

LOW ASH OR ASHLESS TWO-CYCLE LUBRICATING OIL
WITH REDUCED SMOKE GENERATION

5 **FIELD OF THE INVENTION**

 This invention relates to a lubricant composition useful as a two-cycle oil. More particularly the invention relates to two-cycle oil characterized in that it is either ashless or contains a relatively low amount of metal detergent, but provides an oil
10 which complies with certain smoke generation test standards and viscosity requirements for land equipment, gasoline fueled, two-cycle engines, such as motorcycle engines, moped engines, snowmobile engines, lawn mower engines and the like.

15 **BACKGROUND OF THE INVENTION**

 Two-stroke-cycle gasoline engines now range from small, less than 50 cc engines, to higher performance engines exceeding 500 cc. The development of such high performance engines has created the need for new two-cycle oil standards and
20 test procedures.

 Traditional two-cycle engines are lubricated by mixing the fuel and lubricant and allowing the mixed composition to pass through the engine. Newer two-cycle engines may involve the use of direct fuel injection to reduce emissions. In either
25 case, the oil passes through the engine and is burned. Various types of two-cycle oils, compatible with fuel, have been described in the art. Typically, such oils contain a variety of additive components in order for the oil to pass industry standard tests to permit use in two-cycle engines.

30 A worldwide demand for fuel economy and environmental cleanliness has spurred manufacturers of two-cycle oils to meet increasingly severe standards for viscosity and smoke production. In many cases, these new standards are conventionally satisfied by employing ever-greater quantities of expensive starting

materials to manufacture new and improved two-cycle oils. Consequently, a need exists for alternative starting materials which meet the new standards for fuel economy and environmental cleanliness.

5 SUMMARY OF THE INVENTION

The present invention is based on the discovery that the use of highly reactive polyisobutylene polymer, solvent and lubricating oil basestock in certain proportions with appropriate amounts of two cycle lubricating oil additive packages can provide a
10 low ash or ashless two-cycle engine oil of suitable viscosity properties which exceeds the JASO (Japan Automobile Standards Organization) M342 Smoke Index test. Highly reactive polyisobutylene polymer, also known as HR-PIB, contains more terminal vinylidene double bonds and is manufactured by a different manufacturing process, as compared to conventional polyisobutylene, which is known as PIB. Two-
15 cycle oils containing HR-PIB are a useful and efficient alternative to conventional two-cycle oils.

In one aspect, the invention is a low ash two-cycle lubricating oil composition having a kinematic viscosity of at least 6.5 mm²/s (cSt) at 100°C and a JASO M342
20 Smoke Index of at least 85. The composition comprises:

- (a) 15 to 35 % by weight of an olefinically unsaturated polymer selected from the group consisting of polybutene, polyisobutylene or a mixture of polybutene and polyisobutylene, which has a number average molecular weight of 400 to 2200 and a terminal vinylidene content of at least 60 mol % based on the total number of double bonds in the polymer;
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- (b) 20 to 30 % by weight of a normally liquid hydrocarbon or mineral oil solvent, which has a viscosity of 1 to 5 cP. at 25°C;
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- (c) 1 to 5% by weight of an additive package for two cycle oils; and

- (d) a mineral or synthetic oil, or a mixture thereof, which has a viscosity of 4 to 15 mm²/s (cSt) at 100°C.

In another aspect, the invention is an ashless two-cycle lubricating oil composition having a kinematic viscosity of at least 6.5 mm²/s (cSt) at 100°C and a JASO M342 Smoke Index of at least 85. The composition comprises:

- (a) 6 to 12 % by weight of a reactive polybutene polymer being a polybutene, polyisobutylene or a mixture of polybutenes and polyisobutylenes having a number average molecular weight of 400 to 2200 and having at least 60 mol % double bonds as terminal vinylidene;
- (b) 18 to 30 % by weight of a normally liquid hydrocarbon or mineral oil solvent having a viscosity of 1 to 5 cP. at 25°C;
- (c) 14 to 25% by weight of a metal-free additive package for two cycle oils; and
- (d) the balance a mineral or synthetic oil, or a mixture thereof, having a viscosity of 4 to 15 mm²/s (cSt) at 100°C.

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

Highly reactive polybutene polymers (hereinafter referred to as "HR-PIB") useful in this invention include polybutylenes, polyisobutylenes, or mixtures thereof, of Mn 400 to 2200, preferably about 800 to 1500, such as about 1000, which have a terminal vinylidene content of at least 60 mol %, based on the total mols of double bonds. The terminal vinylidene content is preferably at least 70%, more preferably at least 80%, most preferably at least 85%. The following issued patents are incorporated by reference in their entirety and specifically for their teaching regarding manufacturing process for highly reactive polyisobutylene: U.S. Pat. Nos. 4,152,499; 5,962,604, 6,562,913, 6,683,138 and 6,710,140. HR-PIB is commercially available under the trade names Glissopal[R] (from BASF) and Ultravis[R] (from BP-Amoco), among other sources.

Solvents useful in the present invention are normally liquid natural or synthetic hydrocarbon or mineral oil solvents having a viscosity of 1 to 5, preferably 1.2 to 2 cP. at 25°C. The solvent should have a flash point in the range of about 60-120°C such that the flash point of the two-cycle oil of this invention is greater than 70°C. Typical examples include paraffinic, isoparaffinic and naphthenic aliphatic hydrocarbon or mineral oil solvents. The solvent may contain functional groups other than carbon and hydrogen provided such groups do not adversely affect performance of the two-cycle oil. Preferred are mineral oils sold as "Exxsol D80" by ExxonMobil Chemical Company and "Shellsol D70" sold by Shell Chemicals.

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The invention may additionally comprise as a third component 1-5% for low ash oils and 14-25% for ashless oils, each by weight, of an additive package which contains one or more conventional two-cycle lubricating oil additives, and these may be any additive normally included in such lubricating oils for a particular purpose. For the ashless package, there will be essentially no metallic additives.

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Conventional additives for the additive package component of this invention include corrosion inhibitors, oxidation inhibitors, friction modifiers, dispersants, antifoaming agents, antiwear agents, pour point depressants, metal detergents, rust inhibitors, lubricity agents, and the like. All percentages are by weight on an active ingredient basis.

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A preferred low ash additive package comprises (i) polyisobutenyl (Mn 400-2500, preferably about Mn 950) succinimide or another oil soluble, acylated, nitrogen containing lubricating oil dispersant present in the amount of 0.2-5 wt.%, preferably 1-3 wt.%. dispersant in the lubricating oil and (ii) a metal phenate, sulfonate or salicylate oil soluble detergent additive. This detergent is a neutral metal detergent or overbased metal detergent of Total Base Number 200 or less, present in the amount of 0.1-2 wt.%, preferably 0.2-1 wt.%. metal detergent additive in the lubricating oil. The metal is preferably calcium, barium or magnesium. Neutral calcium salicylates are preferred and may be present in amounts of about 0.5 to 1.5 wt.% in the lubricating oil.

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A preferred ashless additive package comprises an ashless lubricating oil dispersant in the oil, in the range of about 5.5 to 17 wt. %, preferably 9 to 15 wt.%, and one or more of the ashless dispersants as disclosed below may be used.

5 Dispersants useful in the present invention include nitrogen-containing, ashless dispersants known to be effective for reducing formation of deposits upon use in gasoline and diesel engines, when added to lubricating oils. These ashless dispersants have an oil soluble polymeric long chain backbone having functional groups capable of associating with particles to be dispersed. Typically, amine, amine-
10 alcohol or amide polar moieties are attached to the polymer backbone, often via a bridging group. The ashless dispersant may be, for example, selected from the group consisting of oil soluble salts, esters, amino-esters, amides, imides and oxazolines of long chain hydrocarbon-substituted mono- and polycarboxylic acids or anhydrides thereof; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic
15 hydrocarbons having polyamine moieties attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

Polyisobutylene polymers that may be employed for making dispersants are
20 generally based on a hydrocarbon chain of from about 400 to 3000 daltons. Methods for making polyisobutylene are publicly known. Polyisobutylene can be functionalized by halogenating (e.g. chlorinating), thermally reacting via the thermal "ene" reaction, or by free radical grafting using a catalyst (for example, peroxide), as described below.

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The functionalized, oil-soluble polymeric hydrocarbon backbones may also be derivatized with hydroxy compounds such as monohydric and polyhydric alcohols, or with aromatic compounds such as phenols and naphthols. Preferred polyhydric alcohols include alkylene glycols in which the alkylene radical contains from 2 to 8
30 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, and mixtures thereof. An ester dispersant may also be derived from unsaturated alcohols, such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-

cyclohexane-3-ol, and oleyl alcohol. Still other classes of alcohols capable of yielding ashless dispersants include ether-alcohols, including oxy-alkylene and oxy-arylene. These ether-alcohols may incorporate up to 150 oxy-alkylene radicals, in which the alkylene radical contains from 1 to 8 carbon atoms. The ester dispersants may be di-esters of succinic acids or acid-esters, such as partially esterified succinic acids, as well as partially esterified polyhydric alcohols or phenols, such as esters having free alcohols or phenolic hydroxy radicals. An ester dispersant may be prepared by any one of several known methods as described, for example, in U.S. Patent No. 3,381,022.

A preferred category of dispersants comprises the succinimides of the highly reactive polyisobutylenes of Mn 400-2200, as described above. These dispersants are typically prepared by reacting a polyisobutenyl succinic anhydride and an alkylene polyamine such as triethylenetetramine or tetraethylene pentamine.

Another class of high molecular weight ashless dispersants comprises Mannich base condensation products. Generally, these products are prepared by condensing about one mole of a long chain alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compound(s) (for example, formaldehyde and paraformaldehyde) and about 0.5 to 2 moles of polyalkylene polyamine, as disclosed, for example, in U.S. Patent No. 3,442,808. Such Mannich base condensation products may include a polymer product of a metallocene catalyzed polymerization as a substituent on the benzene group, or may be reacted with a compound containing such a polymer substituted on a succinic anhydride in a manner similar to that described in U.S. Patent No. 3,442,808.

Corrosion inhibitors may be present in the oil in amounts of 0.01-3 wt.%, preferably 0.01-1.5 wt.%, and are illustrated by phosphosulfurized hydrocarbons and the products obtained by reacting a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide.

Oxidation inhibitors may be present in the oil in amounts of 0.01-5 wt.%, preferably 0.01-1.5 wt.%. Suitable oxidation inhibitors include alkaline earth metal

salts of alkylphenol thioesters having preferably C₅-C₁₂ alkyl side chain such as calcium nonylphenol sulfide, barium t-octylphenol sulfide, and dioctylphenylamines. Also included are oil soluble sulfurized or phosphosulfurized hydrocarbons and antioxidant copper compounds, such as copper salts of C₁₀ to C₁₈ oil soluble fatty acids.

Friction modifiers may be present in the oil in amounts of 0.01-3 wt.%, preferably 0.01-1.5 wt.%, and include fatty acid esters and amides, glycerol esters of dimerized fatty acids and succinate esters or metal salts thereof.

Pour point depressants, also known as lube oil flow improvers, may be included in the oil in amounts of 0.01-2 wt.%, preferably 0.01-1.5 wt.%. Suitable pour point depressants are C₈-C₁₈ or C₁₄ dialkyl fumarate vinyl acetate copolymers, which are preferred, polymethacrylates and wax naphthalene.

Foam control can also be provided by an anti-foamant of the polysiloxane type such as silicone oil and polydimethyl siloxane; acrylate polymers are also suitable. These are used in the oil in amounts of 0.01-5 wt.%, preferably 0.01-1.5 wt.%.

Anti-wear agents reduce wear of metal parts and representative materials are zinc dialkyldithiophosphate, zinc diaryl diphosphate, and sulfurized isobutylene. These may be used in the oil in amounts of 0.01-5 wt.%.

Lubricity agents useful in this invention include a wide variety of oil soluble materials. Generally, they are used in the oil in an amount of 1-20 wt.%, preferably 1-7% by weight. Lubricity agents include polyol ethers and polyol esters, such as polyol esters of C₅-C₁₅ monocarboxylic acids, particularly pentaerythritol trimethylol propane and neopentyl glycol synlube esters of these acids, wherein the ester has a viscosity of at least 9 mm²/s (cSt) at 100°C, natural oils such as bright stock, which is preferred, and is the highly viscous mineral oil fraction derived from the distillation residues formed as a result of the preparation of lubricating oil fractions from petroleum.

Lubricating compositions of this invention normally include an oil of lubricating viscosity, that is, a viscosity of about 4-15, preferably 12-15 mm²/s (cSt) at 100°C, to provide a finished two-cycle oil having a KV in the range of 6.5-14 mm²/s (cSt) at 100°C.

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These oils of lubricating viscosity can be natural or synthetic oils. Mixtures of such oils are also often useful. Blends of oils may also be used so long as the final viscosity of the blend is 4-15 mm²/s (cSt) at 100°C.

10 Natural oils include mineral lubricating oils, which are preferred, such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

15 Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof.

Oils made by polymerizing olefins of less than 5 carbon atoms and mixtures
20 thereof are typical synthetic polymer oils. Methods of preparing these polymer oils are well known to those skilled in the art, as is shown for example by U.S. Patent Nos. 2,278,445; 2,301,052; 2,318,719; 2,329,714; 2,345,574; and 2,422,443.

Alkylene oxide polymers (such as, for example, homopolymers,
25 interpolymers, and derivatives thereof in which the terminal hydroxyl groups have been modified by esterification, etherification, etc.) constitute a preferred class of known synthetic lubricating oils for the purpose of this invention, especially for use in combination with alkanol fuels. They are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these
30 polyoxyalkylene polymers (e.g., methyl polypropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the

acetic acid esters mixed C₃-C₈ fatty acid esters, or the C₁₃ Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of
5 dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, octyl alcohol, dodecyl alcohol, tridecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene
10 glycol monoether, propylene glycol, etc.). Specific examples of these esters include dioctyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two
15 moles of 2-ethylhexanoic acid and the like. Preferred esters will have a viscosity of 5-12 mm²/s (cSt) at 100°C;

Esters useful as synthetic oils also include those made from C₅ to C₁₈ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol,
20 trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the lubricant compositions of the present invention. Unrefined oils are those
25 obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or an ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been
30 further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those of skill in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to

obtain refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

5 The lubricating oil compositions of the present invention will mix freely with the fuels used in such two-cycle engines. Admixtures of such lubricating oils with fuels comprise a further embodiment of this invention. The fuels useful in two-cycle engines are well known to those skilled in the art and usually contain a major portion of a normally liquid fuel such as a hydrocarbonaceous petroleum distillate fuel, e.g.,
10 motor gasoline as defined by ASTM specification D-439-73. Such fuels can also contain non-hydrocarbonaceous materials such as alcohols, ethers, organo nitro compounds and the like. For example, methanol, ethanol, diethyl ether, methylethyl ether, nitro methane and such fuels are within the scope of this invention as are liquid fuels derived from vegetable and mineral sources such as corn, alpha shale and coal.
15 Examples of such fuel mixtures are combinations of gasoline and ethanol, diesel fuel and ether, gasoline and nitro methane, etc. Gasoline is preferred. Gasoline means a mixture of hydrocarbons having an ASTM boiling point of 60°C at the 10% distillation point to about 205°C at the 90% distillation point. Lead-free gasoline is particularly preferred.

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The lubricants of this invention are used in admixture with fuels in amounts of about 20 to 250 parts by weight of fuel per 1 part by weight of lubricating oil, more typically about 30-100 parts by weight of fuel per 1 part by weight of oil.

25 The invention is further illustrated by the following examples which are presented to better communicate the invention and not to limit the scope of the invention in any way. Percentages are by weight.

Example

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An oil of the invention containing reactive HR-PIB, designated "Invention" in the Table below, and a conventional oil containing conventional polyisobutylene, designated "Conventional" in the Table below, were evaluated in accordance with

JASO M345 test procedures JASO M340, M341, M342 and M343. These are engine tests established by the Society of Automotive Engineers of Japan (JSAE) for two-cycle gasoline engine oils. As of July 1, 1994, oils used in two-cycle engines are being labeled in accordance with the JASO-M345 standards as announced by the Japan Automobile Standards Organization (JASO). JASO published the JASO M345 standards in April, 1994 and updated them in 2004. "EGD Detergency" is a reference to a further modification of the normal JASO M341 detergency test (1 hour) procedure in which the test is run for 3 hours. This is a more stringent standard adopted by ISO (the International Organization for Standardization). "FC" was the highest performance standard for the JASO M345 standards prior to the update. The update in 2004 created an "FD" classification, analogous to ISO-EGD. Results of this testing are presented in the Table below.

TABLE

<u>Mass %</u>	<u>Invention</u>	<u>Conventional</u>
Low ash additive package	2.25	2.25
PIB (Polyisobutylene, Mn 950)	0	25.00
HR-PIB (Glissopal 1000, Mn 1000)	25.00	0
Aliphatic solvent (Shellsol D70)	25.00	25.00
Mineral oil (Shell HVI 160B)	47.50	47.50
<u>Results</u>		
Kinematic viscosity @ 100°C, cSt (JASO ≥ 6.5)	7.25	7.30
M342 Smoke Index (JASO FD/FC/ISO-EGD ≥ 85)	89	88

Inspection of the data in Table reveals that the viscosity and smoke index performance of a low ash two-cycle oil containing HR-PIB are practically identical to those of a conventional low ash two-stroke oil containing a corresponding amount of PIB. Accordingly, the data demonstrates that HR-PIB is a useful alternative to PIB for formulating and manufacturing low ash two-stroke oils.

CLAIMS:

1. A low ash two-cycle engine lubricating oil composition having a kinematic viscosity of at least $6.5 \text{ mm}^2/\text{s}$ (cSt) at 100°C and a JASO M342 Smoke Index of at least 85, which composition comprises:
 - (a) 15 to 35 % by weight of an olefinically unsaturated polymer being polybutene, polyisobutylene or a mixture of polybutene and polyisobutylene, which has a number average molecular weight of 400 to 2200 and a terminal vinylidene content of at least 60 mol %, based on the total number of double bonds in the polymer;
 - (b) 20 to 30 % by weight of a normally liquid hydrocarbon or mineral oil solvent, which has a viscosity of 1 to 5 cP. at 25°C ;
 - (c) 1 to 5% by weight of an additive package for two cycle oils; and
 - (d) a mineral or synthetic oil, or a mixture thereof, which has a viscosity of 4 to $15 \text{ mm}^2/\text{s}$ (cSt) at 100°C .

2. An ashless two-cycle engine lubricating oil composition having a kinematic viscosity of at least $6.5 \text{ mm}^2/\text{s}$ (cSt) at 100°C and a JASO M342 Smoke Index of at least 85, which composition comprises:
 - (a) 6 to 12% by weight of an olefinically unsaturated polymer being polybutene, polyisobutylene or a mixture of polybutene and polyisobutylene, which has a number average molecular weight of 400 to 2200 and a terminal vinylidene content of at least 60 mol %, based on the total number of double bonds in the polymer;
 - (b) 18 to 30 % by weight of a normally liquid hydrocarbon or mineral oil solvent, which has a viscosity of 1 to 5 cP. at 25°C ;
 - (c) 14 to 25% by weight of a metal-free additive package for two cycle oils; and
 - (d) a mineral or synthetic oil, or a mixture thereof, which has a viscosity of 4 to $15 \text{ mm}^2/\text{s}$ (cSt) at 100°C .

3. The composition of claim 1 or 2 wherein the olefinically unsaturated polymer has an Mn of 800 to 1500.

4. The composition of claim 1 or 2 wherein the solvent has a viscosity of 1.2 to 2 cP. at 25°C.
5. The composition of claim 1 or 2 wherein the mineral or synthetic oil or mixture thereof has a viscosity of 12 to 15 mm²/s (cSt) at 100°C.
6. The composition of claim 1 or 2 wherein the additive package comprises a succinimide dispersant made from highly reactive polyisobutylene polymer.