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TWO-STROKE LUBRICANT COMPOSITION FOR REDUCED SMOKE

The present invention relates to a two-cycle engine oil composition, more particularly to a two-cycle engine oil composition comprising a major amount by weight of at least one oil of lubricating viscosity and a minor amount, sufficient to reduce smoke emission in the exhaust gases of two-cycle engines, of at least one oil-soluble manganese carbonyl compound.

As is well known to those skilled in the art, two-cycle, or two-stroke, engine lubricating oils are often added directly to fuel to form a mixture which is then introduced into the engine cylinder. However, the incorporation of a lubricant component into such fuel leads to substantial problems of (blue) smoke being produced in the exhaust gases on combustion. Mineral lubricating oils presently in general use for two-stroke applications exacerbate the smoke emission problem.

As the use of two-cycle internal combustion engines has increased significantly, due to their application in a wide variety of equipment such as motorcycles, marine outboard engines, snowmobiles, power mowers, snow blowers, chain saws, and the like, the amount of smoke generated has become a major environmental concern to engine manufacturers and to fuel and lubricant suppliers. While the unique problems and techniques associated with the lubrication of two-cycle engines has led to the recognition



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by those skilled in the art of two-cycle engine lubricants as a distinct lubricant type (see, for example, U. S. Patent 4,708,809) to date there are few commercially available smoke reducing additives.

U S Patent 5,108,462 addresses the smoke emission problem of using an oil-soluble hydrocarbyl-substituted amine salt. It is also known that polybutenes, usually composed mainly of isobutylene and therefore also referred to as polyisobutylene (PIB), may be used in two-stroke fuels for the express purpose of improving the smoke emission problem. PIBs have found application in two-stroke lubricant formulations because of their ability to depolymerize and burn completely without leaving any deposits. Further, PIBs are compatible with mineral oils and confer good metal-wetting properties and improved film strength. Thus, in two-stroke lubricants, the use of PIBs helps to alleviate problems of smoke formation and deposits commonly seen with mineral oil lubricants, while providing protection against wear and scuffing.

However, with increasing environmental concerns and the establishment of stricter standards regarding smoke emissions, it is essential to develop two-stroke lubricant formulations which provide an improved reduction in smoke emissions from the combustion of the fuel/lubricant mixture in internal combustion two-stroke engines.

A lubricating oil composition for two-cycle engines providing important reduction in smoke produced in exhaust

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gases from combustion of fuel/lubricant mixtures in two-cycle engines is disclosed.

The lubricating oil composition comprises a major amount of a base lubricating oil and a minor amount of an oil-soluble and fuel-soluble manganese carbonyl compound, for example a cyclopentadienyl manganese tricarbonyl compound such as methylcyclopentadienyl manganese tricarbonyl, in a smoke reducing amount. The base lubricating oil preferably is a blend of a mineral oil of lubricating viscosity and a polybutene of lubricating viscosity and optionally contains additional additive components such as ashless dispersant and alkali or alkaline earth metal-containing detergent.

The two-cycle engine lubricant composition of this invention requires a major amount of a lubricating oil basestock suitable for two-stroke applications and a minor smoke emission reducing amount of at least one fuel-soluble manganese carbonyl compound. However, if desired, other lubricant and fuel additives may be present in the composition as well. The composition of the invention generally comprises more than 50% wt of base lubricating oil and upto 30% wt preferably 10 to 25% wt of solvent based on the weight of the total composition. The lubricating oil composition of the invention, when incorporated into a fuel suitable for use in two-cycle engines, may be used as a method of reducing the amount of smoke produced in the exhaust gases of two-cycle engines.

Base Lubricating Oil. The lubricating oil basestock can be derived from natural lubricating oils, synthetic lubricating oils, or mixtures thereof. In general, the lubricating oil basestock will have a kinematic viscosity ranging from about 5 to about 10,000 cSt at 40°C., although

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typical applications will require an oil having a viscosity ranging from about 10 to about 1,000 cSt at 40°C.

Natural lubricating oils include mineral or petroleum oils, and oils derived from coal or shale as well as animal oils and vegetable oils (e.g., castor oil and lard oil). The base oil may be any of a wide variety of oils of lubricating viscosity. Thus the base oil can be a refined paraffin type base oil, a refined naphthenic base oil, or be derived from unrefined, refined, rerefined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment, for example a shale oil obtained directly from a retorting operation or a petroleum oil obtained directly from distillation, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Rerefined oils are obtained by treating refined oils in processes similar to those used to obtain the refined oils. These rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

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Synthetic oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g. polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc., and mixtures thereof); alkylbenzenes; polyphenyls; alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogs, and homologs thereof; and the like. Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups have been modified such as by esterification or etherification.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids, etc.) with a variety of alcohols e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.). Esters useful as synthetic oils also include those made from C5 to C12 monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, and the like.

The base oil can also be a mixture of two or more of the natural and synthetic oils. Mineral lubricating oils are presently in more general use, and a preferred base oil for purposes of this invention comprises a mixture or blend of at least one mineral oil and at least one polymerized olefin, particularly polybutene, as the base oil.

5 Polybutenes are currently used in two-stroke lubricants for the express purpose of reducing visible exhaust smoke. Polybutenes are usually composed mainly of isobutylene, and are therefore also referred to as polyisobutylenes or PIBs. Lower molecular weight PIB fluids in the number average molecular weight of range 400 - 1300 , though rarely used as true base fluids, have found application in two-stroke  
10 lubricant formulations where their ability to depolymerize and burn completely without leaving any deposits is advantageous. PIBs are compatible with mineral oils and confer good metal-wetting properties and improved film strength. Lubricants blended with PIB, which is more tacky than mineral oil, form a tough lubricating film even under severe conditions. In two-stroke lubricants, the use of PIBs helps  
15 alleviate problems commonly seen with mineral oil lubricants associated with deposits, such as port blocking and smoke formation, while providing protection against wear and scuffing. The good lubricating properties of PIBs leads to lower oil:fuel ratio requirements in two-stroke applications relative to mineral oil. Generally, the composition of the invention comprises upto 40% wt,

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preferably 15 to 35% wt of PIB based on weight of the total composition.

Manganese Carbonyl Compounds. The manganese carbonyl compounds to be employed in the compositions of this invention are characterized by being oil soluble and fuel soluble and by having at least one carbonyl group bonded to a manganese atom. "Oil-soluble" or "fuel-soluble", as used herein, means that the compound or component under discussion is sufficiently soluble in the lubricating oil composition or the lubricant:fuel mixture respectively at ambient temperature to provide a homogeneous solution containing the compound or component in at least the lowest concentration of the concentration ranges specified herein for such compound or component.

The most desirable general type of manganese carbonyl compounds utilized in accordance with this invention comprise organomanganese polycarbonyl compounds. For best results, use should be made of a cyclopentadienyl manganese tricarbonyl compound of the type described in U. S. Pat. Nos. 2,818,417 and 3,127,351. Thus use can be made of such compounds as cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, butylcyclopentadienyl manganese

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tricarbonyl, pentylcyclopentadienyl manganese tricarbonyl, hexylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, dimethyloctylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and like compounds in which the cyclopentadienyl moiety contains up to about 18 carbon atoms. A preferred organomanganese compound is cyclopentadienyl manganese tricarbonyl. Particularly preferred for use in the practice of this invention is methylcyclopentadienyl manganese tricarbonyl. Methods for the synthesis of cyclopentadienyl manganese tricarbonyls are well documented in the literature. In addition to U. S. Pat. Nos. 2,818,417 and 3,127,351 noted above, see U. S. Pat. Nos. 2,868,816; 2,898,354; 2,960,514; and 2,987,529, among others.

Other less preferable organomanganese compounds which may be employed include the non-ionic diamine manganese tricarbonyl halide compounds such as bromo manganese dianiline tricarbonyl and bromo manganese dipyridine tricarbonyl, described in U. S. Pat. No. 2,902,489; the acyl manganese tricarbonyls such as methylacetyl cyclopentadienyl manganese tricarbonyl and benzoyl methyl cyclopentadienyl manganese tricarbonyl, described in U. S. Pat. No. 2,959,604; the aryl manganese pentacarbonyls such as phenyl manganese pentacarbonyl, described in U. S. Pat. No. 3,007,953; and the aromatic cyanomanganese dicarbonyls such

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as mesitylene cyanomanganese dicarbonyl, described in U. S. Pat. No. 3,042,693. Likewise, use can be made of cyclopentadienyl manganese dicarbonyl compounds of the formula  $\text{RMn}(\text{CO})_2\text{L}$ , where R is a substituted or unsubstituted cyclopentadienyl group having 5 to 18 carbon atoms, and L is a ligand, such as an olefin, an amine, a phosphine,  $\text{SO}_2$ , tetrahydrofuran, or the like. Such compounds are referred to, for example, in Herberhold, M., Metal  $\pi$ -Complexes, Vol. II, Amsterdam, Elsevier, 1967 or Giordano, P. J. and Weighton, M.S., Inorg. Chem., 1977, 16, 160. Manganese pentacarbonyl dimer (dimanganese dicarbonyl) can also be employed if desired.

Solvent. A hydrocarbonaceous solvent may be used in the lubricant composition to accelerate dissolution of the lubricating oil in the lubricant:fuel mixture prepared for two-stroke application. The hydrocarbonaceous solvent for the present invention may be a petroleum or synthetic hydrocarbonaceous solvent having a boiling point not higher than  $300^\circ\text{C}$  at atmospheric pressure. Typical examples of the petroleum hydrocarbonaceous solvent include kerosene, gasoline, and gas oil. Typical examples of the synthetic hydrocarbonaceous solvent include dimer to hexamer of olefin such as propylene and butene. Kerosene is often used.

Additional Additives. If desired, other additives known in the art may be added to the lubricating base oil for purposes of obtaining or improving performance

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properties. Such additives include dispersants, antiwear agents, antioxidants, corrosion inhibitors, detergents, pour point depressants, extreme pressure additives, viscosity index improvers, friction modifiers, and the like.

Examples of suitable metal-containing detergents include, but are not limited to, such substances as lithium phenates, sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulphurised lithium phenates, sulphurised sodium phenates, sulphurised potassium phenates, sulphurised calcium phenates, and sulphurised magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility; the basic salts of any of the foregoing phenols or sulphurised phenols (often referred to as "overbased" phenates or "overbased sulphurised phenates"); lithium sulphonates, sodium sulphonates, potassium sulphonates, calcium sulphonates, and magnesium sulphonates wherein each sulphonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; the basic salts of any of the foregoing sulphonates (often referred to as "overbased sulphonates"); lithium salicylates, sodium salicylates, potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility; the basic salts of any of the

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foregoing salicylates (often referred to as "overbased salicylates"); the lithium, sodium, potassium, calcium and magnesium salts of hydrolysed phosphosulphurised olefins having 10 to 2000 carbon atoms or of hydrolysed phosphosulphurised alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2000 carbon atoms; lithium, sodium, potassium, calcium and magnesium salts of aliphatic carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids; the basic salts of the foregoing carboxylic acids (often referred to as "overbased carboxylates" and many other similar alkali and alkaline earth metal salts of oil-soluble organic acids. Mixtures of salts of two or more different alkali and/or alkaline earth metals can be used. Salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more calcium phenates with one or more calcium sulphonates) can also be used. While rubidium, cesium and strontium salts are feasible, their expense renders them impractical for most uses. While barium salts are effective, barium's toxicology as a heavy metal renders barium salts less preferred for present-day usage.

Ashless dispersants are described in numerous patent specifications, mainly as additives for use in lubricant compositions, but their use in hydrocarbon fuels has also been described. Ashless dispersants leave little or no metal-containing residue on combustion. They generally contain only carbon, hydrogen, oxygen and in most cases

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nitrogen, but sometimes contain in addition other non-metallic elements such as phosphorus or sulphur.

A preferred ashless dispersant is an alkenyl succinimide of an amine having at least one primary amino group capable of forming an imide group. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with an amine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of olefin and maleic anhydride to about 180°-220°C. The olefin is preferably a polymer or copolymer of a lower monoolefin such as ethylene, propylene, isobutene and the like.

Another class of useful ashless dispersants includes alkenyl succinic acid esters and diesters of alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups. The alkenyl succinic portion of these esters corresponds to the alkenyl succinic portion of the succinimides described above. The succinic esters are readily made by heating a mixture of alkenyl succinic acid, anhydrides or lower alkyl (e.g., C<sub>1</sub>-C<sub>4</sub>) ester with the alcohol while distilling out water or lower alkanol. In the case of acid-esters less alcohol is used. In fact, acid-esters made from alkenyl succinic anhydrides do not evolve water. In another method the alkenyl succinic acid or anhydrides can be merely reacted with an appropriate alkylene oxide such as ethylene

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oxide, propylene oxide, and the like, including mixtures thereof.

In another embodiment the ashless dispersant is an alkenyl succinic ester-amide mixture. These may be made by heating alkenyl succinic acids, anhydrides or lower alkyl esters with an alcohol and an amine either sequentially or in a mixture.

Such ashless dispersants containing alkenyl succinic residues may, and as is well known, be post-reacted with boron compounds, phosphorus derivatives and/or carboxylic acid acylating agents, e.g. maleic anhydride. Typical post-treated ashless dispersants such as succinimides and Mannich condensates are described in the literature. All the aforesaid types of ashless dispersants are described in the literature and many are available commercially. Mixtures of various types of ashless dispersants can, of course, be used.

Because of environmental concerns it is desirable to employ ashless dispersants which contain little, if any, halogen atoms such as chlorine atoms. Thus, in order to satisfy such concerns, it is desirable (although not necessary from a performance standpoint) to select ashless dispersants (as well as the other components used in the compositions of this invention) such that the total halogen content of the overall composition is acceptably low. Indeed, the lower the better. Most desirably, the additive composition contains no detectable amount of halogen.

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Typical halogen (chlorine)-free ashless dispersants suitable for use in the compositions of this invention include, in addition to various types described hereinabove, those described in the following published applications: WO 9003359 and EP 365288.

As is well known to those skilled in the art, two-cycle engine lubricating oils are usually added directly to the fuel to form a mixture of oil and fuel which is then introduced into the engine crankcase and cylinder. Such lubricant-fuel blends generally contain about 10-200 parts fuel per 1 part of oil, typically they contain about 25 to 100 parts fuel per 1 part oil. According to the present invention the amount of manganese carbonyl compound in the mixture can vary broadly depending on the lubricant-fuel mixture ratio. Accordingly, only an amount effective in reducing the smoke resulting from combustion of the mixture need be added. In practice, however, the amount of manganese carbonyl compound added will range from about 0.1 to about 2.0 weight percent, preferably from about 0.4 to about 1.0 weight percent, based on weight of lubricant in the lubricant-fuel mixture.

The distillate fuels used 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 hydrocarbonaceous petroleum distillate fuel (e.g., motor gasoline as defined by ASTM Specification D-439-73). A

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preferred fuel is gasoline, that is, 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. Such fuels can also contain non-hydrocarbonaceous materials such as alcohols, ethers, organo-nitro compounds and the like (e.g. methanol, ethanol, diethyl ether, methyl ethyl ether, nitromethane), which are also within the scope of this invention as are liquid fuels derived from vegetable or mineral sources such as corn, alfalfa, shale, and coal. Examples of suitable fuel mixtures are combinations of gasoline and ethanol, diesel fuel and ether, gasoline and nitromethane, etc. Two-cycle fuels may also contain other additives which are well known to those skilled in the art. These can include anti-knock agents such as tetra-alkyl lead compounds, lead scavengers such as halo-alkanes (e.g., ethylene dichloride and ethylene dibromide), dyes, cetane improvers, anti-oxidants such as 2,6-di-tertiary-butyl-4-methylphenol, rust inhibitors such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal deactivators, demulsifiers, upper cylinder lubricants, antiicing agents, and the like. This invention is useful with lead-free as well as lead containing fuels.

The invention will be further understood by reference to the following Example, which includes a preferred embodiment of the invention.

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EXAMPLES 1-5

Japan is one of the highest volume producers of two-stroke engines. A Two-Cycle Engine Oil Subcommittee was formed in the Motorcycle Technical Committee within the Japanese Automobile Standards Organization (JASO) to address and establish quality standards and test procedures for two-stroke lubricants. JASO M 342-92 is a test procedure to evaluate smoke formation.

In Table I, lubricating oil compositions 1-5 were prepared by blending the components given in Table I, the amount of each component being provided as a weight percent based on the weight of the finished lubricant composition. The additive package identified contains a metallic detergent, an ashless succinimide dispersant and antioxidants. Mineral base oil (a) is a 350 grade solvent refined mineral base oil. PIB is a polyisobutylene of 950 molecular weight number average determined by ASTM D 3592. Kerosene is a standard commercial grade. Mineral base oil (b) is a 100 grade solvent refined mineral base oil. The manganese carbonyl used is methylcyclopentadienyl manganese tricarbonyl (MMT) in the form of a blend of 62% MMT and 38% diluent (mainly aromatic solvent). Each of the blending components is commercially available.

The lubricant compositions 1-5 were evaluated for smoke formation by utilizing the procedure of JASO M 342-92, a test procedure using a Suzuki SX-800R test engine to measure formation of exhaust smoke during a specified test

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cycle. A full flow light extinction smoke meter connected to a chart recorder was used to measure the smoke density. Lubricant composition and fuel were premixed at a fuel/oil ratio of 10:1. In Table II, the test fuel/oil blends A-E correspond to oils 1-5 respectively in Table I at the 10:1 fuel/oil ratio. The level of MMT additive for the fuel/oil mixture in examples C, D and E is expressed as weight of manganese in parts per million (Mn, ppm). The lubricant compositions were evaluated against Jatre 1 (J1), a reference oil provided by JASO for two-cycle engine testing, which was also mixed with the fuel in the same ratio. For the examples A-E and for the J1 reference the fuel utilized was Coordinating European Council (CEC) reference fuel RF83/A/91. The test sequence for the JASO Smoke (1) run was J1 - A(Oil 1) - B(Oil 2) - J1 - D(Oil 4). The test sequence for the JASO Smoke (2) run was J1 - B(Oil 2) - D(Oil 4) - E(Oil 5) - J1. Five specified stages for test conditions are repeated three times for each test fuel/oil blend, with peak smoke density measured for each repeat. The average smoke density of the J1 reference oil for the two JASO tests is calculated, and the Smoke Index of the candidate oil is calculated :

Average smoke density % J1  
Index

Average smoke density % candidate oil

$$\times 100 = \text{Smoke}$$

The Smoke Index for the oils tested are reported in Table II. Test B, with Oil 2, represents a typical good quality low-smoke oil formulation and provided a passing Smoke

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Index (currently greater than 85 when run in the JASO M 342 smoke test procedure). Tests D and E, with Oils 4 and 5 with MMT, demonstrated a significant benefit with an improved Smoke Index over Test B. This would enable meeting a more stringent Smoke Index requirement, or permit a reduction in the amount of PIB in the formulation to meet the present Smoke Index requirement.

TABLE I.

| Oil                | 1     | 2     | 3     | 4     | 5     |
|--------------------|-------|-------|-------|-------|-------|
| Additive Package   | -     | 5.00  | 5.00  | 5.00  | 5.00  |
| Mineral oil (a)    | 47.62 | 44.48 | 44.48 | 44.48 | 44.48 |
| PIB                | 31.22 | 29.16 | 29.16 | 29.16 | 29.16 |
| KEROSENE           | 21.16 | 19.76 | 19.76 | 19.76 | 19.76 |
| Mineral oil (b)    | -     | 1.60  | 1.424 | 0.72  | 0.015 |
| Manganese carbonyl | -     | -     | 0.176 | 0.88  | 1.585 |

TABLE II.

| Test Fuel/Oil Blend  | A  | B  | C | D  | E  |
|----------------------|----|----|---|----|----|
| Oil (Table I)        | 1  | 2  | 3 | 4  | 5  |
| Mn, ppm              | -  | -  | 2 | 10 | 18 |
| JASO Smoke index (1) | 71 | 86 | - | 95 | -  |
| JASO Smoke index (2) | -  | 88 | - | 95 | 93 |

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CLAIMS

1. Two-cycle engine lubricating oil composition comprising a major amount of a base lubricating oil characterised in that it further comprises a smoke reducing amount of at least one oil-soluble and fuel-soluble manganese carbonyl compound.

2. The composition of claim 1 wherein the manganese carbonyl compound is a cyclopentadienyl manganese tricarbonyl compound.

3. The composition of claim 2 wherein the cyclopentadienyl manganese tricarbonyl compound is selected from cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, butylcyclopentadienyl manganese tricarbonyl, pentylcyclopentadienyl manganese tricarbonyl, hexylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, dimethyloctylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and mixtures thereof.

4. The composition of claim 3 wherein the cyclopentadienyl manganese tricarbonyl compound is

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methylcyclopentadienyl manganese tricarbonyl or cyclopentadienyl manganese tricarbonyl.

5. The composition of claim 1 wherein the manganese carbonyl compound is a non-ionic diamine manganese tricarbonyl halide compound, an acyl manganese tricarbonyl compound, an aryl manganese pentacarbonyl compound, or an aromatic cyanomanganese dicarbonyl compound.

6. The composition of claim 1 wherein the manganese carbonyl compound is a cyclopentadienyl manganese dicarbonyl compound is of the formula  $\text{RMn}(\text{CO})_2\text{L}$ , in which R is a substituted or unsubstituted cyclopentadienyl group having 5 to 18 carbon atoms, and L is a ligand selected from olefin, amine, phosphine,  $\text{SO}_2$  and tetrahydrofuran.

7. The composition of claim 1 wherein the manganese carbonyl compound is manganese pentacarbonyl dimer .

8. The composition of any one of claims 1 to 7 wherein the base lubricating oil comprises a blend of at least one mineral oil of lubricating viscosity and at least one polybutene.

9. The composition of any one of claims 1 to 8 wherein the manganese carbonyl compound is present in an amount of from about 0.1 to about 2.0 weight percent based on the weight of the lubricating oil composition.

10. The composition of claim 9 wherein the manganese carbonyl compound is present in an amount of from about 0.4 to about 1.0 weight percent based on the weight of the lubricating oil composition.

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11. The composition of any one of claims 1 to 10 which further comprises kerosene in an amount effective to accelerate dissolution of the lubricating oil composition in fuel.

12. Two-cycle engine fuel comprising a mixture of two-cycle distillate fuel and lubricating oil composition characterised in that the lubricating oil composition is as claimed in any one of claims 1 to 11.

13. The fuel of claim 12 comprising from 10 to 200 parts by weight of fuel per 1 part by weight of lubricating oil composition.

14. A method of reducing the amount of smoke produced in the exhaust gases of a two-cycle engine on fuel combustion which comprises incorporating in the fuel a lubricating oil composition as claimed in any one of claims 1 to 11.

15. The composition of claim 1 substantially as hereinbefore described.

16. The fuel of claim 12 substantially as hereinbefore described.

17. The method of claim 14 substantially as hereinbefore described.