP 5996. The amount of coke formed on the stainless steel tubes after 20 hours was weighed and the visual appearance of the tubes was noted. The results are shown in Table 6.

TABLE 6

Example	Coke formed/mg	Visual appearance of tube
Comparative Example A	0.27	Significant levels of coke in centre of tube
Example 1 (0.2% MOAac)	0.24	Reduced levels of coke along the length of the tube compared to Comparative Example A
Example 4 (0.2% HDPimid)	0.19	Significantly reduced levels of coke in centre of tube compared to Comparative Example A

Measurement of Load Carrying Capability

[0073] To measure the load carrying capability & anti-wear properties of the lubricating compositions according to the present invention, Examples 7-12 and Comparative Example A were subjected to the four-ball test (IP 239) and the maximum weld load of each sample measured (10 second duration at each load stage). The results are shown in Table 7 below.

TABLE 7

Example	Wear Scar (60 min, ambient, 1500 rpm, IP 239) (mm)	Weld Load (10 secs at each load stage) (kg)
A	0.41	140
7 (0.2% HMI BF4)	0.32	160
8 (0.5% HMI BF4)	0.31	170
9 (1% HMI BF4)	0.33	210
10 (0.2% HMI PF6)	0.36	200
11 (0.5% HMI PF6)	0.32	230
12 (1% HMI PF6)	0.33	270

Discussion

[0074] The results shown in Table 4 demonstrate that the introduction of low levels of ionic liquids into a turbine engine oil do not detrimentally effect the physical properties of the turbine engine oil (as required by military and civilian specifications, namely MIL-PRF-23699 and SAE-AS-5780, respectively).

[0075] As can be seen from Table 5, the lubricating compositions of Example 1 (containing 0.2% of MOAac), Example 4 (containing 0.2% HDPimid) and Example 16 (containing 0.2% EMIM MSU) exhibit a reduction in the build-up of sludge compared to Comparative Example A (containing no ionic liquid).

[0076] As can be seen from Table 6, the lubricating compositions of Example 1 (containing 0.2% MOAac) and Example 4 (containing 0.2% HDPimid) exhibit a reduction in coking compared to Comparative Example A (containing no ionic liquid). Example 4 (containing 0.2% HDPimid) exhibits a bigger reduction in coking than Example 1 (containing 0.2% MOAac).

[0077] As can be seen from Table 7, the lubricating compositions of Examples 7-12 exhibit an increase in weld load and comparable wear scar diameter compared to Comparative Example A.

1. A lubricating composition comprising:

- (i) from 50% to 99% by weight of base oil;
- (ii) from 0.01% to 5% by weight of ionic liquid; and
- (iii) from 0.01% to 10% by weight of additive;

wherein the lubricating composition has a pour point of less than -54°C ., a flashpoint of greater than 246°C . and a kinematic viscosity at 100°C . in the range of from 4.9 to $5.4\text{ mm}^2/\text{s}$.

2. A lubricating composition according to claim 1 comprising from 0.01% to 1% by weight of ionic liquid.

3. The lubricating composition according to claim 1 comprising from 0.05% to 0.5% by weight ionic liquid.

4. A lubricating composition wherein the ionic liquid is a salt of general formula C^+A^- wherein the cation C^+ is selected from a quaternary ammonium cation, a phosphonium cation, an imidazolium cation, a pyridinium cation, a pyrazolium cation, an oxazolium cation, a pyrrolidinium cation, a piperidinium cation, a trialkylsulfonium cation, a thiazolium cation, a guanidinium cation, a morpholinium cation, a sulfonium cation and a triazolium cation and wherein the anion A^- is selected from $[\text{PF}_6]^-$, $[\text{CF}_3\text{CO}_2]^-$, $[\text{CF}_3\text{SO}_3]^-$, as well as its higher homologues, $[\text{C}_4\text{F}_9\text{SO}_3]^-$ or $[\text{C}_8\text{F}_{17}\text{SO}_3]^-$ and

higher perfluoroalkylsulfonates, $[(\text{CF}_3\text{SO}_2)_2\text{N}]$, $[(\text{CF}_3\text{SO}_2)(\text{CF}_3\text{COO})\text{N}]^-$, Cl^- , Br^- , I^- , $[\text{C}(\text{CN})_3]^-$, SCN^- , $[\text{B}(\text{C}_2\text{O}_4)_2]^-$, $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$, $[\text{R}^4\text{SO}_3]^-$, $[\text{R}^4\text{OSO}_3]^-$, $[\text{R}^4\text{COO}]^-$, $[\text{NO}_3]^-$, $[\text{N}(\text{CN})_2]^-$, $[\text{HSO}_4]^-$, $\text{PF}_{6-x}\text{R}_x^6$ or $[\text{R}^4\text{R}^5\text{PO}_4]^-$, wherein R^4 and R^5 are independently selected from hydrogen, linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms; heteroaryl, heteroaryl- C_1 - C_6 -alkyl groups with 3 to 8 carbon atoms in the hetero aryl residue and at least one heteroatom selected from N, O and S, which can be substituted with at least one group selected from C_1 - C_6 alkyl groups and/or halogen atoms; aryl-aryl- C_1 - C_6 -alkyl groups with 5 to 12 carbon atoms in the aryl residue, which can be substituted with at least one C_1 - C_6 -alkyl group, R^6 can be a perfluoroethyl or a higher perfluoroalkyl group, and x is an integer of from 1 to 4.

5. The lubricating composition according to claim 4 wherein the ionic liquid is selected from butyl methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide, methylpropylpyrrolidinium-bis(trifluoromethylsulfonyl)imide, tris-hexylmethylimidazolium (perfluoroethylene)-trifluorophosphate, hexylmethylimidazolium-bis(trifluoromethylsulfonyl)imide, hexylmethylpyrrolidinium-bis(trifluoromethylsulfonyl)imide, tris-tetrabutylphosphonium(perfluoroethylene)trifluorophosphate, octylmethylimidazolium-hexafluorophosphate, hexylpyridinium-bis(trifluoromethylsulfonyl)imide, methyltrioctylammonium-trifluoroacetate, butylmethylpyrrolidinium tris (pentafluoroethyl)trifluorophosphate, trihexyl (tetradecyl)phosphonium-bis(trifluoromethylsulfonyl)imide, hexylmethylimidazolium tetrafluoroborate, hexylmethylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium diethylphosphate, 1-ethyl-3-methylimidazolium methyl sulphate, 1-ethyl-3-methylimidazolium bis[oxalate(2-)-O,O+]borate and mixtures thereof.

6. The lubricating composition according to claim 4 wherein the ionic liquid is selected from methyltrioctylammonium-trifluoroacetate and trihexyl (tetradecyl)phosphonium-bis(trifluoromethylsulfonyl)imide, hexylmethylimidazolium tetrafluoroborate, hexylmethylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium diethylphosphate, 1-ethyl-3-methylimidazolium methyl sulphate and mixtures thereof.

7. The lubricating composition according to claim 4 wherein the ionic liquid is selected from trihexyl (tetradecyl)phosphonium-bis(trifluoromethylsulfonyl)imide, hexylmethylimidazolium hexafluorophosphate, and mixtures thereof.

8. The lubricating composition according to claim 4 wherein the base oil is a synthetic ester formed by the reaction of a polyol with a carboxylic acid of formula RCOOH wherein R is a straight or branched chain hydrocarbyl group having from 5 to 10 carbon atoms.

9. The use of a lubricating composition according to claim 4 for lubricating a turbine engine.

10. The use of an ionic liquid according to claim 4 to reduce the sludge content of a lubricating composition comprising (i) a base oil, (ii) an ionic liquid and (iii) one or more additives.

11. The use of an ionic liquid to according to claim 4 reduce the coking of a lubricating composition comprising (i) a base oil, (ii) an ionic liquid and (iii) one or more additives.

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