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FUEL COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

A liquid fuel composition containing as a smoke suppressant an overbased carbonated, alkaline earth metal sulfurized phenate or naphtholate.

This invention relates to improving the combustion characteristics of fuels. More particularly it relates to the reduction of smoke tendencies of hydrocarbon oil fuels.

It is well known that fuel oils, including the middle distillate and heavier fuel oils, that can be burned both in automotive engines and oil burners, are often accompanied by the formation of smoke. Generally, smoke formation accompanies the combustion of hydrocarbon oils when the combustion conditions are not at an optimum, for example when the air-fuel mixture is not uniform. Improvements in engine or burner design cannot always inhibit smoke.

The problem is notably present in the operation of diesel engines. Very often diesel fuels are burned with an excessive amount of smoke and soot formation and there is a corresponding noticeable decrease in engine efficiency and power in engine performance.

It is therefore a primary object of this invention to inhibit the tendency for fuel oils to form smoke during combustion. A further object is to provide novel hydrocarbon oil fuel compositions. Another object is to provide diesel fuels which will not undergo undue loss of engine power in operation. These other objects will become more apparent from the following disclosure.

According to the present invention it has been discovered that the desired improvements in liquid fuels, such as non-lubricating petroleum distillates and heavier fuel oils, are obtained by incorporating in such liquid fuels a minor proportion of an overbased, sulfurized alkaline earth metal organophenate or organonaphtholate. The preferred compositions of this invention contain a product obtained by reacting together an anhydrous mixture of carbon dioxide, alkaline earth metal oxide and methanol wherein the mole ratio of carbon dioxide to metal oxide is in the range of 0.4 to 0.8 and then by reacting the product of this reaction with an organo-substituted phenol or naphthol sulfide. Preferably the metal is calcium and the organo substituent is an alkyl group having from 4 to 30 carbon atoms, although overbased salts of other metals or of non-alkyl substituents may be employed. For the purpose of this invention, the salts may alternatively be referred to as sulfurized organophenates or organophenol sulfides. Either term is acceptable.

The preferred calcium derivatives found useful in this invention are the overbased, sulfurized calcium organophenates described in U.S. patent application No. 500,258 filed on Oct. 21, 1965, now U.S. 3,350,310. In the above-mentioned application the organophenol sulfide contains from about 5% to over 15% sulfur. The phenol sulfide reactants have been previously described in U.S. Patent No. 2,916,454. The corresponding phenol is reacted with a sulfur-containing reagent in a mole ratio of phenol:sulfur reagent ranging from 1:1 to 2:1.

The preferred phenol sulfides, namely the alkylphenol sulfides, contain from 8 to 16 carbon atoms in the organic substituent. Nonylphenol sulfide and dodecylphenol sulfide are particularly preferred according to this invention. In addition to alkyl, other suitable groups on the phenol nucleus include aryl, aralkyl, alkaryl, haloalkyl, haloaryl; alkoxy and aryloxy; alkenyl; and the like.

The calcium oxide-methanol-carbon dioxide reaction product may be formed separately and then combined with the phenol sulfide or all four reactants may be mixed together. The temperature during the initial stage of this reaction may range from about 10° C. to 30° C.; if a diluent is present in the reaction mixture during carbonation the temperature may range up to about 65° C. These diluents include mineral oil, or hydrocarbons, both alkyl aromatic hydrocarbons, or halogenated hydrocarbons, which are non-reactive with the reaction mixture under the conditions used to form the products. Solvent refined mineral oils are most conveniently used. High calcium containing salts may require a solvent for both the reaction mixture and the product. Such a solvent is called a "co-solvent" for the purpose of this invention. Hydrocarbon fluids and halogen-containing fluids which are inert to the reaction mixture are used. Chlorobenzene and carbon tetrachloride are of special interest as co-solvents.

It may be also desirable to treat the finished product with a further carbon dioxide charge. It has been found that this "after-carbonation" step provides additional improvements in the product, such as storage clarity.

The amount of additive used in fuel compositions of this invention may range from about 0.05% to about 10% by weight and preferably from about 0.1% to about 2% by weight. The base fluid may include diesel fuels or other hydrocarbon fractions heavier than gasoline ordinarily employed as fuels in compression-ignition engines. Contemplated in this invention are the number 1, 2 and 3 fuel oils used in heating and also jet combustion fuels.

The following example is presented for the purpose of illustrating the invention more clearly although this invention is not to be limited by any specific example. Parts and percentages are deemed to be on a weight basis.

EXAMPLE

Into a reaction vessel were added 182 grams of dodecylphenol sulfide (as a 50% solution in solvent-refined mineral oil), 100 ml. of anhydrous methanol and 100 ml. of chlorobenzene. This mixture was stirred and a homogeneous solution was obtained. Into the solution was added 45 grams (0.79 mole) of calcium oxide. Carbon dioxide was introduced into the reaction vessel at a rate of about 400 ml. per minute for 23 minutes providing an uptake of 20 grams (0.555 mole) of carbon dioxide, the temperature having been maintained in the range of about 41° to 54° C. The CO_2/Ca mole ratio was about 0.57. The methanol was removed by distillation and 20 grams of a solvent refined mineral oil were added. The resulting product after filtration had the following analysis:

	Percent
Calcium	8.61
Carbon dioxide	6.2
TBN	250

EVALUATION OF PRODUCT

To show that the fuel compositions of this invention are capable of combustion at optimum conditions, a test sample fuel was evaluated in a diesel engine, in this case a General Motors 6V71 engine, for smoke rating and power output.

A typical test procedure is as follows: The engine is started and warmed up using the uninhibited base fuel with the cooling water in the engine controlled to 165° F. After the warm-up is reached, the power output and

smoke rating and fuel time are checked at 1800 r.p.m. with a wide open throttle. The throttle is then set to obtain a 20.5 p.s.i. load at 1800 r.p.m. Smoke and power ratings are taken at 1000 r.p.m., 1800 r.p.m. and 2100 r.p.m. The engine is then operated with the test fuel for five minutes. The power and smoke measurements and fuel time are then taken at 1000, 1200, 1400, 1600, 1800, 2000 and 2100 r.p.m. The engine is then operated again on the uninhibited base fuel, and the power and smoke ratings and the fuel time are checked again at 1800 r.p.m.

The diesel fuel used in this test is a 100% straight-run diesel fuel in the boiling range of approximately 300° to 650° F. The additive is the same as that prepared in the above example. The results are as follows:

Fuel	Additive conc., percent	Smoke rating at 1,800 r.p.m., smoke units*	Power output at 1,800 r.p.m., horsepower
Uninhibited base	0	64	137
Base+additive	0.89	51	167
Base+additive	1.33	44	168

*Smoke rating scale is from 0-clear to 100-black.

The above results show that the uninhibited diesel fuel when consumed in the test engine produces relatively dark smoke; moreover, the power output is low. By the addition of small amounts of the additives of this invention, the color and the intensity of the smoke formed during the combustion of the fuel mixture is substantially reduced and the power output is increased.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of this invention as those skilled in the art will readily understand. Such variations and modifications are said to be within the scope of the appended claims.

I claim:

1. A fuel composition comprising a major proportion of a liquid hydrocarbon base fuel which normally forms smoke during the combustion thereof and a minor proportion sufficient to reduce the said smoke formation of an overbased, sulfurized alkaline earth metal salt prepared by forming an anhydrous mixture of alkaline earth metal oxide, methanol and carbon dioxide at a temperature of

up to about 65° C., wherein the mole ratio of carbon dioxide to metal is in the range of 0.4 to 0.8, and reacting said mixture with a member selected from the group consisting of an organophenol sulfide and an organonaphthol sulfide having from 4 to 30 carbon atoms in the organo group.

2. The composition of claim **1** wherein the overbased, sulfurized alkaline earth metal organophenate is an overbased, sulfurized calcium alkylphenate having from 4 to 30 carbon atoms in the alkyl group.

3. The composition of claim **2** wherein the alkyl group contains 8 to 16 carbon atoms.

4. The composition of claim **3** wherein the overbased, sulfurized calcium alkylphenate is calcium dodecylphenol sulfide.

5. The composition of claim **1** wherein the base fuel is a diesel fuel.

6. The composition of claim **1** wherein the base fuel is a fuel oil.

7. The composition of claim **1** wherein the base fuel is a jet fuel.

8. The composition of claim **1** wherein the base fuel is a heating fuel.

9. The composition of claim **1** wherein said organo group is alkyl.

10. The composition of claim **1** wherein the alkaline earth metal oxide is calcium oxide.

11. The composition of claim **1** wherein the said anhydrous mixture is reacted with an organophenol sulfide.

12. The composition of claim **1** wherein the said anhydrous mixture is reacted with an organonaphthol sulfide.

13. The composition of claim **3** wherein the overbased, sulfurized calcium alkylphenate is calcium nonylphenol sulfide.

14. The composition of claim **1** wherein the said four reactants are combined as one reaction mixture.

References Cited

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