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3,585,012

JET FUEL ADDITIVE

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11 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 modified by adding a sulfinyl amine to the organomanganese-containing fuel. The manganese-containing deposits are thereby reduced.

Cyclopentadienyl manganese tricarbonyl compounds are useful organomanganese compounds; N-sulfinyl anilines are useful sulfinyl amines.

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.

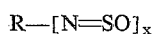
This exhaust smoke may be reduced by adding suitable additives to the fuel. Especially effective additives are certain cyclopentadienyl manganese tricarbonyls, such as (methylcyclopentadienyl)manganese tricarbonyl. U.S. 2,818,417 provides a thorough list of useful compounds of this type, and includes 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 sulfinyl amine in an amount sufficient to reduce the build-up of said manganese-containing deposit.

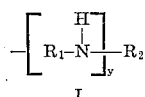
DESCRIPTION OF PREFERRED EMBODIMENT

An 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 sulfinyl amine having the formula



wherein x is an integer from 1 to 4 inclusive and R is selected from

- $C_{11}-C_{18}$ alkyl groups,
- C_6-C_{30} aryl groups,
- C_3-C_{18} alkenyl groups, and
- alkylene amino groups having the formula

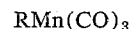


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wherein R_1 and R_2 are independently selected from hydrocarbon alkyl groups having from 2 to about 4 carbon atoms, and y is 0 to 6, and burning the fuel in said engine.

Fuel compositions which are used in the preferred method contain 0.025 to about 6.45 grams of manganese per gallon as a cyclopentadienyl manganese tricarbonyl and sufficient sulfinyl amine of Formula I so that the molar ratio of cyclopentadienyl manganese tricarbonyl:sulfinyl amine is from about 1:1 to about 3:1; a molar ratio of about 2:1 is preferred. N-sulfinyl aniline 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.

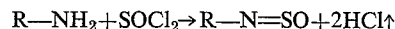
(Methylcyclopentadienyl)manganese tricarbonyl is an especially effective smoke reducer.

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.

The N-sulfinyl amines used in the invention are defined by Formula I above. Methods of preparing these compounds are available in the art. A representative method of preparing these compounds is direct treatment of the parent primary amine with thionyl chloride in a suitable solvent. The reaction is illustrated by the following equation:



As the equation illustrates, an N-sulfinyl amine is a derivative of a primary amine in which the two amine hydrogens are replaced by the $=SO$ radical. In general then, the N-sulfinyl derivative of any suitable primary amine can be used as an additive in the practice of this invention.

Preferred N-sulfinyl amines are those in which the R in Formula I above is selected from the groups (a)-(d) listed above. N-sulfinyl amines in which R is a $C_{11}-C_{18}$ alkyl group include linear, cyclic, and branched alkyl groups with one or more sulfinyl moieties. Representative examples of N-sulfinyl amines are:

- N-sulfinyl-n-methylamine,
- N-sulfinyl-n-octadecylamine,
- N-sulfinyl-2-ethyl-n-hexylamine,
- N-sulfinyl-2,4,4,6,6-pentamethyl-n-heptylamine,
- N-sulfinyl cyclohexylamine,
- N-sulfinyl cyclopentylamine,

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N-sulfinyl cycloctylamine,
N-sulfinyl laurylamine,
and the like.

Representative examples of N-sulfinyl alkyl amines having more than one sulfinyl group are:

N,N'-disulfinyl-1,5-pentanediamine,
N,N'-disulfinyl-1,10-decanediamine,
N,N',N'',N'''-tetrasulfinyl-(2,3-methylamine)
1,4-butanediamine,
N,N',N''-trisulfinyl-1,6,12-dodecanetriamine,
N,N'-disulfinyl-1,18-octadecanediamine,
and the like.

N-sulfinyl amines wherein R in Formula I is a C₆-C₃₀ aryl group can have one or more sulfinyl groups; and R can be an unsubstituted aryl group, substituted aryl group, alkaryl and aralkyl group, mononuclear as well as polynuclear aryl group. Representative examples of these N-sulfinyl aryl amines are:

N-sulfinyl-4-cyclohexylaniline,
N-sulfinyl-2,6-dichloroaniline,
N-sulfinyl-β-naphthylamine,
N-sulfinyl-4-diphenylamine,
N-sulfinyl-4-dodecylaniline,
N-sulfinyl-2,4-didodecylaniline,
N-sulfinyl-2,4-dimethylamine,
N-sulfinyl benzylamine,
N-sulfinyl-α-anthracenylamine,
N-sulfinyl-2-isopropylaniline,
N-sulfinyl-4-octadecylaniline,
N-sulfinyl-2,4,6-triethylaniline,
N-sulfinyl-N'-phenyl-phenylenediamine,
N,N'-disulfinyl-4,4'-diphenyldiamine,
N,N',N''-trisulfinyl-1,3,5-benzenetriamine,
N,N',N'',N'''-tetrasulfinyl-1,2,4,6-benzene tetramine,
N,N'-disulfinyl-benzidine,
N,N'-disulfinyl-3,3'-dichlorobenzidine,
and the like.

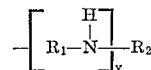
More preferred N-sulfinyl aryl amines are those derived from lower aryl mononuclear mono- and diamines having from 6 to about 18 carbon atoms. Representative examples of these N-sulfinyl aryl amines are:

N-sulfinyl-2-methylaniline,
N-sulfinyl-2-chloroaniline,
N-sulfinyl-4-chloroaniline,
N-sulfinyl-2-sec-butylaniline,
N-sulfinyl-6-tert-butylaniline,
N-sulfinyl-2,6-dimethylaniline,
N-sulfinyl-2,4-dimethylaniline,
N-sulfinylaniline,
N-sulfinylphenethylamine,
N-sulfinyl-3-dodecylaniline,
N-sulfinyl-2,4,6-tribromoaniline,
N-sulfinyl-p-anisidine,
N-sulfinyl-o-nitroaniline,
N-sulfinyl-2,6-diisopropylaniline,
N,N'-disulfinyl-o-phenylenediamine,
N,N'-disulfinyl-2-methyl-p-phenylenediamine,
N-sulfinyl-2,6-dimethylaniline,
N-sulfinyl-3-dimethylaniline,
N-sulfinyl-4-dimethylaniline,
N-sulfinyl-2,4-di-tert-butylaniline,
N,N'-disulfinyl-p-phenylenediamine,
and the like.

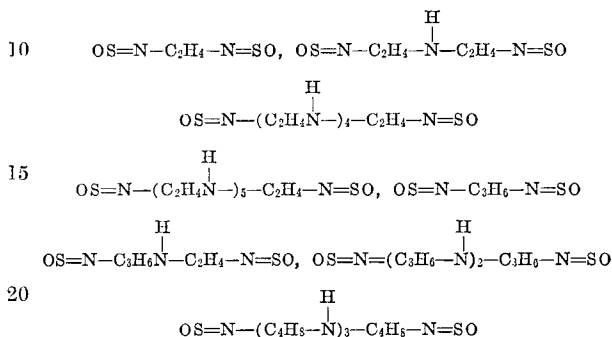
N-sulfinyl amines where R in Formula I is an alkenyl group include mono- as well as poly-unsaturated alkenyl compounds. Representative examples of these N-sulfinyl alkenyl amines are N-sulfinyl allylamine, N-sulfinyl oleylamine, N-sulfinyl linoleylamine, N-sulfinyl-4-pentenyl amine, N-sulfinyl-2-heptenyl amine, N,N'-disulfinyl-6-dodecenyl-1,12-diamine, N-sulfinyl-2-propenylamine, and the like.

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N-sulfinyl amines where R is the group represented by



wherein R₁, R₂ and y are as defined above, are derived from C₂-C₄ alkylene diamines and polyamines. Representative examples of these types of N-sulfinyl amines are:



and the like.

Mixtures of N-sulfinyl amine compounds described above can also be used in the fuels of the present invention.

The amount of the N-sulfinyl amine described above which is added to the organomanganese-containing fuel may be varied. It is preferred that sufficient N-sulfinyl amine is added to the fuel so that the molar ratio of cyclopentadienyl manganese tricarbonyl:N-sulfinyl amine is 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 3.27 grams/gallon of N-sulfinyl aniline.

The cyclopentadienyl manganese tricarbonyl:N-sulfinyl aniline molar ratio of this composition is 2:1.

EXAMPLE 2

To a JP-5 base fuel were added 2.58 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 6.54 grams/gallon of N-sulfinyl aniline.

The cyclopentadienyl manganese tricarbonyl:N-sulfinyl aniline molar ratio of this composition is 1:1.

EXAMPLE 3

To a JP-5 base fuel were added 2.58 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 2.18 grams/gallon of N-sulfinyl aniline.

The cyclopentadienyl manganese tricarbonyl:N-sulfinyl aniline molar ratio of this composition is 3:1.

EXAMPLE 4

To a JP-5 base fuel were added 2.58 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 3.62 grams/gallon of N-sulfinyl-4-methylaniline.

The cyclopentadienyl manganese tricarbonyl:N-sulfinyl amine molar ratio of this composition is 2:1.

EXAMPLE 5

To a JP-5 base fuel are added 1.29 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 11.9 grams/gallon of N-sulfinyl 2,6-didodecylaniline.

The cyclopentadienyl manganese tricarbonyl:N-sulfinyl amine molar ratio of this composition is about 1:1.

EXAMPLE 6

To a JP-5 base fuel are added 5.19 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 15.35 grams/gallon of N-sulfinyl 6-dodecylaniline.

The cyclopentadienyl manganese tricarbonyl:N-sulfinyl amine molar ratio of this composition is about 2:1.

EXAMPLE 7

To a JP-5 base fuel are added 2.58 grams/gallon of Mn as (methylcyclopentadienyl)manganese tricarbonyl and 2.9 grams/gallon of N-sulfinyl 2-ethylhexylamine.

The cyclopentadienyl manganese tricarbonyl:N-sulfinyl amine molar ratio of this composition is 3:1.

Useful jet fuel compositions having the deposit modifying characteristics described below are also prepared (a) 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 N-sulfinyl laurylamine, N-sulfinyl pentylamine, N-sulfinyl octadecylamine, N-sulfinyl 3-pentenylamine, N-sulfinyl linoleylamine, N-sulfinyl β -naphthylamine, $\text{OS}=\text{N}-(\text{C}_2\text{H}_4)_2-\text{C}_2\text{H}_4\text{N}=\text{SO}$, N-sulfinyl 3-nitroaniline, N-sulfinyl N'-sulfinyl-p-phenylenediamine, and the like, in place of the N-sulfinyl amines in the above examples.

These jet fuel compositions are prepared by simply blending the required amount of manganese-containing smoke reducer and N-sulfinyl-containing deposit modifier 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.

Quite unexpectedly, by adding a small amount of an N-sulfinyl amine of Formula I to the fuel before burning, the deposit formed is substantially reduced.

This unexpected deposit-reducing effect of N-sulfinyl amines 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 fuel 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 amount of deposit was determined by subtracting the weight of the clean metal test specimen from the exposed metal test piece.

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.

A second clean test specimen was placed in the exhaust opening of the jet burner, now fueled with the fuel composition of Example 1 (JP-5+Mn compound+N-sulfinyl aniline). 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 weighed. The amount of deposit was obtained by subtracting the weight of the clean test piece from the coated test piece.

Data obtained for these runs is tabulated below.

TABLE 1.—EFFECT OF N-SULFINYL AMINE ON DEPOSIT

Test	Fuel composition	Amount of deposit, mg.	Percent deposit reduction
1	JP-5 plus Mn compound ¹	82	—
2	Example 1	72	12

¹ 2.58 grams of manganese as (methylcyclopentadienyl)manganese tricarbonyl.

The data in Table 1 clearly shows the deposit-reducing effect of the N-sulfinyl amine additive. Comparable deposit reduction is obtained using other N-sulfinyl amines as herein disclosed.

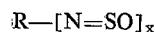
Thus, the additives of the present invention substantially reduce the manganese-containing deposit build-up

in jet engines. This deposit reduction improves the efficiency and increases the life of the jet engine.

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 following claims.

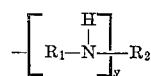
I claim:

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-reducing amount of a sulfinyl amine having the formula



wherein x is an integer from 1 to 4 inclusive and R is selected from

- C_1-C_{18} alkyl groups,
- C_6-C_{30} aryl groups,
- C_3-C_{18} alkenyl groups, and
- alkylene amino groups having the formula



wherein R_1 and R_2 are independently selected from hydrocarbon alkyl groups having from 2 to about 4 carbon atoms, and y is 0 to 6, and burning the fuel containing said cyclopentadienyl manganese tricarbonyl and sulfinyl amine in said engine.

2. The method of claim 1 wherein the amount of said sulfinyl amine present is sufficient to give a molar ratio of said manganese tricarbonyl to sulfinyl amine of from about 1:1 to about 3:1.

3. The method of claim 1 wherein said cyclopentadienyl manganese tricarbonyl is (methylcyclopentadienyl)manganese tricarbonyl.

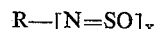
4. The method of claim 3 is a C_6-C_{30} aryl group and said molar ratio is about 2:1.

5. The method claim 4 wherein x is an integer from 1 to 2 inclusive.

6. The method of claim 5 wherein R is a C_6-C_{18} mono-nuclear aryl group.

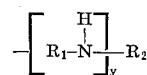
7. The method of claim 5 wherein said organic compound is N-sulfinyl aniline.

8. 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 sulfinyl amine having the formula



wherein x is an integer from 1 to 4 inclusive and R is selected from

- C_1-C_{18} alkyl groups,
- C_6-C_{30} aryl groups,
- C_3-C_{18} alkenyl groups, and
- alkylene amino groups having the formula



wherein R_1 and R_2 are independently selected from hydrogen alkyl groups having from 2 to about 4 carbon atoms, and y is 0 to 6,

such that the molar ratio of said cyclopentadienyl manganese tricarbonyl to said sulfinyl amine is from about 1:1 to about 3:1.

9. Jet fuel of claim 8 wherein said cyclopentadienyl manganese tricarbonyl is (methyl-cyclopentadienyl)manganese tricarbonyl.

10. Jet fuel of claim 9 wherein R is C_6-C_{30} aryl group and said molar ratio is about 2:1 and x is an integer 1 to 2 inclusive.

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11. Jet fuel of claim 10 wherein said sulfinyl amine is N-sulfinyl aniline.

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DANIEL E. WYMAN, Primary Examiner
Y. H. SMITH, Assistant Examiner

U.S. Cl. X.R.

44—72

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,585,012 Dated June 15, 1971

Inventor(s) George C. Licke

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

In Column 5, line 18, that part of the composition
"N'-sulfinyl" should read -- N'-cyclohexyl --;

In Claim 4, line 1, after 3, the phrase -- wherein R --
should be added.

Signed and sealed this 12th day of October 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents