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3,442,631

JET ENGINE DEPOSIT MODIFICATION

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U.S. Cl. 44-68

6 Claims

ABSTRACT OF THE DISCLOSURE

A method of modifying manganese containing deposits formed on the surfaces of jet engines from burning fuel containing organomanganese compound as a smoke reducer is described. The deposits are modified by adding a silicone to the organomanganese containing fuel. The manganese containing deposit is so modified by the silicone additive that its cohesive and adhesive tendencies are reduced.

Cyclopentadienyl manganese tricarbonyl compounds are useful organomanganese compounds; methyl polysiloxanes having a viscosity at 25° C. of from about 0.6 to about 100,000 centistokes are useful silicones.

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 formed on the engine surface which are contacted by the exhaust products. As with many engine deposits, an effective method of modifying these manganese containing deposits so that they may be more readily removed from said engine surfaces is desirable.

SUMMARY OF THE INVENTION

A method of modifying 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 modifying amount of a methyl polysiloxane in an amount sufficient to reduce the cohesive and adhesive tendency of said manganese containing deposit.

By so modifying the manganese containing deposits mentioned above, the deposits are more readily removed from the engine surfaces.

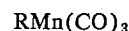
DESCRIPTION OF THE PREFERRED EMBODIMENTS

An embodiment of this invention is a method of modifying manganese containing deposits formed on the surfaces of jet engines which burn fuel containing organomanganese smoke reducers, especially cyclopentadienyl manganese tricarbonyls having up to 17 carbon atoms, which comprises adding a deposit modifying amount of a methyl polysiloxane having a viscosity at 25° C. of from about 0.6 to about 150,000 centistokes. The deposit modifying amount of methyl polysiloxane is sufficient to give an atomic ratio of Mn:Si of from about 0.5:1 to about 1:0.01. In a preferred embodiment the methyl polysiloxane has a viscosity at 25° C. of from about 0.6

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to about 60,000 centistokes. In a more preferred embodiment, the preferred methyl polysiloxanes are present in the fuel in amounts sufficient to give an Si:Mn atomic ratio of about 1:1. In a most preferred embodiment, the Si:Mn atomic ratio is 1:1 and the methyl polysiloxane has a viscosity at 25° C. of about 0.6 centistoke.

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.

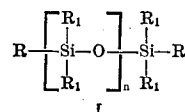
(Methylcyclopentadienyl)manganese tricarbonyl is an especially effective smoke reducer.

The concentration of the manganese tricarbonyl in the jet fuel 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; ASTM Type-A fuel and the like.

Silicones used in this invention are the alkyl polysiloxanes. These polysiloxanes are characterized in that they contain as a repeating unit a silicon atom which is bound directly to two alkyl radicals and to at least one oxygen atom which is in turn bound to a second silicon atom. Their characteristic structure is represented by the following formula:



wherein R₁ is a C₁-C₄ hydrocarbon alkyl group, R is selected from C₁-C₄ hydrocarbon alkyl groups, C₁ to C₄ alkoxy groups, and the hydroxy group, and n is an integer from 1 to about 2,000. Alkyl polysiloxanes (also referred to herein as silicones) of Formula I in which R₁ is methyl are preferred silicones. The term methyl polysiloxanes is also used to designate these preferred silicones. The end groups, that is, the R groups in Formula I, in these preferred silicones can be alkoxy groups such as methoxy, ethoxy, butoxy, and the like, and methyl groups.

Especially preferred silicones are the methyl polysiloxanes in which R and R₁ of Formula I are methyl groups.

These alkyl polysiloxanes vary in consistency from very low viscosity, water-like fluids to heavy, grease-like materials. The consistency of these silicones is related directly to their molecular weight—the higher the molecular weight, the higher the viscosity. Thus, the higher the value of n in Formula I, the greater the number of siloxane units and, therefore, the greater the molecular weight. Since the molecular weight is directly related to the viscosity

of the silicones, these materials are also characterized by their viscosity. The silicones having Formula I which are useful are those having a viscosity at 25° C. of from about 0.6 to about 100,000 centistokes. Silicones having a viscosity at 25° C. of from about 0.6 to about 60,000 centistokes are preferred. Formula I silicones, and especially the methyl polysiloxanes described above, having a viscosity at 25° C. of from about 0.6 to about 3,000 centistokes are especially preferred.

Methyl polysiloxanes wherein R and R₁ in Formula I are methyl groups and which have a viscosity at 25° C. of about 0.6 to about 1,000 centistokes are most preferred.

The amount of silicone having Formula I which is added to the cyclopentadienyl manganese tricarbonyl containing fuel may be varied. In general, sufficient silicone is added to the fuel so that the atomic ratio of silicon (Si):manganese (Mn) in the fuel is about 0.01:1 to about 1:0.5. It is preferred that the amount of silicone added gives an atomic ratio of Si:Mn in the fuel of about 1:1.

Following are examples of jet fuel compositions useful in this invention. These examples illustrate but do not limit this invention.

All silicone (or polysiloxane) viscosities given below are at 25° C. unless otherwise specified.

EXAMPLE 1

To an ASTM-Type A base fuel were added 2.58 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 1.3 grams/gallon of Dow-Corning-200, 0.65 centistoke viscosity silicone fluid. Dow-Corning-200 is the trade name for a series of methyl polysiloxanes of different molecular weight, further identified by their viscosity.

The Mn:Si atomic ratio of this composition is 1:1.

EXAMPLE 2

To an ASTM-Type A base fuel were added 2.58 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 0.65 gram/gallon of Dow-Corning-200, 0.65 centistoke viscosity, silicone fluid.

The Mn:Si atomic ratio of this composition is 1:0.5.

EXAMPLE 3

To a JP-5 base fuel are added 1.29 grams/gallon of (methylcyclopentadienyl)manganese tricarbonyl and 1.3 grams/gallon of Dow-Corning-200, 0.65 centistoke viscosity, silicone fluid.

The Mn:Si atomic ratio of this composition is 0.5:1.

EXAMPLE 4

To a JP-5 base fuel are added 2.58 grams/gallon of (methylcyclopentadienyl)manganese tricarbonyl and 0.13 gram/gallon of Dow-Corning-200, 0.65 centistoke viscosity, silicone fluid.

The Mn:Si atomic ratio of this composition is 1:0.1.

EXAMPLE 5

To a JP-5 base fuel are added 2.58 grams/gallon of (methylcyclopentadienyl)manganese tricarbonyl and 0.065 gram/gallon of Dow-Corning-200, 0.65 centistoke viscosity, silicone fluid.

EXAMPLE 6

To a JP-5 base fuel are added 2.58 grams/gallon of (methylcyclopentadienyl)manganese tricarbonyl and 0.033 gram/gallon of Dow-Corning-200, 0.65 centistoke viscosity, silicone fluid.

The Mn:Si atomic ratio of this composition is 1:0.025.

EXAMPLE 7

To a JP-5 base fuel are added 2.58 grams/gallon of (methylcyclopentadienyl)manganese tricarbonyl and 0.013 gram/gallon of Dow-Corning-200, 0.65 centistoke viscosity, silicone fluid.

The Mn:Si atomic ratio of this composition is 1:0.01.

Useful jet fuel compositions are also prepared (a) by using JP-4, JP-3 and the like in place of the base fuel

in the above examples, and (b) by using equivalent amounts of methyl polysiloxanes having viscosities of about 65,000 centistokes (cs.), about 3,000 cs., about 15 cs., about 20 cs., about 5 cs., about 2 cs., and the like in place of the 0.65 cs. silicone fluid in the above examples.

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

Often, 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. This deposit is light colored, is dense (good cohesion) and generally adheres to the metal surface it contacts. It is not friable, does not readily flake, and can be removed from the metal surface only with difficulty, as for example, by heavy mechanical brushing.

In direct contrast and quite unexpectedly, by adding a small amount of silicone of Formula I to the fuel before burning, the deposit formed is modified so that it becomes soft (low cohesion), and friable; it tends to flake readily. Thus modified, the deposit is more easily removed from the metal surface, as for example, by light brushing or by rice blasting.

This unexpected deposit modifying 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, ASTM-Type A fuel 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 examined.

This control test specimen was coated with a light tan colored, dense, hard deposit. Analysis of the deposit showed that it contained manganese oxides primarily. This deposit did not flake off; it could not be removed by directing a stream of air at it nor by light hand brushing. In other words, the manganese containing deposit showed good cohesion and good adhesion and, therefore, could be removed only with difficulty.

A second clean test specimen was placed in the exhaust opening of the tubular burner, now fueled with the fuel composition of Example 1 (fuel+Mn compound+silicone). The jet burner was ignited and the test piece was exposed to the exhaust stream until an amount of Example 1 fuel equivalent to the control fuel was burned. The coated test piece was then removed from the exhaust stream and examined.

The modified deposit obtained from burning Example 1 fuel was a fluffy, soft, brown colored material. It tended to flake off easily; it tended to be readily removed from the metal surface by directing a light stream of air at it or by light hand brushing.

The modified deposit obtained from burning the Example 2 fuel composition was identical in nature to that obtained from burning Example 1 fuel.

Thus, this clearly shows that the addition of a small amount of a silicone to a fuel containing a cyclopentadienyl manganese tricarbonyl smoke reducer significantly alters the nature of the manganese-containing deposit formed on a jet engine metal surface from burning the fuel. The modified deposit affords the advantage of being more readily removed or less readily retained. Thus, the modified deposit can be removed from the engine surfaces by relatively mild means such as by using a jet of air or a stream of water to blow it off or by light mechanical brushing. In either case, the danger of damaging the engine surface during the cleaning operation would be reduced.

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Besides being easier to remove from the engine surface after operation, the modified deposit offers a self-cleaning feature. Thus, because of its tendency to flake readily, the deposit may be loosened by mechanical forces resulting from normal engine operation and/or blown out of the engine by aerodynamic forces.

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 modifying 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 modifying amount of a methyl polysiloxane having a viscosity at 25° C. of from about 0.6 to about 100,000 centistokes, and burning said fuel containing said cyclopentadienyl manganese tricarbonyl and said methyl polysiloxane in said engine.

2. The method of claim 1 wherein the amount of methyl polysiloxane present is sufficient to give an atomic ratio of manganese:silicon of from 0.5:1 to about 1:0.01.

3. The method of claim 2 wherein said methyl polysiloxane has a viscosity at 25° C. of from about 0.6 to about 60,000 centistokes.

4. The method of claim 3 wherein said cyclopentadienyl manganese tricarbonyl is (methylcyclopentadienyl) manganese tricarbonyl and said methyl polysiloxane has

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a viscosity at 25° C. of about 0.65 centistokes, and said atomic ratio of silicon:manganese is about 1:1.

5. Jet fuel containing a smoke reducing quantity of (methylcyclopentadienyl)manganese tricarbonyl and methyl polysiloxane having a viscosity at 25° C. of about 0.65 centistoke, in an amount sufficient to give an atomic ratio of silicon:manganese of about 1:1.

6. Jet fuel containing a smoke reducing quantity of a cyclopentadienyl manganese tricarbonyl wherein the cyclopentadienyl radical has up to 17 carbon atoms and methyl polysiloxane, having a viscosity at 25° C. of from about 0.6 to about 60,000 centistokes, in an amount sufficient to give an atomic ratio of manganese:silicon of from 0.5:1 to about 1:0.01.

References Cited

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U.S. Cl. X.R.

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PO-1050
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,442,631 Dated May 6, 1969

Inventor(x) Martin E. Gluckstein

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Example 5, column 3, after line 59, the following paragraph should be added -- The Mn:Si atomic ratio of this composition is 1:0.05. --. In Claim 4, column 5, line 30, "methylcyclopentarienyl" should read -- (methylcyclopentadienyl) --.

SIGNED AND
SEALED
MAR 3 - 1970

(SEAL)
Attest:

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