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3,554,801

METHOD OF REMOVING MANGANESE OXIDE DEPOSITS

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10 Claims

A method of removing manganese containing deposits formed on the surfaces of jet engines from burning fuel containing a cyclopentadienyl manganese tricarbonyl as a smoke reducer, by treating the deposit coated surfaces with an aqueous solution of hydroxylamine salt.

Hydroxylamine salts of carboxylic acids are examples of useful compounds.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of Ser. No. 692,321, filed Dec. 21, 1967, now abandoned.

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 are contacted by the exhaust products. As with many engine deposits, an effective method of removing these manganese containing deposits is desirable.

SUMMARY OF THE INVENTION

A method of removing manganese containing deposits formed on the surface of jet engines which burns fuels containing organomanganese compounds, which comprises treating the deposit coated surfaces with an aqueous solution of a salt of hydroxylamine and an acid.

Thus, manganese containing deposits formed in jet engines can be removed by treating the deposit coated surfaces with an aqueous solution of a hydroxylamine salt such as hydroxylamine oxalate. This provides a simple and effective method for cleaning the engine; it is especially advantageous because the engine can be cleaned without disassembling it.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

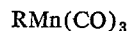
An embodiment of this invention is a method of removing manganese containing deposits formed on the surfaces of a jet engine from burning a fuel containing a smoke reducing quantity of a cyclopentadienyl manganese tricarbonyl having up to 17 carbon atoms, which comprises treating said surfaces with an aqueous solution of a salt of hydroxylamine and an organic acid having up to 18 carbon atoms.

Another embodiment of said method comprises treating the manganese containing deposit coated surface with an

aqueous solution containing up to about 20 percent by weight of the hydroxylamine compounds described above.

In a preferred embodiment the acid portion of the hydroxylamine salt is derived from an organic acid selected from hydrocarbon, alkyl mono- and dicarboxylic acids. The total number of carbon atoms in said organic acids ranges from two to about 18 carbon atoms. In a more preferred embodiment, said organic acids have from 2 to 8 carbon atoms. A most preferred embodiment utilizes the salt of hydroxylamine and oxalic acid.

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 naphtha and blends of the above, including blends with light 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 manganese containing deposit which is formed on the jet engine surfaces comprises a mixture of compounds. Principal components of this mixture are the oxides such as Mn_2O_3 and Mn_3O_4 .

Organic acids which are useful to prepare hydroxylamine salts suitable for the present invention may contain the carboxyl group, the sulfonic acid functional group, the phosphonic acid functional group, the phosphoric acid functional group, and the like. The carboxylic acids, that is, acids containing carboxyl functional groups include monocarboxylic acids and dicarboxylic acids. These carboxylic acids may contain other substituents besides carbon, hydrogen and the carboxyl group, such as for example, hydroxy groups, halogens and the like. Examples of some useful carboxylic acids are trichloroacetic acid, α -bromopropionic acid, 4-hydroxy hexanoic acid, decenoic acid, m-nitrobenzoic acid, glycolic acid, sebacic acid, oleic acid, cyanoacetic acid, cyclohexene carboxylic acid, and the like.

Preferred carboxylic acids are hydrocarbon, alkyl, mono- and dicarboxylic acids having from 2 to 18 carbon atoms. Preferred monocarboxylic acids are propionic acid, stearic acid, dodecanoic acid, 2-ethylhexanoic acid, butanoic acid, 2,4,4-trimethylpentanoic acid, trimethylacetic acid, undecanoic acid, tetradecanoic acid and the like. Preferred dicarboxylic acids are tetradecenedioic acid, octadecanedioic acid, nonanedioic acid, undecanedioic acid, sebacic acid and the like. More preferred carboxylic acids are those having from 2 to about 8 carbon atoms. They are exemplified by acetic acid, octanoic acid, iso-

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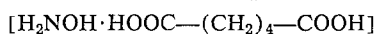
butyric acid, pentanoic acid, adipic acid, suberic acid, malonic acid, glutaric acid, pimelic acid and the like. A most preferred carboxylic acid is oxalic acid.

Sulfonic acids which are useful include the alkyl as well as the benzene and alkyl benzene sulfonic acids. Examples of useful sulfonic acids are dodecylbenzene sulfonic acid, benzene sulfonic acid, 1-octane sulfonic acid, 2-propane sulfonic acid, 2-octadecane sulfonic acid, 1-(4,6-dimethyl) heptane sulfonic acid, p-toluene sulfonic acid and the like. Phosphorus containing organic acids are also useful. Ex-

amples of these phosphorus containing acids are methyl phosphonic acid, octyl dihydrogen phosphate, phenyl phosphonic acid, butyldecylhydrogen phosphate, octadecyl phosphonic acid, dodecyl dihydrogen phosphate, and the like.

Although salts of hydroxylamine and strong mineral acids such as sulfuric acid also remove manganese deposits, they are not as effective as the salts of the preferred organic acids. Data will be presented below illustrating the greater effectiveness of the organic acid hydroxylamine salts.

Hydroxylamine salts useful in this invention include fully neutralized salts and partially neutralized salts. A fully neutralized salt is one in which one molecule of hydroxylamine is provided for each acid hydrogen in the acid molecule. Thus, salts of hydroxylamine and adipic acid can be prepared which contain (1) one mole of hydroxylamine and one mole of adipic acid



or (2) two moles of hydroxylamine and one mole of adipic acid $[(\text{H}_2\text{NOH})_2\cdot\text{HOOC}-(\text{CH}_2)_4-\text{COOH}]$. The former salt is partially neutralized, while the latter salt is fully neutralized. Only acids having more than one acid hydrogen can form partially neutralized salts. A preferred partially neutralized salt is the salt of one mole of hydroxylamine and one mole of oxalic acid.

The concentrations of hydroxylamine salts which are used in the present process may be varied. In general, concentrations of from about 0.001 percent to about 20 percent by weight are useful. Saturated solutions are especially useful.

An outstanding feature of the present invention is that it offers a method of removing manganese containing deposits in a jet engine without requiring its disassembly or its removal from its mounting. Thus, the engine can be cleaned while it is still in place in an airplane fuselage for example, by simply spraying the solution of hydroxylamine salt described above, through the engine, while the engine is being cranked. "Cranking" a jet engine means that the engine is turning but the fuel is not ignited. By cranking the engine, all the engine surfaces which may have a manganese containing deposit become exposed to the spray.

Another method of spraying the solution into the jet engine is to feed it through the fuel feed system between the fuel tank and the combustion area. Using this procedure, the solution will contact only those engine surfaces on which the fuel and exhaust products would impinge. The engine is cranked to insure better contact. In either case, the spray may be continuously recycled if desired, to reduce the volume of solution required. Besides the spraying technique, the engine can be cleaned by immersing it in a suitably designed vessel containing the acid/hydroxyl amine compound solution for a period of time sufficient to dissolve the manganese containing deposits. After such an immersion or after a spray treatment, the engine is generally rinsed with a pure water. A combination of the spray-soak procedure can also be used.

The engine treatment can be carried out either before or after the engine has cooled after being in operation. The solution with which the treatment is carried out may also be warmed, if desired. By treating the engine while hot or by using a hot solution, treatment time to clean

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the engine can be reduced. Heating either the engine surfaces or the solution, however, is not required. Whatever means is used to carry out the engine treatment, the only requirement is that a solution, as herein described contact the manganese containing deposits on the engine surfaces.

The effectiveness of the aqueous solution of hydroxylamine salt treatment was determined in a laboratory procedure using a metal test specimen on which was deposited a manganese-containing deposit. The test specimen was prepared by allowing the exhaust stream from burning a jet fuel containing about 0.1 volume percent (1.29 g./gal. of manganese) of (methylcyclopentadienyl) manganese tricarbonyl, to impinge on the metal piece. The manganese containing deposit appeared as a brownish deposit on the metal surface. This test specimen was then placed in a chamber where it was subjected to an alternate spray/soak treatment. This treatment consists of (a) spraying (1.48 gal. per hour at 10 p.s.i.g.) the test piece with the test solution for five minutes while the test piece is spinning and (b) then allowing the wet specimen to set for an additional five minutes; this spray/soak cycle is repeated three times. At the end of the treatment cycle, the test piece is rinsed with clear water and is then allowed to dry. The treated test piece is then weighed. The loss in deposit weight (the amount of deposit dissolved) is recorded as percent deposit loss.

Aqueous solutions of hydroxylamine sulfate (for comparison) and hydroxylamine oxalate (one mole hydroxylamine: one mole oxalic acid), where evaluated using this spray/soak test procedure. The data obtained is presented in the following table. All percentages are by weight.

TABLE 1.—DEPOSIT REMOVAL IN SPRAY/SOAK TREATMENT

Test solution	Test solution temperature	Percent Mn containing deposit removed
Water.....	R. T. ¹	0
Water plus 10 percent $(\text{H}_2\text{NHO})_2\cdot\text{H}_2\text{SO}_4$	R. T. ¹	31
Water plus 10 percent $\text{H}_2\text{NOH}\cdot\text{HOOC}-\text{COOH}$	R. T. ¹	46

¹ R.T. = Room temperature.

The data in Table 1 shows that the



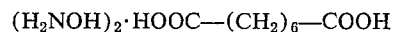
solution removes 46% of the manganese containing deposit whereas the $(\text{H}_2\text{NOH})_2\cdot\text{H}_2\text{SO}_4$ solution removes only 31% of the deposit.

Similar deposit removal is obtained using any of the following aqueous solutions instead of the

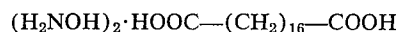


solutions.

- (1) 20% solution of $\text{H}_2\text{NOH}\cdot\text{CH}_3-\text{COOH}$
- (2) 0.001% solution of $\text{H}_2\text{NOH}\cdot\text{CH}_3-(\text{CH}_2)_{16}-\text{COOH}$
- (3) 0.05% solution of $\text{H}_2\text{NOH}\cdot\text{CH}_3-(\text{CH}_2)_7-\text{COOH}$
- (4) 1.0% solution of $\text{H}_2\text{NOH}\cdot\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$
- (5) 3.0% solution of



- (6) 12% solution of



- (7) 4% solution of salt of H_2NOH and benzenesulfonic acid
- (8) 6% solution of $\text{H}_2\text{NOH}\cdot\text{Cl}_3\text{C}-\text{COOH}$
- (9) 1.5% solution of salt of H_2NOH and octyl phosphonic acid.

The results presented above clearly demonstrate that the manganese containing deposits formed on jet engine parts can be very effectively removed by treatment with an aqueous solution of a hydroxylamine salt of an organic acid as herein described. The manganese containing deposit has been described as that being formed from burning jet fuel containing a cyclopentadienyl manganese tri-

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carbonyl. However, it is considered within the scope of the present invention that the present method will be effective for removing manganese containing deposits obtained on burning jet fuel containing other manganese bearing additives.

The process of the present invention is described above. It is intended that the present invention be limited only within the lawful scope and extent of the following claims.

What is claimed is:

1. A method of removing manganese containing deposits formed on surfaces of a jet engine from burning a fuel containing a cyclopentadienyl manganese tricarbonyl compound, wherein the cyclopentadienyl radical has up to 17 carbon atoms, which comprises treating said surfaces with an aqueous solution of a salt of hydroxylamine and an organic acid having from 2 to about 18 carbon atoms selected from the group consisting of

- (a) hydrocarbon alkyl carboxylic acids containing up to two carboxyl groups,
- (b) alkyl and aryl sulfonic acids,
- (c) alkyl and aryl phosphonic acids, and
- (d) alkyl phosphoric acids.

2. The method of claim 1 wherein said cyclopentadienyl manganese tricarbonyl is (methylcyclopentadienyl) manganese tricarbonyl at a concentration in said fuel of from 0.025 to about 6.45 grams of manganese per gallon.

3. The method of claim 2 wherein said aqueous solution contains from 0.001% to about 20% by weight of said hydroxylamine salt.

4. The method of claim 1 wherein said aqueous solution contains from 0.001% to about 20% by weight of said hydroxylamine salt.

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5. The method of claim 4 wherein said acid is a hydrocarbon alkyl carboxylic acid having from 2 to about 18 carbon atoms.

6. The method of claim 4 wherein said acid is a hydrocarbon alkyl carboxylic acid having from 2 to about 8 carbon atoms.

7. The method of claim 6 wherein said acid is a dicarboxylic acid.

8. The method of claim 7 wherein said acid is oxalic acid.

9. The method of claim 8 wherein said salt is $H_2NOH \cdot HOOC-COOH$.

10. The method of claim 9 wherein said fuel contains about 1.29 grams per gallon of manganese as (methylcyclopentadienyl)manganese tricarbonyl and said aqueous solution contains 10% by weight of said salt.

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