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2-STROKE LUBRICANT

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This invention relates to improved lubricant compositions and fuels suitable for use in 2-stroke internal combustion engines.

It is common practice to supply a two-stroke engine with a mixture of fuel and lubricating oil composition, such a mixture often being called a "petroil" mixture. Admixture of the fuel and lubricating oil composition is usually effected immediately before supply to the tank of the engine and in proportions depending upon the particular requirements of the engine. In general, a "petroil" mixture comprises at least 10 parts by volume of gasoline per volume of base lubricating oil and as examples there may be mentioned "petroil" mixtures having 16, 24, 50 or even greater volumes of fuel per volume of base lubricating oil. Although this practice simplifies the design of the engine, such engines are prone to greater fouling of the combustion chamber compared with engines having separate supplies of fuel and lubricant. These disadvantages are commonly alleviated by increasing the amount of scavenger available to the engine over that normally present in the gasoline and also by incorporating in the oil a metallic additive of high basicity. An increase in the amount of scavenger available to the engine is most economically effected by incorporating a scavenger in the lubricant, thereby avoiding manufacture, supply and distribution problems associated with the provision of a separate grade of gasoline of enhanced scavenger content, although from the point of view of engine operation, incorporation of increased amounts of scavenger in the fuel would be equally effective. A recent proposal has been to decrease engine fouling still further by replacing at least part of the metallic base additive by an ashless, nitrogenous, oil soluble organic base, a course which presents additional advantages, e.g. improved piston skirt cleanliness and anti-rust performance. However, it has now been found that the alkyl halide scavenger reacts in the oil with the organic base additive to deplete said base and furthermore, such reaction may result in the formation of products which are harmful to the engine at operating temperatures.

I have now discovered that this difficulty can be overcome by the use in the oil, in conjunction with the aforesaid organic base, of an organic halide wherein each halogen atom is attached directly to an unsaturated carbon atom, in place of an alkyl halide.

Accordingly, in one of its aspects, the present invention provides a lubricant composition suitable for use in "petroil" systems, comprising a base lubricating oil, an ashless, nitrogenous, oil soluble organic base and an organic halide wherein each halogen atom is attached directly to an unsaturated carbon atom. In another of its aspects the present invention provides a "petroil" mixture comprising an ashless, nitrogenous, oil soluble organic base, a lead tetra-alkyl, an alkyl halide and an organic halide wherein each halogen atom is attached directly to an unsaturated carbon atom. In a further aspect the present invention provides a method of operating a 2-stroke

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internal combustion engine by having an ashless, nitrogenous, oil soluble organic base and an organic halide wherein each halogen atom is attached directly to an unsaturated carbon atom present in the "petroil" mixture.

In this specification, the term "lubricating oil" is intended to mean any hydrocarbon oil known to be suitable for lubricating metal surfaces and especially internal combustion engines, e.g. such as are obtained by the refining of petroleum, and having a viscosity in the range specified in the S.A.E. Crankcase Oil Classification, i.e. oils which have a viscosity in the range 4 centistokes to 25 centistokes at 210° F., which oils may also contain any of the fortifying agents at present known to the art, for example, viscosity index improvers (e.g. polymeric acrylic esters), pour point depressants (e.g. methacrylate polymers), oxidation inhibitors (e.g. bis(2,6-di-t-butyl-4-hydroxy phenyl)methane), metal deactivators (e.g. di-salicylal ethylene diimine), rust inhibitors (e.g. the condensation product of maleic anhydride and long chain alkenes), anti-foaming agents (e.g. silicone polymers), EP additives, provided that such EP additives do not contain halogens (e.g. triphenyl phosphate), and anti-seizure agents (e.g. acidless tallow or a non-drying fatty oil e.g. castor oil). The term "gasoline" is intended to mean a hydrocarbon oil, or a mixture of a hydrocarbon oil with an alcohol, distilling substantially continuously at atmospheric pressure throughout the temperature range 10° C. to 250° C. and containing a lead tetra-alkyl, for example tetra-ethyl lead, tetra-methyl lead, ethyl trimethyl lead, diethyl dimethyl lead, triethyl methyl lead or mixtures thereof. The hydrocarbon oil will normally be derived from petroleum but may be derived from other sources, e.g. from coal or from synthetic processes. The gasoline may contain other anti-knock agents, for example methyl cyclopentadienyl manganese tricarbonyl, and any of the additives or fortifying agents known to the art, e.g. vapour pressure modifiers such as butanes, co-anti knock agents, e.g. tertiary butyl acetate, scavengers, e.g. alkyl halides, deposit modifiers e.g. tritoyl phosphate, anti-icing additives e.g. isopropyl alcohol, anti-foaming agents e.g. silicones, anti-oxidants e.g. 2,4-methyl-6-tertiary butyl phenol or di sec. butyl para phenylene diamine and dyestuffs or colouring agents.

Preferred lubricating oils are those having viscosities in the range 8 to 20 centistokes at 210° F., while particularly preferred are lubricating oils having viscosities in the range 8 to 17 centistokes at 210° F. Preferred gasolines for admixture with the lubricant composition of the present invention are gasolines which distil in the temperature range 25 to 205° C. while particularly preferred gasolines are those which distil in the temperature range 30 to 180° C.

While a wide range of ashless nitrogenous oil soluble materials may be used as the organic base in lubricant compositions according to the present invention, the present invention is of greatest interest in relation to ashless, nitrogenous oil soluble materials derived from alkylene polyamines, particularly the products of reacting branched chain carboxylic acids with polyalkylene polyamines and more particularly still the products of reacting branched chain carboxylic acids with tetra ethylene pentamine. Thus there can be used as the ashless nitrogenous oil soluble material the diamide of a polyalkylene polyamine and iso-oleic acid or dimerized or trimerized unsaturated fatty acids having from 16-22 carbon atoms such as dimerized

oleic and linoleic acids, or mixtures of said unsaturated acids and/or hydrogenated derivatives thereof such as isostearic acid and straight chain C₁₂₋₂₀ saturated fatty acids such as lauric, myristic, palmitic and/or stearic acids. When mixtures are used, the straight chain fatty acids comprise 5-30 mole percent and the balance (70-95 mole percent) being the branch-chain acids. The polyamines used to form the diamides can be alkylene polyamines such as ethylene diamine, diethylene triamine, triethylene tetramine, 1-methyl ethylene diamine, 1-ethyl ethylene diamine, propylene diamine, butylene diamine, trimethyl trimethylene diamine, tetramethylene diamine, diaminopentane or pentamethylene diamine, diamino-hexane, hexamethylene diamine, heptamethylene diamine, diamino-octane, decamethylene diamine, and the higher homologues up to 18 carbon atoms, phenylene diamine, the alkylated phenylene diamines having nuclear substituents such as methyl, ethyl, propyl, butyl, etc., naphthalene diamine, and the alkylated naphthalene diamines; N,N'-dimethyl ethylene diamine, N,N'-(diethylethylene)-diamine, N,N'-(dipropyl)-ethylene diamine, N,N'-(2-hydroxypropyl)-ethylene diamine, N,N'-(diethylpropylene)-diamine, N,N'-(dipropyl)-propylene diamine, N,N'-(dimethyl)butylene diamine, N,N'-(diethyl)-butylene diamine; penta-(1-methylpropylene)hexamine; tetrabutylene-pentamine; hexa-(1,1-dimethylethylene)heptamine; di-(1-methyl-butylene)triamine; pentaamylenehexamine; tri(1,2-trimethylethylene)-tetramine; di-(1-methylamylene)triamine; tetra-(1,3-dimethylpropylene)-pentamine; penta-(1,5-dimethylamylene)hexamine; di-(1-methyl-4-ethylbutylene)triamine; penta-(1,2-dimethyl-1-isopropylethylene)-hexamine; tetraoctylene-pentamine and the like but preferred polyamines are ethylene diamine, propylene diamine, diethylene triamine, triethylene tetraamine, trimethylene diamine, hexamethylene diamine, and the like. The diamides are formed by reacting approximately equimolecular quantities of a polyamine and saturated and/or unsaturated fatty acids, e.g. iso-oleic acid or dimerized oleic acid or isostearic acid or mixture of stearic and isostearic acids at between 120° C. and 250° C. for a period of 10 or more hours, preferably under atmospheric pressure. For example, 1 mole of alkyl substituted diethylene triamine H₂N-CH₂CH₂-N(C₄H₉)CH₂CH₂NH₂ and two moles of iso-oleic acid were mixed and heated at 175-200° C. for about 10-15 hours in an enclosed vessel under atmospheric conditions until the diamide was formed, after which the reaction was cooled and the end product has the following formula: (Ia)



where R is oleyl radical. Other diamides include (Ib) diisooleylamide of ethylene diamine, (Ic) dimerized oleic amide of diethylene triamine, (Id) dimerized linoleyl amide of diethylene triamine, (Ie) mixed di- and trimerized oleyl amide of diethylene triamine, (If) diisooleylamide of diethylene triamine, (Ig) diisooleylamide of N-2-aminoethyl piperazine, (Ih) diamide of tetraethylene pentamide and isostearic acid, (Ij) diamide of tetraethylene pentamine and a mixture of 10 mole percent stearic acid and 90 mole percent isostearic acid, and mixtures thereof. Materials sold under the Registered Trade Mark "OLOA 340D" are suitable.

Amounts of ashless, nitrogenous oil soluble organic base up to 20% by weight, based on the lubricant composition, are useful for the purpose of the present invention but amounts in the range of 2-10% wt., especially 2-5% wt., are preferred. If desired, replacement of metallic base additive by the aforesaid organic base need not be complete and a proportion of the metallic base additive may remain, in which case the amount of organic base may be correspondingly reduced but not necessarily in proportion.

A wide range of organic halides may be used in lubricant compositions according to the present invention provided that in the halide chosen each halogen atom is

attached directly to an unsaturated carbon atom and the halide is oil soluble. As examples of useful oil soluble organic halides wherein each halogen atom is attached directly to an unsaturated carbon atom there are mentioned haloalkenes wherein the alkene is a lower alkene such as haloethylenes (i.e. haloethenes), e.g. iodoethylene, 1,1-dichloroethylene, 1,2-dichloroethylene, 1,2-dibromoethylene, trichloroethylene, tetrachloroethylene, halogen derivatives of butadiene, e.g. 1-chloro-1,3-butadiene, 2-chloro-1,3-butadiene, 1,1,2,3,4,4-hexachlorobutadiene, aryl halides, e.g. chlorobenzene, bromobenzene, dichlorobenzene, dibromobenzene, diiodobenzene, trichlorobenzene, tribromobenzene, tetrachloro benzene, tetrafluoro benzene, hexafluoro benzene, halogen derivatives of unsaturated heterocyclic compounds, e.g. 2-chloro pyridine, 3-chloro pyridine, 4-chloro pyridine, 3-bromo pyridine, 3-chloro pyrrole, 2-chloro thiophene and certain substituted haloacetylenes, e.g. 1-chloro hexyne-1, although halogen derivatives of the acetylenes are in general unlikely to be suitable. Preferred halides are those which contain the greatest amount of halogen per unit weight of halide, consistent with adequate oil solubility.

The amount of oil soluble organic halide wherein each halogen atom is attached directly to an unsaturated carbon atom used in lubricant compositions according to the present invention will not in general exceed 15% by weight, based on the lubricant composition and will more usually lie in the range 0.25 to 10% wt., depending, for example, upon the nature of the gasoline with which it is intended to mix the lubricant composition and the type of said halide employed.

Examples of the benefits to be obtained from the present invention will now be described with reference to the accompanying examples.

A lubricant composition in accordance with the present invention, designated as Example I in Table I below, was maintained in a closed container at a temperature of 60° C. for 14 days, the total base number of the formulation being determined before and after the storage period. A similar test was carried out, for comparative purposes, on lubricant formulations, designated as Examples II and III in Table I below, not in accordance with the present invention. The results obtained are set out in Table I below.

TABLE I

Ex. No.	Oil	Scavenger	Organic base	Total base number	
				Before test	After test
I....	SAE 30	1.05% wt. tribromo benzene.	3% wt. OLOA 340D.	1.95	1.45
II....	SAE 30	1% wt. ethylene dibromide.*	3% wt. OLOA 340D.	1.90	0.25
III....	SAE 30	1% wt. ethylene dibromide.	6% wt. Lubrizol 224.	2.15	0.35

*I.e., 1,2-dibromoethane.

The data of Table I show that whereas the composition of Example I changed relatively little in basicity over the test period, each of the comparative formulations suffered a severe decrease in basicity over the same period, thereby indicating substantial depletion in storage of the organic basic additive.

A lubricant formulation in accordance with the present invention and consisting of an SAE 30 lubricating oil, 3% weight of OLOA 340D and 1.06% weight of tribromobenzene was divided into 3 portions and tested as follows:

Portion I (Example IV) was mixed with gasoline at 20/1 gasoline/lubricant ratio and the resulting "petroil" mixture used to operate a Fichtel and Sachs 2-stroke engine for a period of 60 hours, after which the piston of the engine was assessed visually for cleanliness.

Portion II (Example V) was aged in a closed container at a temperature of 100° C. for a period of 2 weeks and similarly mixed with gasoline and used to operate a Fichtel and Sachs engine. Portion III (Example VI) was similarly aged for a period of 6 weeks and again similarly mixed with gasoline and used to operate a Fichtel and Sachs engine.

TABLE II

Lubricant Formulation	Piston Cleanliness (10=clean)
Example IV.....	7.4
Example V.....	7.5
Example VI.....	7.7

The results obtained are summarised at Table II from which it can be seen that all 3 portions gave high values for piston cleanliness and moreover maintained such high values even after six weeks of severe ageing.

By way of contrast a lubricant formulation not in accordance with the present invention and consisting of an identical SAE 30 lubricating oil, 3% weight of OLOA 340D and 1% weight of ethylene dibromide was divided into 2 portions and tested as follows:

Portion I (Example VII) was mixed with gasoline and tested as has been described for Example IV above while Portion II (Example VIII) was aged for a period of four days at a temperature of 100° C. and again mixed with gasoline and tested as is described for Example IV above. As before piston cleanliness was assessed at the end of the engine test and the results obtained are summarised at Table III.

TABLE III

Lubricant Formulation	Piston Cleanliness (10 = clean)
Example VII.....	8.0
Example VIII.....	6.7

The results given at Table III show that whereas the formulation of Example VII gives a high value for piston cleanliness, ageing for as little as four days at 100° C. causes a substantial decrease in the degree of piston cleanliness.

In a further series of storage tests, samples of the compositions set forth in Table IV were stored in closed containers for periods up to eight weeks at either or both of two temperatures, viz 60° C. and 100° C., the total base numbers of portions of the samples being determined before and at convenient intervals during the storage period. Similar tests were carried out for comparative purposes on lubricant formulations (designated as Examples XVI-XVIII in Table IV) not in accordance with the present invention. The results of the storage tests are set forth in Table V, from which it can again be seen that whereas the formulation of Examples IX-XV changed relatively little in basicity during storage, either at 60° C. or at 100° C., each of the comparative formulations suffered a severe decrease in basicity over the same

periods, thereby indicating substantial depletion in storage of the organic base additive.

TABLE IV

Ex. No.	Oil	Seavenger	Organic base
IX.....	SAE 30	0.94% wt. 1,2-dibromo-ethylene.*	3% wt. OLOA-340D
X.....	SAE 30	1.06% wt. tribromobenzene.	3% wt. OLOA-340D
XI.....	SAE 30	0.61% wt. trichlorobenzene.	3% wt. OLOA-340D
XII.....	SAE 30	0.55% wt. tetrachlorobenzene.	3% wt. OLOA-340D
XIII.....	SAE 30	0.38% wt. tetrafluorobenzene.	3% wt. OLOA-340D
XIV.....	SAE 30	0.31% wt. hexafluorobenzene.	3% wt. OLOA-340D
XV.....	SAE 30	1.63% wt. di-iodobenzene.	3% wt. OLOA-340D
XVI.....	SAE 30	0.95% wt. ethylene dibromide.†	3% wt. OLOA-340D
XVII.....	SAE 30	0.87% wt. tetra bromoethane.	3% wt. OLOA-340D
XVIII.....	SAE 30	0.5% wt. ethylene dichloride.	3% wt. OLOA-340D

*I.e., 1,2-dibromoethene. †I.e., 1,2-dibromoethane.

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TABLE V

Example No.	Total Base Number					
	Storage time (weeks) at 60° C.			Storage time (weeks) at 100° C.		
	0	4	8	0	4	8
IX.....				1.95	1.10	0.85
X.....	1.95	1.85	1.60	1.95	1.65	1.2
XI.....	1.95	1.30	1.20			
XII.....	1.95	1.35	1.70			
XIII.....	1.95	1.55	1.55	1.95	1.10	
XIV.....	1.95	1.45	1.45			
XV.....				1.95	1.65	1.00
XVI.....	1.95	0.45	0.20	1.95	0.25	0.25
XVII.....				1.95		0.25
XVIII.....				1.95	0.63	0.5

Further examples of lubricant compositions in accordance with the present invention were aged in closed containers at a temperature of 100° C. for periods of up to 6 months and thereafter mixed with gasoline at 20/1 gasoline/lubricant ratio, the resulting "petroil" mixture then being used to operate a Fichtel and Sachs 2-stroke engine for a period of 60 hours, after which the piston of the engine was assessed visually for cleanliness. The results obtained are set out in Table VI and are therein compared with the results obtained for a correspondingly tested lubricant composition not in accordance with the present invention and identified as Example No. XXI.

TABLE VI

Example No.	XIX	XX	XXI
Composition.....	1.06% wt. tribromo benzene. 4% wt. OLOA 340D. SAE 30 oil to 100% wt.	0.94% wt. 1,2-dibromo ethylene. 3% wt. OLOA 340D. SAE 30 oil to 100% wt.	0.95% wt. ethylene dibromide. 4% wt. OLOA 340D. SAE 30 oil to 100% wt.
Piston cleanliness after storage of lubricant composition at 100° C.			
Storage time in weeks:			
0.....	7.2	8.0	9.3
2.....	7.5	7.5	1.9
6.....	7.2		
26.....	6.9		

From Table VI it is seen that the lubricant composition in accordance with the present invention (Examples XIX and XX) gave high values for piston cleanliness when the lubricant composition was in the unaged condition and moreover maintained high piston cleanliness after periods of severe ageing, whereas the comparative (non-inventive)

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formulation (Example XXI) suffered a drastic loss in piston cleanliness after two weeks ageing.

Similar engine and ageing tests were carried out on yet another lubricant composition in accordance with the present invention, in which part of the ashless nitrogenous oil soluble organic base was replaced by a proportion of a metallic base additive. The metallic base additive selected was a highly basic form of calcium alkyl salicylate, herein designated as "AC45C" and as before a comparative test was made using a lubricant composition not in accordance with the present invention and containing "AC45C." The results obtained are set out in Table VII from which it is again seen that whereas the lubricant composition in accordance with the present invention maintained a high level of piston cleanliness even after severe ageing, the comparative (non-inventive) lubricant composition (Example XXIII) gave a substantially lower piston cleanliness value after only a short period of ageing.

TABLE VII

Example No.	XXII	XXIII
Composition.....	1.06% wt. tribromo benzene. 1% wt. OLOA 340D..... 1.75% wt. AC45C..... SAE 30 oil to 100% wt....	0.95% wt. ethylene dibromide. 1% wt. OLOA 340D. 1.75% wt. AC45C. SAE 30 oil to 100% wt.
Piston cleanliness after storage of lubricant composition at 100° C.		
Storage time in weeks:		
0.....	9.0	8.3
1.....		6.9
2.....	9.1	

What I claim is:

1. A lubricating composition for two-stroke engines comprising lubricating oil and from 2% to 20% of an oil-soluble diamide of a polyalkylene polyamine and a fatty acid having from 12-22 carbon atoms and from 0.25% to 15% of a haloalkene wherein the halogen atoms are attached directly to an unsaturated carbon atom and wherein the alkene is a lower alkene.

2. The composition of claim 1 wherein the diamide is derived from a fatty acid which is a branch-chained fatty acid having 12-22 carbon atoms.

3. The composition of claim 1 wherein the diamide is derived from a mixture of straight and branch-chain fatty acids having from 12-22 carbon atoms.

4. A lubricating composition for two-stroke engines comprising mineral lubricating oil and from 2% to 10% of an oil-soluble diamide of tetraethylene pentamine and an iso-fatty acid having from 12 to 22 carbon atoms and from 1% to 10% of a haloalkene wherein the halogen atoms are attached to unsaturated carbon atoms and wherein the alkene is a lower alkene.

5. The composition of claim 4 wherein the haloalkene is 1,2-dibromoethylene.

6. A lubricating composition for two-stroke engines comprising mineral lubricating oil and from 2% to 10% of the diamide of tetraethylene pentamine and isooleic acid and from 1% to 10% of 1,2-dibromoethylene.

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