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(54) **SMOKE REDUCING ADDITIVES FOR TWO-CYCLE ENGINE LUBRICANT-FUEL MIXTURE**

RAUCHVERRINGERNDE ADDITIVE FÜR SCHMIER- UND KRAFTSTOFF- MISCHUNGEN FÜR
ZWEITAKTKRAFTMASCHINEN

ADDITIFS POUR MELANGES CARBURANT/LUBRIFIANT DIMINUANT LES EMISSIONS DE
FUMÉES DES MOTEURS DEUX TEMPS

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EP 0 580 587 B1

DescriptionBACKGROUND OF THE INVENTION5 1. Field of the Invention

10 This invention relates to a lubricant-fuel mixture for two-cycle internal combustion engines in which the mixture has reduced smoke emission due to the presence of an amine salt and/or amide of a derivative of benzoic acid or thiobenzoic acid, a hydrocarbyl substituted amine salt of a derivative of phosphoric acid, or certain quaternary ammonium hydroxides.

20 2. Description of Related Art

15 In the last several years, the use of spark-ignited two-cycle internal combustion engines has increased significantly. This is due to their use in a variety of garden and recreational equipment such as motorcycles, marine outboard engines, snowmobiles, power mowers, snow blowers, chain saws, and the like. As such, the amount of smoke released from two-cycle engines has become a major environmental concern to engine manufacturers and fuel suppliers. However, few smoke reducing additives are commercially available, and the few that are contain metals, which are environmentally undesirable.

20 Amine salts of certain benzoic acid derivatives have been used as extreme pressure (EP) agents for water-based metal cutting fluids (see for example, Japanese Patent No. 55023132). Substituted benzoic acids have also been used as EP agents in water-based fluids (see for example, U.S. Patent 4,569,776). U.S. Patent No. 4,434,066 discloses a water based hydraulic fluid containing a combination of a hydroxyl-substituted aromatic acid component and a nitroaromatic compound component. U.S. Patent No. 4,012,331 discloses a lubricating oil composition comprising a sulfur compound prepared by reacting a trithiolan compound with a thiol compound in the presence of a base.

25 Similarly, U.S. Patents 4,787,916 and 4,902,437, together with the patents disclosed therein, describe the use of quaternary ammonium hydroxides in fuels and in lubricating oils, respectively.

30 More recently, the use of a hydrocarbyl substituted amine salt and/or amide of benzoic acid as an antioxidant in lubricating oils and as a flow improver in middle distillates has been disclosed in copending applications U.S. -A-5 076 949 and US-A-5 094 666 respectively.

35 However, none of these publications suggest the particular ashless two-cycle engine lubricant-fuel mixture disclosed herein or its effectiveness in reducing the smoke formed during combustion of the mixture.

SUMMARY OF THE INVENTION

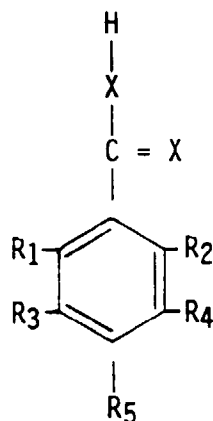
35 In one embodiment, this invention concerns a two-cycle engine lubricant-fuel mixture that comprises

(a) a lubricating oil basestock,

40 (b) a distillate fuel, and

(c) the following oil-soluble additive:

45 a hydrocarbyl substituted amine salt and/or amide of a compound having the formula



wherein X is oxygen or sulfur, and R₁, R₂, R₃, R₄ and R₅ are selected from hydrogen; a hydrocarbyl group containing from 1 to 24 carbon atoms; a hydroxy group; and an oxygen-containing hydrocarbyl group containing from 1 to 24 carbon atoms and at least one of the radicals R₁, R₂, R₃, R₄ or R₅ is a hydrocarbyl group containing from 1 to 24 carbon atoms;

In another embodiment, this invention concerns a method for reducing smoke emission from a two-cycle internal combustion engine by operating the engine with the lubricant-fuel mixture described above.

DETAILED DESCRIPTION OF THE INVENTION

The two-cycle engine lubricant-fuel mixture of this invention requires a lubricating oil basestock, a distillate fuel, and an amine salt and/or amide of a derivative of benzoic acid or dithiobenzoic acid as defined above. However, if desired, other lubricant and distillate fuel additives may be present in the mixture as well.

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 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 animal oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale.

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 (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzene, etc.); polyphenyls (e.g. biphenyls, terphenyls, alkylated polyphenyls, etc.); 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 by esterification, etherification, etc. This class of synthetic oils is exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene 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); and mono- and polycarboxylic esters thereof (e.g., the acetic acid esters, mixed C₃-C₈ fatty acid esters, and C₁₃ oxo acid diester of tetraethylene glycol).

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.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, diicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid, and the like.

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.

Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. These oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxy)-disiloxane, poly(methyl)-siloxanes and poly(methylphenyl) siloxanes, and the like. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid), polymeric tetrahydrofurans, polyalphaolefins, and the like.

The lubricating oil may be derived from unrefined, refined, rerefined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, 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.

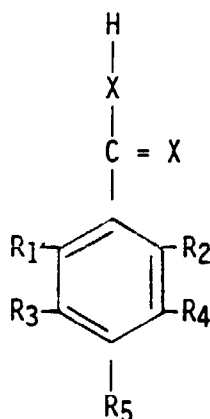
If desired, other additives known in the art may be added to the lubricating base oil. Such additives include dispersants, antiwear agents, antioxidants, corrosion inhibitors, detergents, pour point depressants, extreme pressure additives, viscosity index improvers, friction modifiers, and the like. These additives are typically disclosed, for example, in "Lubricant Additives" by C. V. Smalhear and R. Kennedy Smith, 1967, pp. 1-11 and in U.S. Patent 4,105,571.

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). 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), 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 such fuel mixtures are combinations of gasoline and ethanol, diesel fuel and ether, gasoline and nitromethane, etc. Particularly preferred 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.

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, anti-icing agents, and the like. This invention is useful with lead-free as well as lead containing fuels.

The lubricant-fuel mixture of this invention will also contain a hydrocarbyl substituted amine salt and/or amide of an oil-soluble benzoic acid or thiobenzoic acid derivative, an amine salt of a phosphoric acid derivative, or a particular class of quaternary ammonium hydroxides.

The hydrocarbyl substituted amine salt and/or amide (preferably an amine salt) of an oil-soluble benzoic acid or thiobenzoic acid derivative has the formula



wherein X is oxygen or sulfur, preferably sulfur, and R₁, R₂, R₃, R₄ and R₅ are selected from hydrogen; a hydrocarbyl

group containing from 1 to 24 carbon atoms, preferably an alkyl group containing from 1 to 18 carbon atoms; a hydroxy group, i.e., -OH; and an oxygen-containing hydrocarbonyl group containing from 1 to 24 carbon atoms and at least one of the radicals R_1 , R_2 , R_3 , R_4 or R_5 is a hydrocarbonyl, preferably an alkyl group, containing from 1 to 24, preferably from 1 to 18 carbon atoms, most preferably from 1 to 6 carbon atoms.

Specific examples of the benzoic or dithiobenzoic acid derivatives include 4-hydroxy 3,5 ditertiary butyl dithiobenzoic acid; 4-hydroxy 3,5 ditertiary butyl benzoic acid; 3,5 dimethyl dithiobenzoic acid; 4-hydroxy 3,5 dimethyl dithiobenzoic acid.

The oil soluble additive is formed in a conventional manner by mixing substantially equimolar amounts of the benzoic acid derivative and a hydrocarbonyl substituted amine at temperatures generally in the range of 20°C - 100°C.

The hydrocarbonyl groups of the amine include groups which may be straight or branched chain, saturated or unsaturated, aliphatic, cycloaliphatic, aryl, alkaryl, etc. Said hydrocarbonyl groups may contain other groups, or atoms, e.g. hydroxy groups, carbonyl groups, ester groups, or oxygen, or sulfur, or chlorine atoms, etc. These hydrocarbonyl groups will usually be long chain, e.g. C_{12} to C_{40} , e.g. C_{14} to C_{24} . However, some short chains, e.g. C_1 to C_{11} may be included as long as the total numbers of carbons is sufficient for solubility. Thus, the resulting compound should contain a sufficient hydrocarbon content so as to be oil-soluble. The number of carbon atoms necessary to confer oil solubility will vary with the degree of polarity of the compound. The compound will preferably also have at least one straight chain alkyl segment extending from the compound containing 8 to 40, e.g. 12 to 30 carbon atoms.

The amines may be primary, secondary, tertiary or quaternary, but preferably are secondary. If amides are to be made, then primary or secondary amines will be used.

Examples of primary amines include n-dodecyl amine, n-tridecyl amine, C_{13} Oxo amine, coco amine, tallow amine, behenyl amine, etc. Examples of secondary amines include methyl-lauryl amine, dodecyl-octyl amine, coco-methyl amine, tallow-methyl amine, methyl-n-octyl amine, methyl-n-dodecyl amine, methyl-behenyl amine, ditallow amine etc. Examples of tertiary amines include coco-diethyl amine, cyclohexyl-diethyl amine, coco-dimethyl amine, tri-n-octyl amine, di-methyl-dodecyl amine, methyl-ethyl-coco amine, methyl-cetyl stearyl amine, etc.

Amine mixtures may also be used and many amines derived from natural materials are mixtures. The preferred amines include the long straight chain alkyl amines containing from 8 to 40, preferably from 12 to 24, carbon atoms. Naturally occurring amines, which are generally mixtures, are preferred. Examples include coco amines derived from coconut oil which is a mixture of primary amines with straight chain alkyl groups ranging from C_8 to C_{18} . Another example is di tallow amine, derived from hydrogenated tallow acids, which amine is a mixture of C_{14} to C_{18} straight chain alkyl groups. Ditallow amine is particularly preferred.

Oil-soluble, as used herein, means that the additive is soluble in the mixture at ambient temperatures, e.g., at least to the extent of about 5 wt.% additive in the mixture at 25°C.

As is well known to those skilled in the art, two-cycle engine lubricating oils are often added directly to the fuel to form a mixture of oil and fuel which is then introduced into the engine cylinder. Such lubricant-fuel blends generally contain per 1 part of oil about 20-250 parts fuel, typically they contain 1 part oil to about 30-100 parts fuel.

The amount of additive in the mixture can vary broadly depending on the lubricant-fuel mixture ratio. Accordingly, only an amount effective in reducing the smoke of the mixture need be added. In practice, however, the amount of additive added will range from about 0.1 to about 5 wt.%, preferably from about 0.5 to about 1 wt.%, based on weight of lubricant in the lubricant-fuel mixture.

The invention will be further understood by reference to the following Example, which include preferred embodiments of this invention.

Example

Three samples of the same lubricant-fuel mixture were tested in a single cylinder Yamaha snowmobile engine to determine the maximum smoke produced by each sample. The mixture comprised a commercially available two-cycle engine lubricating oil and a commercially available unleaded gasoline having an RON of 91 and an oil to fuel ratio of 1 to 33. The samples tested were the lubricant-fuel mixture without additives, the mixture with a conventional smoke reducing additive (barium sulfonate), and the mixture with dihydrogenated tallow amine:4-hydroxy-3,5-ditert-butylidithiobenzoate (DTA:DTB). The maximum smoke produced when operating the engine at 4500 rpm and applying a 10 Nm (Newton meter) load was measured by inserting an optical opacity smoke meter into the exhaust system. The results of these tests are shown in Table 1 below.

Table 1

Test No.	Additive	Conc., wt. %	Max. Smoke, %	Smoke Reduction, %
1	None	--	49.6	--

Table 1 (continued)

Test No.	Additive	Conc., wt. %	Max. Smoke, %	Smoke Reduction, %
2	DTA:DTB	1.0	39.4	21
3	Ba Sulfonate	1.0	39.8	20

The data in Table 1 show that the additive of this invention provide a reduction in smoke comparable with that of barium sulfonate (a commercially available additive) without the formation of ash.

Claims

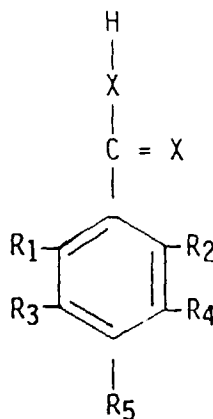
1. A lubricating oil-fuel mixture comprising

(a) a lubricating oil basestock,

(b) a distillate fuel, and

(c) the following oil-soluble additive;

a hydrocarbyl substituted amine salt and/or amide of a compound having the formula



wherein X is oxygen or sulfur, and R₁, R₂, R₃, R₄ and R₅ are selected from hydrogen; a hydrocarbyl group containing from 1 to 24 carbon atoms; a hydroxy group; and an oxygen-containing hydrocarbyl group containing from 1 to 24 carbon atoms and at least one of the radicals R₁, R₂, R₃, R₄ or R₅ is a hydrocarbyl group containing from 1 to 24 carbon atoms.

2. The mixture of claim 1 wherein the oil-soluble additive in (c) is an amine salt.

3. The mixture of claim 1 or claim 2 wherein X in (c) is sulfur.

4. The mixture of any of the preceding claims wherein the hydrocarbyl substituted amine in (c) is a tallow amine.

5. The mixture of claim 4 wherein the tallow amine is a ditallow amine salt of 4-hydroxy-3, 5-di-tert-dibutyldithio-benzoic acid.

6. The mixture of any of the preceding claims wherein from 0.1 to 5 wt.% of the oil-soluble additive is present therein and the volume ratio of lubricant to fuel ranges from 1:20 to 1:250.

7. The mixture of claim 6 wherein fuel is gasoline.

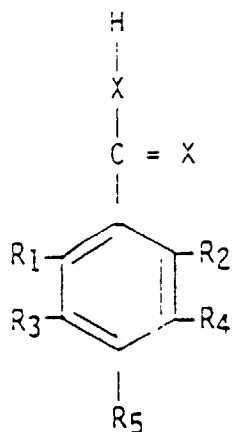
8. A method for reducing the smoke emitted from a two-cycle internal combustion engine by operating the engine

with the mixture of any of the preceding claims.

Patentansprüche

1. Schmieröl/Brennstoff-Mischung, die

- (a) Schmieröleinsatzmaterial,
- (b) Destillatbrennstoff und
- (c) das folgende öllösliche Additiv umfaßt:
ein mit Kohlenwasserstoff substituiertes Aminsalz und/oder Amid einer Verbindung der Formel



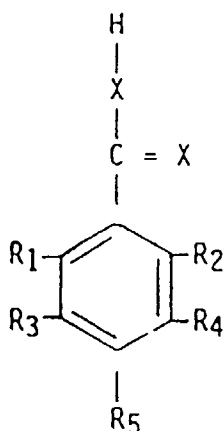
in der X Sauerstoff oder Schwefel ist und R_1 , R_2 , R_3 , R_4 und R_5 ausgewählt sind aus Wasserstoff, einer Kohlenwasserstoffgruppe, die 1 bis 24 Kohlenstoffatome enthält, einer Hydroxygruppe und einer Sauerstoff enthaltenden Kohlenwasserstoffgruppe, die 1 bis 24 Kohlenstoffatome enthält, wobei mindestens einer der Reste R_1 , R_2 , R_3 , R_4 oder R_5 eine Kohlenwasserstoffgruppe ist, die 1 bis 24 Kohlenstoffatome enthält.

- 2. Mischung nach Anspruch 1, bei der das öllösliche Additiv in (c) ein Aminsalz ist.
- 3. Mischung nach Anspruch 1 oder Anspruch 2, bei der X in (c) Schwefel ist.
- 4. Mischung nach einem der vorhergehenden Ansprüche, bei der das mit Kohlenwasserstoff substituierte Amin in (c) ein Talgamin ist.
- 5. Mischung nach Anspruch 4, bei der das Talgamin ein Ditalgaminsalz von 4-Hydroxy-3,5-ditert.-dibutyldithiobenzoesäure ist.
- 6. Mischung nach einem der vorhergehenden Ansprüche, bei der 0,1 bis 5 Gew.% des öllöslichen Additivs darin vorhanden sind und das Volumenverhältnis von Schmiermittel zu Brennstoff im Bereich von 1:20 bis 1:250 liegt.
- 7. Mischung nach Anspruch 6, bei der der Brennstoff Benzin ist.
- 8. Verfahren zur Verringerung des Rauchs, der aus einem Zweitaktverbrennungsmotor emittiert wird, bei dem der Motor mit der Mischung gemäß einem der vorhergehenden Ansprüche betrieben wird.

Revendications

1. Mélange huile lubrifiante-combustible, comprenant

- (a) une huile lubrifiante de base,
 (b) un combustible distillé, et
 (c) l'additif, soluble dans l'huile, suivant :
 un sel d'amine et/ou amide, à substituant hydrocarbyle, d'un composé répondant à la formule



dans laquelle X représente l'oxygène ou le soufre, et R₁, R₂, R₃, R₄ et R₅ sont choisis entre l'hydrogène ; un groupe hydrocarbyle contenant 1 à 24 atomes de carbone ; un groupe hydroxyle ; et un groupe hydrocarbyle, renfermant de l'oxygène, contenant 1 à 24 atomes de carbone, et au moins un des radicaux R₁, R₂, R₃, R₄ et R₅ représentant un groupe hydrocarbyle contenant 1 à 24 atomes de carbone.

2. Mélange suivant la revendication 1, dans lequel l'additif soluble dans l'huile en (c) est un sel d'amine.
3. Mélange suivant la revendication 1 ou la revendication 2, dans lequel X en (c) représente le soufre.
4. Mélange suivant l'une quelconque des revendications précédentes, dans lequel l'amine à substituant hydrocarbyle en (c) est une amine dérivée du suif.
5. Mélange suivant la revendication 4, dans lequel l'amine dérivée du suif est un sel de diamine dérivée du suif d'acide 4-hydroxy-3,5-di-tertio-dibutyldithiobenzoïque
6. Mélange suivant l'une quelconque des revendications précédentes, dans lequel une quantité de 0,1 à 5 % en poids de l'additif soluble dans l'huile est présente dans ce mélange et le rapport volumique du lubrifiant au combustible est compris dans l'intervalle de 1:20 à 1:250.
7. Mélange suivant la revendication 6, dans lequel le combustible est l'essence.
8. Procédé pour réduire la fumée émise par un moteur à combustion interne à deux temps, en faisant fonctionner le moteur avec le mélange suivant l'une quelconque des revendications précédentes.