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3,558,292

JET FUEL ADDITIVE

Richard G. Abowd, Jr., Farmington, Mich., assignor to Ethyl Corporation, New York, N.Y., a corporation of Virginia

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9 Claims

ABSTRACT OF THE DISCLOSURE

A method of reducing manganese-containing deposits formed on the surfaces of jet engines from burning fuel containing organomanganese compounds as a smoke reducer is described. The deposits are reduced by adding a non-metallic organic sulfur compound to the organomanganese-containing fuel. The manganese-containing deposit is substantially reduced by the sulfur additive.

Cyclopentadienyl manganese tricarbonyl compounds are useful organomanganese compounds; dialkylxanthates are useful organic sulfur compounds.

BACKGROUND OF THE INVENTION

Smoke produced during the operation of a distillate fuel burning engine, such as a jet engine, is undesirable. It contributes to air pollution. It indicates reduced engine efficiency.

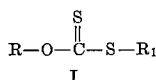
This exhaust smoke may be reduced by adding suitable additives to the fuel. Especially effective additives are certain cyclopentadienyl manganese tricarbonyls, such as (methylcyclopentadienyl)manganese tricarbonyl. U.S. 2,818,417 provides a thorough list of useful compounds of this type, and includes methods of preparing them. Although use of these manganese additives substantially reduces the exhaust smoke, a secondary problem may arise in some instances. On combustion of the fuel containing the manganese compound, manganese-containing deposits are formed on the engine surface which was contacted by the exhaust products. As with many engine deposits, an effective method of reducing these manganese-containing deposits is desirable.

SUMMARY OF THE INVENTION

A method of reducing manganese-containing deposits formed on the surfaces of jet engines which burn fuel containing organomanganese compounds, which comprises adding to said fuel prior to burning a deposit-reducing amount of a non-metallic organic sulfur compound in an amount sufficient to reduce the quantity of said manganese-containing deposit.

DESCRIPTION OF PREFERRED EMBODIMENT

A preferred embodiment of this invention is a method of reducing manganese-containing deposits formed on the surface of a jet engine from burning a fuel containing a smoke-reducing quantity of a cyclopentadienyl manganese tricarbonyl, wherein the cyclopentadienyl radical has up to 17 carbon atoms; which comprises adding to said fuel prior to burning, a deposit-reducing amount of a non-metallic organic sulfur compound having the formula

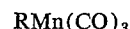


wherein R and R₁ are selected from C₆-C₁₈ aryl groups and C₁-C₁₂ hydrocarbon alkyl groups, and burning the fuel in said engine. Fuel compositions which are used in the preferred method contain 0.025 to about 6.45 grams

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of manganese per gallon as a cyclopentadienyl manganese tricarbonyl and sufficient sulfur compound of Formula I so that the molar ratio of manganese compound:sulfur compound is from about 1:1 to about 3:1. A molar ratio of manganese compound to sulfur compound of about 1:1 to about 2:1 is preferred. Ethyl ethylxanthate and (methylcyclopentadienyl)manganese tricarbonyl in the preferred ratio in the fuel is a most preferred embodiment.

Manganese compounds which are useful as smoke reducers in jet fuels are cyclopentadienyl manganese tricarbonyls having the formula



wherein R is a cyclopentadienyl hydrocarbon radical having from 5 to 17 carbon atoms. U.S. 2,818,417, issued Dec. 31, 1957, contains an extensive disclosure of the type of manganese compounds which are useful. This listing of compounds is incorporated by reference.

(Methylcyclopentadienyl)manganese tricarbonyl is an especially effective smoke reducer.

The concentration of the manganese tricarbonyl in the jet fuels may be varied. Concentrations from 0.025 to about 6.45 grams of manganese per gallon as a cyclopentadienyl manganese tricarbonyl are useful.

By jet fuels, we include distillate hydrocarbons and blends which are useful as fuel for jet engines. These fuels are principally hydrocarbon distillates heavier than gasoline. In other words, they are distillate hydrocarbon fuels having a higher end point than gasoline. They are generally composed of distillate fuels and naphthas and blends of the above, including blends with lighter hydrocarbon fractions. The end point of preferable jet fuels is at least 435° F., and more preferably, greater than 470° F.

Typical jet fuels include JP-3, a mixture of about 70 percent gasoline and 30 percent light distillate having a 90 percent evaporation point of 470° F.; JP-4, a mixture of about 65 percent gasoline and 35 percent light distillate especially designed for high altitude performance; JP-5, an especially fractionated kerosene, and the like.

Non-metallic organic sulfur compounds useful in the present invention are represented by Formula I above. These compounds are oil-dispersible or oil-soluble. By oil-soluble is meant solubility in jet fuels in an amount sufficient to effect deposit reduction as described herein. Oil-soluble organic sulfur compounds of Formula I are preferred.

The compounds of Formula I can also be described as xanthates. Useful xanthates include aryl or alkyl xanthates and mixed alkyl/aryl xanthates. Examples of useful aryl xanthates are:

phenyl phenylxanthate
cresyl cresylxanthate
xylyl xylylxanthate
p-tolyl p-tolylxanthate
3-nitrophenyl 3-nitrophenylxanthate
2-chlorophenyl 2-chlorophenylxanthate
4-aminophenyl 4-aminophenylxanthate
4-hydroxyphenyl 4-hydroxyphenylxanthate
di-4-dodecylphenylxanthate
2-tert-butylphenyl phenylxanthate
phenyl 2-octylphenylxanthate and the like.

Mixed alkyl/aryl xanthates are exemplified by the following compounds:

ethyl-phenylxanthate
phenyl-butylxanthate
indenyl-dodecylxanthate
methyl 2-chlorophenylxanthate
isobutyl- α -naphthylxanthate
tolyl-dodecylxanthate and the like.

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Useful alkyl xanthates are represented by:

n-butyl n-butylxanthate
isopropyl isopropylxanthate
ethyl (2-ethyl-n-hexyl) xanthate
dodecyl dodecylxanthate
methyl-ethylxanthate
tert-butyl-nonylxanthate
ethyl-cyclohexylxanthate and the like.

Ethyl ethylxanthate is a most preferred sulfur compound.

The amount of the sulfur compounds described above which is added to the organomanganese containing fuel may be varied. In general, sufficient sulfur compound is added to the fuel so that the molar ratio of manganese compound to sulfur compound in the fuel is about 1:1 to about 3:1. It is preferred that the amount of organo sulfur compound added give a molar ratio of manganese compound to sulfur compound in the fuel of from about 1:1 to about 2:1.

The following examples illustrate but do not limit jet fuel compositions useful in this invention.

Example 1

To a JP-5 (ASTM-Type A) base fuel was added 2.58 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 11.38 grams/gallon of diethylxanthate.

The manganese compound:sulfur compound molar ratio of this composition is 1:1.

Example 2

To a JP-5 base fuel were added 2.58 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 5.69 grams/gallon of diethylxanthate.

The manganese compound:sulfur compound molar ratio of this composition is 2:1.

Example 3

To a JP-5 base fuel were added 2.58 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 22.76 grams/gallon of diethylxanthate.

The manganese compound:sulfur compound molar ratio of this composition is 1:2.

Example 4

To a JP-5 base fuel are added 1.29 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 5.69 grams/gallon of ethyl ethylxanthate.

The manganese compound:sulfur compound molar ratio of this composition is 1:1.

Example 5

To a JP-5 base fuel are added 3.22 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 5.69 grams/gallon of ethyl ethylxanthate.

The manganese compound:sulfur compound molar ratio of this composition is 2.5:1.

Example 6

To a JP-5 base fuel are added 3.87 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 11.38 grams/gallon of ethyl ethylxanthate.

The manganese compound:sulfur compound molar ratio of this composition is 1.5:1.

Example 7

To a JP-5 base fuel are added 5.16 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 22.76 grams/gallon of ethyl ethylxanthate.

The manganese compound:sulfur compound molar ratio of this composition is 1:1.

Useful jet fuel compositions having the deposit modifying characteristics described below are also prepared (a)

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by using JP-4, JP-3, and the like, in place of JP-5 in the above examples, (b) by using equivalent amounts of compounds such as dodecyl dodecylxanthate, phenyl phenylxanthate, methyl ethylxanthate, cyclohexyl octylxanthate, 2-ethyl-n-hexyl butylxanthate, nonyl nonylxanthate, isopropyl tert-butylxanthate, and the like, in place of the ethyl ethylxanthate in the above examples.

These jet fuel compositions are prepared by simply blending the required amount of manganese-containing smoke reducer and sulfur-containing deposit reducer with the base jet fuel. Conventional fuel blending apparatus and techniques are used.

When a jet fuel containing an organomanganese compound as a smoke reducer is burned in a jet engine, a manganese-containing deposit is formed on parts of the engine which come in contact with the burning fuel and/or its combustion products.

By adding a small amount of a non-metallic sulfur compound to the fuel before burning, the deposit formed is substantially reduced. The reduction in deposit improves engine efficiency and reduces maintenance.

This unexpected deposit-reducing effect was demonstrated by using the following laboratory procedure. This test procedure was designed to simulate jet engine conditions.

A clean metal test specimen was placed in the exhaust opening of a tubular burner fueled with the control fuel, JP-5 containing 2.58 grams/gallon of manganese as (methylcyclopentadienyl)manganese tricarbonyl. The burner was ignited and the test specimen was exposed to the exhaust stream until a certain amount of fuel was burned. The test specimen was then removed from the exhaust stream and weighed. The deposit weight was determined by subtracting the weight of the clean metal test piece from the coated piece.

This control test specimen was coated with a tan-colored, dense, hard deposit. Analysis of the deposit showed that it contained manganese oxides primarily.

A second clean test specimen was placed in the exhaust opening of the jet burner, now fueled with JP-5 fuel containing (methylcyclopentadienyl)manganese tricarbonyl and ethyl ethylxanthate. The jet burner was ignited and the test piece was exposed to the exhaust stream until an amount of this fuel composition equivalent to the control fuel was burned. The coated test piece was then removed from the exhaust stream and weighed. The amount of deposit formed was obtained by subtracting the weight of the clean test specimen from the coated test piece.

Data from a series of such tests is tabulated below.

TABLE 1.—EFFECT OF XANTHATE ON DEPOSIT

	Fuel composition	Amount of deposit, mg.	Percent deposit reduction
Test:			
1.....	JP-5+Mn compound ¹ ..	82	-----
2.....	Example 1.....	63	23
3.....	Example 2.....	60	27

¹ 2.58 grams of manganese (Mn) per gallon as (methylcyclopentadienyl)manganese tricarbonyl.

This data clearly shows the significant reduction in deposit formation effected by the xanthate additives of the present invention. Comparable deposit reduction is obtained using other xanthate additives herein described.

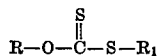
The method and fuels of the present invention are fully described above. It is intended that this invention be limited only within the spirit and lawful scope of the claims which follow.

I claim:

1. A method of reducing manganese containing deposits formed on the surface of a jet engine from burning a fuel containing a smoke-reducing quantity of a cyclopentadienyl manganese tricarbonyl, wherein the cyclopentadienyl radical has up to 17 carbon atoms; which comprises adding to said fuel prior to burning a deposit-

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reducing amount of a non-metallic organic sulfur compound having the formula



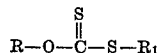
wherein R and R₁ are independently selected from C₆-C₁₈ aryl groups and C₁-C₁₂ hydrocarbon alkyl groups, and burning the fuel containing said cyclopentadienyl manganese tricarbonyl and said non-metallic organic sulfur compound in said engine.

2. The method of claim 1 wherein the amount of sulfur compound present is sufficient to give a molar ratio of manganese compound to sulfur compound of from about 1:1 to about 3:1.

3. The method of claim 2 wherein said sulfur compound is diethyl xanthate.

4. The method of claim 3 wherein said cyclopentadienyl manganese tricarbonyl is (methylcyclopentadienyl)manganese tricarbonyl and said molar ratio is 1:1 to 2:1.

5. Jet fuel containing a smoke reducing quantity of a cyclopentadienyl manganese tricarbonyl wherein the cyclopentadienyl radical has up to 17 carbon atoms and a deposit reducing amount of a non-metallic organic sulfur compound having the formula



wherein R and R₁ are independently selected from C₆-C₁₈

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aryl groups and C₁-C₁₂ hydrocarbon alkyl groups, such that the molar ratio of said cyclopentadienyl manganese tricarbonyl to said organic sulfur compound is from about 1:1 to about 3:1.

6. Jet fuel of claim 5 wherein said cyclopentadienyl manganese tricarbonyl is (methylcyclopentadienyl)manganese tricarbonyl.

7. Jet fuel of claim 5 wherein said organic sulfur compound is diethyl xanthate.

8. Jet fuel of claim 7 wherein said cyclopentadienyl manganese tricarbonyl is (methylcyclopentadienyl)manganese tricarbonyl.

9. Jet fuel of claim 8 wherein said molar ratio is 1:1 to about 2:1.

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DANIEL E. WYMAN, Primary Examiner

Y. H. SMITH, Assistant Examiner

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