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METHOD OF REMOVING MANGANESE OXIDE DEPOSITS

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27 Claims

ABSTRACT OF THE DISCLOSURE

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 a mineral acid, an organic acid having an ionization constant at 25° C. greater than 10⁻³, either in the presence or absence of H₂O₂ or an H₂O₂ source as a promoter.

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 surfaces of jet engines which burn fuels containing organo manganese compounds, which comprises treating the deposit coated surfaces with an aqueous solution of a mineral acid, a halogenated monocarboxylic acid, or an alkyl or aryl sulfonic acid, either with or without hydrogen peroxide as a promoter.

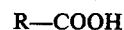
Thus, manganese containing deposits formed in jet engines can be removed for example, by treating the deposit coated surfaces with an aqueous solution of trichloroacetic acid or trichloroacetic acid and hydrogen peroxide. This provides a simple and effective method for cleaning the engine; it is especially 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 surface with an aqueous solution of an acid selected from simple inorganic mineral acids and organic acids (a) having an ionization constant, at 25°

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C., greater than 10⁻³ and (b) having a formula selected from



(I)

wherein R is a group selected from halogen-substituted C₂-C₆ alkyl and halogen-substituted phenyl, and



(II)

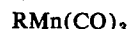
wherein R₁ is a group selected from C₂-C₁₈ hydrocarbon alkyl, phenyl, and C₁-C₁₈ hydrocarbon alkyl-substituted phenyl.

Another embodiment of said method comprises treating the manganese containing deposit coated surface with an aqueous solution containing up to about 30 percent by weight of the acids described above.

In another embodiment, the method described above is carried out using the aqueous acid solution containing a promoter quantity of hydrogen peroxide. The promoter is present in a quantity by weight from 0.1 to 1 times the weight of the acid.

In a preferred embodiment using either the promoted or unpromoted aqueous solution, the acid is a mineral acid selected from sulfuric acid and phosphoric acid. In another preferred embodiment the acid is a halogenated acetic 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 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 includes 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 can comprise a mixture of compounds. Principle components of this mixture are the oxides such as Mn₂O₃ and Mn₃O₄.

Acids which are used in this invention include inorganic mineral acids as well as organic acid. Useful inorganic mineral acids are exemplified by sulfuric acid, sulfurous acid, the hydrohalide acids such as HCl, HBr, and the like, orthophosphoric acid, pyrophosphoric acid, phos-

phorous acid and the like, nitric acid, orthoboric acid, metaboric acid and the like. Sulfuric acid and orthophosphoric acid are preferred acids.

Organic acids which are useful (1) have an ionization constant (K_1) at 25° C. greater than 10^{-3} and (2) contain the elements C, H, O and X, where X is a halogen. This invention can also be extended to acids such as 2-methyl-6-nitrobenzoic acid, picric acid, glycerophosphoric acid, o-nitrobenzoic acid, ethyl dihydrogen phosphate, dibutyl hydrogen phosphate, propyl phosphonic acid and the like.

Preferred organic acids are the halogen-substituted monocarboxylic acids having Formula I. The halogen substituent can be iodine, fluorine, chlorine or bromine. The acid may contain one or more halogen atoms. Examples of useful acids are o-iodobenzoic acid, α -bromopropionic acid, α,α -difluorohexanoic acid, β -iodobutyric acid, α -fluoropentanoic acid, β,β -dichlorohexanoic acid, 3,5-diodobenzoic acid and the like. More preferred organic acids are the halogenated acetic acids. These include chloroacetic acid, dichloroacetic acid, bromoacetic acid, iodoacetic acid, fluoroacetic acid, difluoroacetic acid, dibromoacetic acid, trifluoroacetic acid, tribromoacetic acid, triiodoacetic acid and the like. A most preferred halogenated acetic acid is trichloroacetic acid.

Another group of preferred organic acids are the sulfonic acids having Formula II. These acids are aryl and alkyl substituted sulfuric acids, characterized generally by good water solubility. Both straight chain and branched chain hydrocarbon alkyl sulfonic acids are useful. Examples of useful alkyl sulfonic acids are ethane sulfonic acid, octadecane sulfonic acid, decane sulfonic acid, 1,1,3,3,5,5-hexamethylpentane sulfonic acid, octane sulfonic acid, tridecane sulfonic acid, 1,1,3,3-tetramethylbutane sulfonic acid, 1-methylundecane sulfonic acid, 2-methylpropane sulfonic acid and the like.

Useful aryl sulfonic acids are benzene and alkyl benzene sulfonic acids. Examples of useful acids are benzene sulfonic acid, p-toluene sulfonic acid, o-isobutylbenzene sulfonic acid, 2,4-diethylbenzene sulfonic acid, dodecylbenzene sulfonic acid, p-(1,1,3,3-tetramethylbutyl) benzene sulfonic acid, o-isopropylbenzene sulfonic acid, p-decylbenzene sulfonic acid, 2,6-dimethylbenzene sulfonic acid and the like.

Phosphorous containing organic acids are also useful. These include the alkyl and aryl esters of orthophosphoric acid, phosphorous acid, phosphonic acid and the like. Examples of useful esters are methyl dihydrogen phosphate, methyl phosphonic acid, dimethyl phosphate, octadecyl phosphoric acid, phenyl dihydrogen phosphate, dibutyl hydrogen phosphate, dodecyl dihydrogen phosphate, octyl phosphonic acid, propyl dihydrogen phosphite, decyl phosphonic acid, phenyl phosphonic acid and the like.

In another embodiment of this invention, a promoter, hydrogen peroxide, is used in combination with either the inorganic or organic acid in aqueous solution. The hydrogen peroxide makes the aqueous acid solution more effective in removing the manganese containing deposit. The data presented below will illustrate this promoter effect.

Although hydrogen peroxide itself is most conveniently used, compounds which will produce hydrogen peroxide or the peroxide ion (OOH^-) in an aqueous medium may also be used as promoters. Examples of such useful materials are inorganic compounds such as sodium peroxide, potassium peroxide, calcium peroxide, barium peroxide, copper peroxide, zinc peroxide, cadmium peroxide, mercury peroxide, super oxides of mono- and divalent metals and the like; and organic peroxide compounds represented by the formula $\text{L}-\text{O}-\text{O}-\text{L}$ and $\text{L}-\text{O}-\text{O}-\text{H}$ where L is a suitable alkyl or aryl radical, examples of which are dicumyl peroxide, cumyl hydroperoxide, perbenzoic acid, peracetic acid, performic acid, and the like.

The concentration of acid in aqueous solution is not critical. It can vary from about 0.001 percent to about

30 percent by weight. Acid concentrations of from 5–10 percent by weight are conveniently used.

The concentration of hydrogen peroxide used as a promoter in this invention is based on the weight of acid used. Generally, the weight of hydrogen peroxide can range from about 0.1 to about one times the weight of acid present. For example, a 10 weight percent aqueous solution of dichloroacetic acid containing from about one percent to about 10 percent hydrogen peroxide is useful. Solutions containing equal amounts by weight of acid and hydrogen peroxide are especially useful. Where a compound which will produce the hydrogen peroxide in situ is used instead of the hydrogen peroxide itself, a sufficient amount of this hydrogen peroxide source is used to provide hydrogen peroxide in the above described concentration range.

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 a solution of acid or acid and hydrogen peroxide 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 or acid/hydrogen peroxide 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 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 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 acid or acid/hydrogen peroxide aqueous solution 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 weight compared with the test piece before

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treatment represents the amount of deposit dissolved. This is recorded as percent deposit loss. Using this test procedure various acid and acid/hydrogen peroxide solutions were evaluated. The results are presented in the following table. All percentages are by weight.

TABLE 1

Example	Aqueous test solution ¹	Manganese containing deposit removed, percent
1	Water	0
2	13% H ₃ PO ₄	36
3	10% H ₃ PO ₄ , 10% H ₂ O ₂	64
4	10% trichloroacetic acid	36
5	10% trichloroacetic acid, 10% H ₂ O ₂	55.6

¹ All test solutions were at room temperature.

The data in Table 1 clearly illustrates the benefits of the present invention. Example 2 shows that a 10 percent aqueous solution of a mineral acid (H₃PO₄) removed 36 percent of the manganese containing deposit. By adding 10 percent H₂O₂ to the 10 percent H₃PO₄, the amount of deposit removed is almost doubled (64 percent). Examples 4 and 5 illustrate the analogous effectiveness for an organic acid, trichloroacetic acid (K₁ at 25° C. = 1.3 × 10⁻¹) and trichloroacetic acid promoted with hydrogen peroxide.

Deposit removal effectiveness similar to that illustrated by examples 2 and 3 and 4 and 5 above is obtained when the following aqueous solutions are used for treating the manganese containing deposits. All percentages are by weight.

TABLE 2

Example:	Aqueous solution
6	0.001% H ₃ BO ₃
7	0.001% H ₃ BO ₃ +0.001% H ₂ O ₂
8	20% H ₂ SO ₄
9	20% H ₂ SO ₄ +10% H ₂ O ₂
10	15% H ₃ SO ₃
11	15% H ₃ SO ₃ +1.5% H ₂ O ₂
12	12% H ₄ P ₂ O ₇
13	12% H ₄ P ₂ O ₇ +2.4% H ₂ O ₂
14	8% HCl
15	8% HCl+4% H ₂ O ₂
16	3% HNO ₃
17	3% HNO ₃ +0.3% H ₂ O ₂
18	1% H ₃ PO ₃
19	1% H ₃ PO ₃ +0.75% H ₂ O ₂
20	0.5% HBr
21	0.5% HBr+0.5% H ₂ O ₂
22	7% p-toluene sulfonic acid
23	7% p-toluene sulfonic acid+2.5% H ₂ O ₂
24	20% dichloro acetic acid
25	20% dichloro acetic acid+15% Na ₂ O ₂
26	0.01% α-bromo propionic acid
27	0.01% α-bromo propionic acid+0.005% H ₂ O ₂
28	30% trifluoro acetic acid
29	30% trifluoro acetic acid+30% H ₂ O ₂
30	12% β-iodo butyric acid
31	12% β-iodo butyric acid+0.65% H ₂ O ₂
32	11% α,α-dichloro hexanoic acid
33	11% α,α-dichloro hexanoic acid+2.8% H ₂ O ₂
34	6% m-bromo benzoic acid
35	6% m-bromo benzoic acid+0.6% H ₂ O ₂
36	1% 2,4-dichloro benzoic acid
37	1% 2,4-dichloro benzoic acid+0.2% H ₂ O ₂
38	1.5% p-iodo benzoic acid
39	1.5% p-iodo benzoic acid+0.45% H ₂ O ₂
40	5% dimethyl hydrogen phosphate
41	5% dimethyl hydrogen phosphate+2% H ₂ O ₂
42	0.07% butyl phosphonic acid
43	0.07% butyl phosphonic acid+0.06% H ₂ O ₂

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44	10% α-iodo pentanoic acid
45	10% α-iodo pentanoic acid+1.5% H ₂ O ₂
46	0.02% octadecane sulfonic acid
47	0.02% octadecane sulfonic acid+0.005% H ₂ O ₂
48	3% nonane sulfonic acid
49	3% nonane sulfonic acid+1.8% Na ₂ O ₂
50	10% butane sulfonic acid
51	10% butane sulfonic acid+4% H ₂ O ₂
52	7% ethane sulfonic acid
53	7% ethane sulfonic acid+7% H ₂ O ₂
54	4% (1,3-dimethyl)butane sulfonic acid
55	4% (1,3-dimethyl)butane sulfonic acid+4% H ₂ O ₂
56	6% (2-methyl-4,4-dimethyl)pentane sulfonic acid
57	6% (2-methyl-4,4-dimethyl)pentane sulfonic acid+6% H ₂ O ₂
58	2.5% (2-methyl-4,4,6,6,8,8-hexamethyl)nonane sulfonic acid
59	2.5% (2-methyl-4,4,6,6,8,8-hexamethyl)nonane sulfonic acid+1% H ₂ O ₂
60	12% benzene sulfonic acid
61	12% benzene sulfonic acid+7% Na ₂ O ₂
62	25% 2,6-dimethyl benzene sulfonic acid
63	25% 2,6-dimethyl benzene sulfonic acid+23% H ₂ O ₂
64	3.5% p-dodecylbenzene sulfonic acid
65	3.5% p-dodecylbenzene sulfonic acid+3% H ₂ O ₂
66	4.5% o-ethyl benzene sulfonic acid
67	4.5% o-ethyl benzene sulfonic acid+4.5% H ₂ O ₂
68	8% p-tert-butyl benzene sulfonic acid
69	8% p-tert-butyl benzene sulfonic acid+5.2% H ₂ O ₂
70	13% decyl benzene sulfonic acid
71	13% decyl benzene sulfonic acid+7.8% H ₂ O ₂
72	16% o-isobutyl benzene sulfonic acid
73	16% o-isobutyl benzene sulfonic acid+16% H ₂ O ₂
74	9% p-hexylbenzene sulfonic acid
75	9% p-hexylbenzene sulfonic acid+7.2% H ₂ O ₂

In each case, the acid solution containing the hydrogen peroxide removes significantly more manganese containing deposit than the acid solution without the promoter; the improvement in effectiveness (or the promoter effect) is of the same order as that illustrated by Examples 2 and 3 and 4 and 5.

The results presented above clearly demonstrate that the manganese containing deposits formed on jet engine parts can be effectively removed by treatment with an aqueous solution of acid as herein described. They further show the promoter effect of hydrogen peroxide in the acid solution. The manganese containing deposit has been described as that being formed from burning jet fuel containing a cyclopentadienyl manganese tricarbonyl. 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 cyclopentadienyl manganese tricarbonyl compounds wherein said cyclopentadienyl radical has up to 17 carbon atoms, which consists essentially of treating said surfaces with an aqueous solution of an inorganic mineral acid selected from the group consisting of sul-

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furic acid, sulfurous acid, the phosphoric acids, phosphorous acid, the boric acids, hydrochloric acid, hydrobromic acid and nitric acid, wherein said aqueous solution contains from about 0.001 percent to about 30 percent by weight of said acid, and a promoter quantity of a compound selected from the group consisting of hydrogen peroxide, peroxides of mono- and divalent metals and organic peroxide compounds selected from the group consisting of dicumyl peroxide, cumyl hydroperoxide, perbenzoic acid, peracetic acid and performic acid, wherein said quantity of promoter compound is from 0.1 to 1 times the weight of said mineral acid.

2. The method of claim 1 wherein said acid weight percent is about 5 percent to about 10 percent.

3. The method of claim 1 wherein said mineral acid is orthophosphoric acid.

4. The process of claim 1 wherein said promoter compound is hydrogen peroxide.

5. The process of claim 4 wherein the weight percent of said mineral acid is from 5 percent to 10 percent.

6. The method of claim 4 wherein said mineral acid is orthophosphoric acid.

7. The method of claim 4 wherein the weight of hydrogen peroxide is substantially equal to the weight of said mineral acid.

8. The method of claim 5 wherein the weight of hydrogen peroxide is substantially equal to the weight of said mineral acid.

9. The method of claim 7 wherein said mineral acid is orthophosphoric acid.

10. The method of claim 8 wherein said mineral acid is orthophosphoric acid.

11. The method of claim 10 wherein said orthophosphoric acid concentration is 10 percent by weight and said hydrogen peroxide concentration is 10 percent by weight.

12. A method of removing manganese containing deposits formed on surfaces of a jet engine from burning a fuel containing cyclopentadienyl manganese tricarbonyl compounds wherein said cyclopentadienyl radical has up to 17 carbon atoms, which comprises treating said surfaces with an aqueous solution of organic acids (a) having an ionization constant, at 25° C., greater than 10^{-3} and (b) having a formula selected from:

(i) $R-COOH$

wherein R is a group selected from halogen-substituted C_2-C_6 alkyl and halogen-substituted phenyl, and

(ii) R_1-SO_3H

wherein R_1 is a group selected from C_2-C_{18} hydrocarbon alkyl, phenyl, and C_1-C_{18} hydrocarbon alkyl-substituted phenyl, wherein said aqueous solution contains from about 0.001 percent to about 30 percent by weight of said acid.

13. The method of claim 12 wherein said organic acid has the formula (ii) R_1-SO_3H .

14. The method of claim 12 wherein said organic acid

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weight percent is from about 5 percent to about 10 percent.

15. The method of claim 12 wherein said organic acid has the formula (i) $R-COOH$.

16. The method of claim 12 wherein said aqueous solution contains a promoter quantity of a compound selected from the group consisting of hydrogen peroxide, peroxides of mono- and divalent metals and organic peroxide compounds selected from dicumyl peroxide, cumyl hydroperoxide, perbenzoic acid, peracetic acid and performic acid, wherein said quantity of promoter compound is from 0.1 to 1 times the weight of said organic acid.

17. The method of claim 14 wherein said organic acid is trichloroacetic acid.

18. The method of claim 15 wherein said organic acid is a halogenated acetic acid.

19. The method of claim 18 wherein said organic acid is trichloroacetic acid.

20. The method of claim 16 wherein said promoter compound is hydrogen peroxide.

21. The method of claim 20 wherein said organic acid is a halogenated acetic acid.

22. The method of claim 20 wherein the weight of hydrogen peroxide is substantially equal to the weight of said organic acid.

23. The method of claim 21 wherein said organic acid is trichloroacetic acid.

24. The method of claim 22 wherein said organic acid is a halogenated acetic acid.

25. The method of claim 24 wherein the weight of said organic acid is 5 percent to 10 percent.

26. The method of claim 25 wherein said acid is trichloroacetic acid.

27. The method of claim 26 wherein said aqueous solution contains 10 percent by weight trichloroacetic acid and 10 percent by weight hydrogen peroxide.

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