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3,192,910 TWO-CYCLE INTERNAL COMBUSTION ENGINE FUEL

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This invention relate to a method of operating a two-cycle internal combustion engine and to compositions having utility in this operation. More particularly, this invention relates to a method of operating a two-cycle engine wherein the lubricant is premixed with the fuel.

Spark ignition engines of the two-cycle type, which 15 have no lubricant reservoir, are generally lubricated by including oil in the fuel which lubricates the engine and is eventually burned in the cylinders. When insufficient oil is employed in the fuel-lubricant mixture, excessive engine wear results. However, fuel/oil ratios sufficiently low to prolong engine life in terms of wear usually lead to excessive deposition and clogging of the intake and exhaust ports of the engine. In overcoming this problem by increasing the fuel/oil ratio, the operation in turn leads to excessive engine wear.

It is, therefore, an object of this invention to provide a method for operating a two-cycle internal combustion engine using a fuel/oil ratio low enough to keep engine wear at an acceptable level and at the same time reduce clogging of the intake and exhaust ports of the engine. A further object of this invention is to provide compositions useful in operating two-cycle spark-ignition internal combustion engines. Other objects will become apparent by the following description of the invention.

It has now been found that intake and exhaust port clogging of two-cycle spark ignition internal combustion engines may be satisfactorily reduced by employing the method and compositions of this invention. Accordingly, an embodiment of this invention is the method of operating a two-cycle spark ignition internal combustion engine which comprises introducing into the combustion chamber a fuel/oil mixture, the weight ratio of said fuel to said oil being at least about 15/1, said mixture containing as an additive therefor a compound having the formula

$$HO R$$
 R
 R
 R
 R
 R
 R

wherein R is an alkyl group of 1–8 carbon atoms and R_1 is an alpha-branched alkyl group of 3–8 carbon atoms, igniting said fuel/oil mixture in said combustion chamber, thereby producing gaseous combustion products, and causing said combustion products to act on a piston, thereby producing a driving force. Such a process effectively reduces intake and exhaust port clogging.

The compositions used in the above method; namely a fuel/oil mixture especially adapted for use in two-cycle 60 engines, said fuel comprising leaded hydrocarbon fuel of the gasoline boiling range and said oil comprising hydrocarbon mineral oil, the weight ratio of said fuel to said oil being at least about 15/1, said composition containing a compound having the formula

$$HO CH_2 R_1$$
 R_2
 OH

wherein R is an alkyl group having 1-8 carbon atoms and

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R₁ is an alpha-branched alkyl group having 3-8 carbon atoms, also comprises an aspect of this invention. In addition, certain oil-additive combinations, described below make up part of this invention.

In general, those fuel-oil mixtures having a ratio of fuel/oil of about 15/1 to about 30/1 are benefited by the practice of this invention. With ratios higher than 30/1 mounts of oil present in the mixture are low enough so that port clogging does not become a serious problem.

Modern practice in two-cycle operation especially with respect to high performance outboard and motor scooter engines is to use leaded fuels-fuels containing alkyl lead antiknock agents—to insure proper engine efficiency and optimum power. The lead-containing products formed by combustion in the engine of such alkyl lead antiknocks substantially increase the magnitude of the wear problems associated with high fuel oil operation. Accordingly, the use of a lower fuel oil mixture is required. An adverse effect of this is the further clogging of intake and exhaust ports of the engine due to the greater amount of oil used. Accordingly, such fuel/oil mixtures are especially benefited by the practice of this invention. Thus another embodiment of this invention is as a new composition of matter a fuel/oil mixture especially adapted for use in two-cycle engines, said fuel comprising leaded hydrocarbon fuel of the gasoline boiling range and said oil comprising hydrocarbon mineral oil, the weight ratio of said fuel to said oil being at least 15/1, said composition containing as an additive therefor a compound hav-30 ing the formula

wherein R is an alkyl group having 1-8 carbon atoms and R_1 is an alpha-branched alkyl group having 3-8 carbon atoms.

By leaded fuel we mean fuel containing from about 0.5 to about 6.0 grams of lead per gallon as an alkyllead antiknock compound, such at tetraethyllead, tetramethyllead, mixtures of tetramethyllead and tetraethyllead, the equilibrium mixtures of tetramethyllead, trimethylethyllead, dimethyldiethyllead, methyltriethyllead and tetraethyllead produced by chemical redistribution of tetraethyllead-tetramethyllead mixtures, such as the 50 mol percent—50 mol percent mixture, the 25 mol percent—75 mol percent mixture, and so forth. Aryllead compounds, such at tetraphenyllead, can also be used.

Although certain of the compounds have been suggested as additives to lubricant compositions and, when in such lubricant compositions, as antioxidants, the present invention and its surprising features are completely unexpected.

For one thing, due to the high dilution of the oil with gasoline in the present compositions, the concentration of the additive in the finished fuel can be miniscule and still permit the realization of the benefits of this invention. For another thing, the additive compounds of this invention serve a purpose entirely unrelated to their recognized use as antioxidants. Antioxidants function to inhibit deterioration of the oil while in storage. In doing so they react with and destroy peroxides slowly formed in the oil over an extended period of time. In the present invention, however, the additive compounds perform an additional and entirely different function. When the additives of this invention are added to the oil even just prior to its use they effectively reduce intake and exhaust port clogging. In addition they help maintain cleanliness

of the piston skirt, piston underhead and cylinder bore. Such utility is completely unrelated to any antioxidant properties the additive may have.

Instructions for preparing the additive compounds of this invention are found in U.S. Patent No. 2,807,653.

Examples of the phenolic additive compounds of this invention are: 4,4'-methylenebis(2-tert-butyl - 6 - methylphenol), 4,4'-methylenebis(2-isopropyl-6-methylphenol), 4,4'-methylenebis(2 - sec-butyl - 6 - methylphenol), 4,4'methylenebis (2,6-di-tert-butylphenol), 4,4' - methylenebis 10 (2,6-diisopropylphenol), 4,4' - methylenebis(2-methyl-6tert-octylphenol, 4,4' - methylenebis[2-ethyl-6-(2'-hexyl) phenol], 4,4' - methylenebis[2-n-butyl - 6 - (3' - heptyl) phenol], 4,4' - methylenebis(2-n-amyl-6-tert-amylphenol), 4,4' - methylenebis(2 - isoamyl - 6-n-propylphenol), 4,4'methylenebis (2-tert-butyl-6-n-hexylphenol), 4,4' - methylenebis(2-isopropyl-6-n-octylphenol), and 4,4'-methylenebis (2-n-heptyl-6-isobutylphenol).

Preferred additives are those compounds of the above formula wherein R and R₁ are alpha-branched alkyl 20 groups containing 3-8 carbon atoms. These are preferred because they are especially effective in reducing port clogging and are more soluble in oil and in gasoline. Examples of these preferred compounds are: 4,4'-methylenebis (2,6-diisopropylphenol), 4,4'-methylenebis (2,6-di-tertbutylphenol), 4,4'-methylenebis(2,6-di-sec-butylphenol), 4,4'-methylenebis(2,6 - di-tert-amylphenol), 4,4'-methylenebis(2,6 - di-tert-octylphenol), 4,4' - methylenebis(2,6diisobutylphenol), 4,4'-methylenebis[2,6 - di - (3'-hexyl) phenol], 4,4'-methylenebis[2,6-di-(2'-heptyl)phenol] and 30 4,4'-methylenebis(2,6-diisoamylphenol).

The most effective phenolic additive compound of this invention is 4,4'-methylenebis(2,6-di-tert-butylphenol) and it constitutes the most preferred compound of this

The compositions of this invention can be prepared by dissolving the phenolic compound of this invention in the oil composition and adding it to fuel, by dissolving the compound in the fuel composition and adding it to oil; or by forming an oil/fuel composition and adding the 40 compound to it. In formulating the compositions of this invention which contain alkyllead compounds the alkyl lead compound can be added to the fuel, to the oil, or to the fuel-oil combination. It is most preferably to add the compound to hydrocarbon mineral oil, in concentrations of about 0.05 to about 10 weight percent, and to add this oil composition to leaded fuel.

The lubricating oil employed in the compositions of this invention is generally a mineral lubricating oil of the type usually employed for the crankcase lubrication 50 of a spark ignition internal combustion engine. Thus, it may be derived from paraffinic, naphtenic, asphaltic or mixed base stocks and in general, has a viscosity varying with temperature over a wide range. It is not necessary to use a pure mineral-derived lubricating oil. The oil may contain other additives and may be blended with other types of oils including vegetable-derived oils such as rapeseed oil and castor oil and synthetic oils such as polymerized olefins and organic polyesters including dioctyl sebacate and trihexyl phosphate.

The fuel employed in the compositions of this invention is primarily a petroleum-derived liquid hydrocarbon of the gasoline boiling range. However, it may, and often does, contain minor proportions of various other ingredients including non-hydrocarbon fuel constituents. Furthermore, the fuel may contain from 0.5 to about 6.5 grams of lead per gallon as an alkyllead antiknock agent to improve the octane quality of the fuel. The compositions of this invention, especially those containing an alkyllead antiknock, may also contain one or more organic halide scavengers. The function of an organic halide scavenger is to convert the lead present in the combustion chamber, after combustion, to lead halide, which is more volatile and more easily exhausted from the engine than lead oxides, which are the normal combustion products 75 carbons because the former are less corrosive to the

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when scavengers are not used. The amount of scavenger employed is such as to provide from about 0.75 to 2.5 or more theories of halogen based on the amount of lead present. A theory of halogen is that amount which is required to quantitatively convert the lead present to lead dihalide. A common example, which is widely used in two-cycle service, is "Motor Mix," which is a tetraethyllead fluid containing 1.0 theory of chlorine as ethylene dichloride and 0.5 theory of bromine as ethylene dibro-

In this connection it has been found that addition to the compositions of this invention of organic halide scavengers in amount greater than normally used in gasoline provides great benefits in terms of reduced combustion chamber deposits and increased spark plug life. in one aspect of my invention we include in the finished composition an organic halide scavenger or mixture of such scavengers, so that the total amount of halogen present in the fuel/oil compositions is as high as 2.5 theories based on the amount of lead present. Ordinary gasoline seldom contains more than 1.5 or 1.6 total theories of halogen. This addition of "extra" scavenger can be conveniently done by blending the organic halide into the oil before the oil is blended with the fuel; into the finished fuel/oil composition; or into the fuel before the fuel is blended with the oil. In any event, the extra scavenger is added in such amount that the total present in the finished fuel/oil composition ranges from about 0.75 to 2.5 theories based on the amount of lead present.

It is usually preferable to blend the organic halide scavenger in the oil prior to addition to the fuel. Ordinarily, we blend so that the scavenger is present in the oil to the extent of about 0.5 to about 7.5 percent by weight of the oil. Thus, an aspect of this invention comprises mineral lubricating oil containing 0.05 to 10.0 weight percent of a phenolic compound of the type described and an organic halide scavenger in amount sufficient to substantially reduce combustion chamber deposit formation and increase spark plug life in the two-cycle engine. This amount of organic halide scavenger will usually range from about 0.25 to about 7.5 percent, preferably 0.25 to 2.5 percent, by weight of the oil. Another embodiment of this invention includes fuel compositions containing oil with the above amounts of phenolic compound and organic halide scavenger, wherein the fuel/oil ratio is at least about 15/1.

Further examples of suitable organic halide scavengers for use in this invention include ethylene dichloride, propylene dichloride, chlorinated benzenes, brominated benzenes and toluenes, brominated propanes, butanes and ethanes. Further scavengers include carbon tetrachloride; propylene dibromide; 2-chloro-2,3-dibromobutane; 1,2,3tribromopropane; hexachloropropylene; mixed bromoxylenes; 1,4-dibromobutane; 1,4-dichloropentane; β,β' -dibromodiisopropyl ether; trichlorobenzene; dibromotoluenes; tert-butyl bromide; 2-methyl-2-bromobutane; 2,3,3 - trimethyl-2-bromobutane; tert-butyl chloride; 2,3-dimethyl-2,3-dibromobutane; 2,3-dimethyl-2,5-dibromohexane; 2methyl-2,3-dibromobutane; 2-methyl-2,3-dichloroheptane; 60 2-methyl-2,4-dibromohexane; 2,4-dibromopentane; 2,5dichlorohexane; 3-methyl-2,4-dibromopentane; 1-phenyl-1-bromoethane; 1-phenyl-1-chloroethane; ethyl-α-bromoacetate; diethyl-dibromomalonate; propyl-α-chlorobutyrate; 1,1-dichloro-1-nitroethane; 1,1-dichloro-2-nitroethane; 1,1-dibromo-1-nitrobutane; 2-chloro-4-nitropentane; 2,4dibromo-3-nitropentane; 1 - chloro-2-hydroxyethane; 1bromo-3-hydroxypropane; 1-bromo-3-hydroxybutane; 3methyl-2-bromo-4-hydroxypentane; 3,4 - dimethyl-2-bromo-4-hydroxypentane; and, in general, scavengers disclosed in U.S. Patents 1,592,954; 1,668,022; 2,364,921; 2,479,900; 2,479,901; 2,479,902; 2,479,903 and 2,496,983. Such products may be used singly or in combination. We prefer the bromohydrocarbons to the chlorohydroaluminum parts which are widely used in two cycle engines. The most preferred compound is ethylene dibromide and we prefer to use this material in concentrations of 0.25 to 2.0 percent in the oil or 0.75 to 2.5 theories in the finished fuel/oil composition.

In a greatly preferred embodiment of this invention the fuel and oil compositions contain, in addition to the phenolic compound of this invention, a detergent additive. Use of such a detergent leads to vastly superior results. Any hydrocarbon-soluble detergent can be used. This includes both the ash-forming type and the ashless type. Ordinarily, the ashless detergents, including surfactants, are preferred.

Examples of suitable detergents include the heavy metal salts of carboxylic or sulfonic acids and the metal alcoholates or phenolates, in all of which the anionic constituent has a large hydrocarbon-soluble radical. The metal constituent is usually an alkaline earth metal, most commonly calcium or barium. The aluminum, zinc and cobalt salts are also used. Other detergents include the metallic salts of the mahogany sulfonic acids, the alkyl phosphoric acids, the alkyl phenols, phthalic monoesters, alkylaryl phosphoroamides, long-chain phenolic ether alcohols, naphthenic acids, amino substituted fatty acids, chlorinated fatty acids and acids containing thioether groups.

Further examples of suitable detergents are the lecithins and various long-chain esters of polyhydric alcohols.

Further examples include reaction products of P_2S_5 with olefins, terpenes and alcohols, as well as salts thereof, the calcium and barium petroleum sulfonates, the calcium and barium alkyl phenol sulfides and methacrylate polymers and co-polymers particularly polymers with vinyl pyridines and vinyl pyrrolidones. Vinyl caprolactams and vinyl valerolactams are also co-monomers used in forming such polymethacrylate detergents. Further useful detergents include polyhydrocarbons, such as low molecular weight polybutenes, and the polyoxyethylene derivatives of various polymers, such as amine-aldehyde, sulfonamide-aldehyde, phenol-aldehyde, alkyd, polyamide and imidazoline resins.

Detergent additives which cooperate in an outstanding way with the phenolic additives of this invention include derivatives of carboxylic acids wherein an amide or imidazoline linkage exists. Especially outstanding are amides made from carboxylic acids of about 6 to about 10 carbon atoms with secondary amines of about the same number of carbon atoms. Such amides have the general formula

$$\begin{array}{c|c}
O & R_1 \\
R-C-N & R_2
\end{array}$$

where R is an unsaturated or, more preferably, a saturated aliphatic radical of 5 to 9 carbon atoms and R1 and R₂ are preferably saturated aliphatic or cycloaliphatic radicals of 6-10 carbon atoms. Such compounds wherein R₁ and R₂ are secondary aliphatic radicals are especially preferred. Thus, an aspect of this invention comprises mineral lubricating oil containing 0.05 to 10.0 weight percent of a phenolic compound of the type described and a hydrocarbon-soluble detergent in amount sufficient to substantially reduce sludge formation in the two-cycle engine. This amount of detergent will usually range from about 0.25 to about 10 percent, preferably 0.5 to 5 percent, by weight of the oil. Another embodiment of this invention includes fuel compositions containing oil with the above amounts of phenolic compound and detergent, wherein the fuel/oil ratio is at least about 15/1.

In order to show the benefits derived from this invention tests were conducted on a two-cycle spark ignition engine. A 125 cc. two-cycle air-cooled single cylinder 75

Lambretta motor scooter engine equipped with induction system and four-speed transmission was mounted on a steel frame in the same relative position as on a motor scooter. The load was absorbed by a 5 horsepower induction motor belted to the exhaust shaft of the transmission. Idle conditions were achieved by allowing the electric motor to free wheel. Engine specifications are shown in Table I.

Table I

ENGINE SPECIFICATIONS

	Engine	
_]	Horsepower	.52 at 5200 r.p.m.
	No. cylindersBore, inches	1.
5	Stroke, inches	2.28.
20]	Displacement, cu. in Horsepower/cu. in	7.47. 0.697.

The test procedure consisted of operating at full throttle at 4500 r.p.m. for 55 minutes followed by a five-minute idle period. This cycle was repeated to accumulate a total of 80 test hours after which the cylinder barrel was removed and the piston and ports were rated for deposit build-up.

A regular grade fuel was blended with test oil at a 24:1 gasoline oil ratio. Table II sets forth the fuel inspection data for this gasoline.

Table II

FUEL INSPECTION DATA

35	TEL content, ml./gal.	12
	Existent gum, mg./100 ml	2.8
	Oxidation stability, min.	1440+
	Sulfur, wt., percent	0.045
	Gravity, ° API	59.5
40	Reid vapor pressure, p.s.i.	8.3
	Hydrocarbon type, vol. percent:	1.3
	Aromatics	24.5
	Olefins	3.8
	Saturates	72.0
45	ASTM Distillation, ° F:	
	10% evaporated	141
	50% evaporated	229
	90% evaporated	318

1 As commercial "Motor Mix" which contains additionally 1.0 theory of chlorine as ethylene dichloride and 0.5 theory of bromine as ethylene dibromide.

Three different solvent-refined oils were used for the investigation. Oil inspection data are listed in Table III.

 $egin{array}{ccc} Table & III \\ ext{OIL INSPECTION DATA} \end{array}$

60	Oil	н	ı	j	
	Type	Solvent Ref., Mixed Base	Solvent Ref., Coastal Neutral	Solvent Ref., Coastal Distillate	
65	Viscosity: At 100° F., SUS At 210° F., SUS Viscosity index Gravity, °API	539 65. 6 97. 0 28. 6	509 58.1 64.0 25.6	901 72. 7 62. 0 25. 0	
70	Ash (D-482) Sulfur, wt. percent Total acid number Total base number Additives Metals	0.020 0.37 0.5 0.1 (1) None	0.046 0.1 0.2 0.3 None None	0.003 0.1 0.1 0.1 0.1 None None	

¹ Commercial ashless additive package.

Each of the three oils was tested alone and then with

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one weight percent 4,4'-methylenebis(2,6-di-tert-butylphenol). Table IV summarizes the test results.

Table IV SUMMARY OF LAMBRETTA ENGINE DATA

Oil	н		I		J	
4,4'-methylenebis(2,6-di- tert-butylphenol)	None	1%	None	1%	None	1%
Cleanliness (10=Clean): Piston skirt Piston underhead Intake ports. Cylinder boro Exhaust ports	6. 0 3. 0 8. 0 8. 0 2. 3	6. 5 3. 0 10. 0 8. 0 5. 2	3. 5 3. 0 8. 0 6. 5 7. 0	3. 5 3. 0 8. 0 6. 5 8. 0	3. 0 2. 0 7. 0 5. 0 4. 8	4. 0 3. 5 7. 8 7. 0 6. 2
Exhaust port clogging, percent	. 55	32	20	15	35	25

It can be seen from the above test results that the addition of one weight percent of 4,4'-methylenebis(2,6-ditert-butylphenol) to each of the oils consistently reduced exhaust port clogging. The greatest amount of port clogging occurred with oil H containing a commercial ashless additive package wherein 55 percent of the exhaust ports were clogged. The addition of one weight percent 4,4'methylenebis(2,6-di-tert-butylphenol) to this oil reduced the clogging to 32 percent. Likewise the addition of 25 one weight percent 4,4'-methylenebis(2,6-di-tert-butylphenol) to oils I and J reduced clogging from 20 to 15 percent and from 35 to 25 percent respectively

The reduction in exhaust port clogging by utilizing an additive of this invention was accompanied by an improvement in intake port cleanliness when oil H and oil J were used. Thus, a clean rating of 10 was obtained with oil H when 4,4'-methylenebis(2,6-di-tert-butylphenol) was used at one weight percent concentration compared to a rating of 8.0 without the additive of this invention. Likewise adding the compound to oil J resulted in an intake port rating of 7.8 compared to 7.0 in the absence of the compound.

The compositions of this invention are illustrated by the following examples, in which all parts and percentages are by weight unless otherwise designated. The oils and fuels in preparing the compositions are identified in Tables V and VI as follows:

EXAMPLE 1

To 100 parts of Oil A is added 0.05 part of 4,4'-methylenebis (2,6-di-tert-butylphenol). This additive-containing oil is then blended with Fuel A in a fuel/oil weight ratio of 15/1 to provide a low clogging two-cycle fuel composition.

EXAMPLE 2

To 100 parts of Oil D is added 0.5 part of 4,4'-methylenebis[2-(3'-heptyl)-6-sec-butylphenol]. This composition is blended with Fuel C in fuel/oil ratio of 20/1.

EXAMPLE 3

To 100 parts of Oil B is added 3 parts of 4,4'-methylenebis(2-tert-butyl-6-methylphenol) and 1 part of calcium petroleum sulfonate. This composition is blended with Fuel F in fuel/oil ratio of 25/1.

EXAMPLE 4

The procedure of Example 3 is followed except that the phenolic compound is 4,4'-methylenebis(2,6-diisopropylphenol) and the detergent is a copolymer of lauryl methacrylate and N,N-dimethylaminoethyl methacrylate.

EXAMPLE 5

To 100 parts of Oil F is added 1 parts of 4,4'-methylenebis(2-ethyl-6-tert-octylphenol), 2.8 parts of a detergent made up of a mixture of octanoic acid and its amide with sec-octyl amine and 1.7 parts of ethylene dibromide. This is blended with Fuel B in fuel/oil ratio of 15/1 and in fuel/oil ratio of 30/1.

EXAMPLE 6

To 100 parts of Oil G are added 1.5 parts of 4,4'methylenebis[2-tert-amyl-6-(2'-hexyl)phenol] and 0.5 part of ethylene dibromide. This composition is blended with Fuel D in fuel/oil ratio of 28/1.

EXAMPLE 7

To 100 parts of Oil A are added 10 parts of 4,4'methylenebis(2,6-di-tert-butylphenol) and 1.5 parts of the amide of decanoic acid with secondary decyl amine. This composition is blended with Fuel C in fuel/oil ratio of 18/1.

Table VLUBRICATING OILS OF THIS INVENTION

	Viscosity SUS at—		Viscosity	Percent	Percent	Percent	Percent	Percent
Oil	100° F.	210° F.	index	sulfate	barium	calcium	phosphorus	zine
A B	307 462	54.3 61.8	108.5 98.5	0. 4 0. 2	0.16	Trace Trace	0. 040	0. 051
D E	749 698 718	59. 5 63. 7 58. 4	4. 0 52. 0 2. 5	$\begin{array}{c} 0.4 \\ 0.2 \end{array}$	0.39	Trace Trace	0.032	
F G	531 484	86. 8 68. 0	129. 5 116. 0	0.38 1.5	0.80	Trace 0. 052		

Table VI

	TY	PICAL FU	ELS OF TH	IIS INVEN	TION		
Fuels	Alkyllead, ml./gallon	Gravity, ° API	Initial boiling temperature, ° F.	Research octane number	Aromatics	Olefins	Saturates
A	3.13 (TML) 2.58 (TEL)	59. 0 60. 2	93 93	\$\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	22. 5 25. 5	30. 5 14. 0	47. 0 60. 5
C	0.05 (TEL)	69.9	94	\$ 58.7 58.8	3.5	0. 0	96.5
D E F	0.84 (TEL) 1.50 (TML) 1.48 (Mixture) None	58.4 63.3 64.3 61.1	100 91 95 97	\$\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	34.9 15.0 9.5 11.5	23. 5 27. 5 28. 0 28. 0	41.6 57.5 62.5 60.5

When alkyllead is present, it is formulated as "Motor Mix." TML=tetramethyllead.
TEL=tetraethyllead.
Mixture=equilibrium mixture of tetramethyllead, trimethylethyllead, dimethyldiethyllead, trimethylethyllead, and tetraethyllead, formed by chemical redistribution of a mixture of 50 mol percent tetramethyllead and 50 mol percent tetraethyllead.

To the oil of Example 7 is added 1.0 percent by weight of ethylene dibromide. This composition is blended with Fuel E in fuel/oil ratio of 20/1.

EXAMPLE 9

The oil of Example 8 is blended with Fuel G in the fuel/oil ratio of 30/1.

We claim:

1. As a new composition of matter a fuel/oil mixture 10 especially adapted for use in two-cycle engines comprising a major proportion of a hydrocarbon fuel of the gasoline boiling range and a minor proportion of a lubricating hydrocarbon mineral oil, the weight ratio of said fuel to said oil being at least above 15/1, said composition containing as an additive therefor from 0.05 to 10.0 weight percent, based on the oil, of a compound having the formula

wherein R is an alkyl group of 1-8 carbon atoms and R₁ is an alpha-branched alkyl group of 3-8 carbon atoms.

2. The composition of claim 1 wherein R and R₁ are alpha-branched alkyl groups containing 3-8 carbon atoms.

3. The composition of claim 2 wherein said compound

is 4,4'-methylenebis(2,6-di-tert-butylphenol).

4. As a new composition of matter a fuel/oil mixture especially adapted for use in two-cycle engines comprising a major proportion of a leaded hydrocarbon fuel of the gasoline boiling range and a minor proportion of a lubricating hydrocarbon mineral oil, the weight ratio of said fuel to said oil being at least about 15/1, said composition containing as an additive therefor from 0.05 to 10.0 weight percent, based on the oil, of a compound having the formula

$$R$$
 CH_2
 CH_3
 CH_3

wherein R is an alkyl group of 1-8 carbon atoms and R₁ is an alpha-branched alkyl group of 3-8 carbon atoms.

5. A composition especially adapted for blending with two-cycle engine fuel, said composition comprising a major proportion of a lubricating hydrocarbon mineral oil containing 0.05 to 10.0 weight percent of a compound having the formula

$$HO \longrightarrow CH_2 \longrightarrow OH$$

wherein R is an alkyl group of 1-8 carbon atoms and R₁ is an alpha-branched alkyl group of 3-8 carbon atoms 60 and additionally containing an oil soluble detergent in amount sufficient to substantially reduce sludge formation in the two-cycle engine.

6. A composition especially adapted for blending with two-cycle engine fuel, said composition comprising a major proportion of a lubricating hydrocarbon mineral oil containing 0.05 to 10.0 weight percent of a compound having the formula

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wherein R is an alkyl group of 1-8 carbon atoms and R₁ is an alpha-branched alkyl group of 3-8 carbon atoms and additionally containing 0.5 to 5 weight percent of an amide having the formula

wherein R₂ is an alphatic hydrocarbon radical of 5-9 carbon atoms and R₃ and R₄ are aliphatic hydrocarbon radicals of 6-10 carbon atoms.

7. A composition especially adapted for blending with two-cycle engine fuel, said composition comprising a major proportion of a lubricating hydrocarbon mineral oil containing 0.05 to 10.0 weight percent of a compound having the formula

$$OH$$
 R_1
 R
 R
 R_1
 R_1

wherein R is an alkyl group of 1-8 carbon atoms and R₁ is an alpha-branched alkyl group of 3-8 carbon atoms, 0.5 to 5 percent of an amide having the formula

$$\begin{array}{cccc}
O & R_3 \\
R_2-C-N & R_4
\end{array}$$

35 wherein R₂ is an aliphatic hydrocarbon radical of 5-9 carbon atoms and R_3 and R_4 are aliphatic hydrocarbon radicals of 6-10 carbon atoms, and additionally containing 0.5 to 7.5 weight percent of ethylene dibromide.

8. The method of operating a two-cycle spark ignition 40 internal combustion engine which comprises as the fuel supplying step introducing into the combustion chamber a fuel/oil mixture, the weight ratio of said fuel to said oil being at least about 15/1, said mixture containing as an additive therefor a compound having the formula

$$R$$
 CH_2
 CH_2
 OH

wherein R is an alkyl group of 1-8 carbon atoms and R₁ is an alpha-branched alkyl group of 3-8 carbon atoms, igniting said fuel/oil mixture in said combustion chamber, thereby producing gaseous combustion products, and causing said combustion products to act on a piston, thereby producing a driving force.

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DANIEL E. WYMAN, Primary Examiner.