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3,506,488

METHOD OF REMOVING MANGANESE CONTAINING DEPOSITS

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7 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 an acidic nitrogen containing chelating compound.

Ethylene diamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and the disodium salt of EDTA are useful chelating 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 are contacted by the exhaust products. As with many engine deposits, an effective method of removing these manganese containing deposits is desirable.

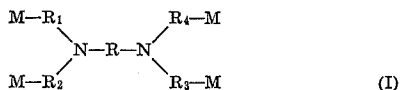
SUMMARY OF THE INVENTION

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 an acidic nitrogen containing chelating compound.

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

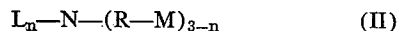
DESCRIPTION OF THE PREFERRED EMBODIMENTS

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 an acidic chelating compound selected from acids having the formulae



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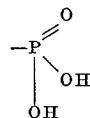
and



wherein R, R₁, R₂, R₃ and R₄ are selected from alkyl groups having from 1 to about 4 carbon atoms; M is selected from



10 and



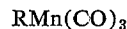
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L is selected from hydrogen, C₁-C₄ alkyl groups and C₆-C₁₂ aryl groups and n is selected from 0 and 1, and partial salts of said acids.

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 chelating compounds described above.

In a preferred embodiment, the chelating compound is nitrilotriacetic acid or ethylenediamine tetraacetic acid (EDTA). A most preferred embodiment utilizes a saturated EDTA solution.

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.

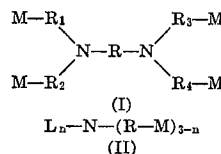
The concentration of the manganese tricarbonyl in the jet fuel may be varied. Concentrations from 0.025 to about 6.45 grams of manganese per gallon as a cyclopentadienyl manganese tricarbonyl are useful.

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 comprises a mixture of compounds. Principal components of this mixture are the oxides such as Mn₂O₃ and Mn₃O₄.

Acidic chelating compounds which are useful in the present method are nitrogen-containing polybasic acids, and partial salts thereof. The acids are represented by the following formulae:



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R, R₁, R₂, R₃ and R₄ are selected from alkyl groups having from 1 to about 4 carbon atoms; M is selected from



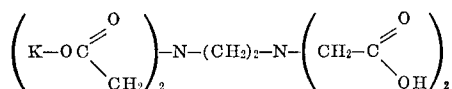
and



L is selected from hydrogen, C₁-C₄ alkyl groups and C₆-C₁₂ aryl groups, n is selected from 0 and 1. Examples of useful chelating acids are trimethylene diamine tetraacetic acid, methylamine-diacetic acid, aminomethylphosphonic acid-N,N-diacetic acid, anilinediacetic acid, butylnitrilaminodimethylenediphosphonic acid, tetramethylene dinitrilotetramethylenetetraphosphonic acid, and the like.

Ethylene diamine tetraacetic acid and nitrilotriacetic acid are preferred chelating acids.

The partial salts of the chelating acids having Formulas I and II are also useful. A partial salt is a salt obtained by using less than the stoichiometric amount of base required to neutralize all the acid groups. For example, four moles of potassium hydroxide are required to fully neutralize one mole of ethylene diamine tetraacetic acid (EDTA). By reacting only two moles of potassium hydroxide with one mole of EDTA, only two acid groups in the EDTA are neutralized. The product obtained is a partial salt as represented by the formula



Thus the partial salts are characterized by having at least one unneutralized acid group.

Bases which can be used to prepare suitable partial salts are inorganic bases such as sodium hydroxide, barium hydroxide, calcium hydroxide, ammonium hydroxide and the like; or organic bases such as dimethylamine, diethylenetriamine, aniline, ethanolamine and the like.

Examples of useful partial salts are mono-calcium salt of ethylenediamine tetraacetic acid, disodium salt of ethylenediamine tetraacetic acid, monosodium salt of nitrilotriacetic acid and the like, mono-potassium salt of trimethylenedinitrilotetraethylenetetraphosphonic acid, monotrimethylamine salt of ethylenediamine tetrabutyrac acid and the like.

The concentrations of acidic chelating compound 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 acidic chelating compound 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

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by immersing it in a suitably designed vessel containing the acidic chelating 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 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 acidic chelating compound 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 tan deposit on the metal surface. This test specimen was then immersed in a vessel containing about 200 part of the aqueous solution of the acidic chelating compound to be tested. The solution was then warmed in a steam bath to above about 70° C. The effect of the solution on the deposit was observed. The effective aqueous acid solutions dissolved a substantial portion of the tan manganese containing deposit, leaving the metal piece partially free of the deposit. This dissolution began almost immediately on placing the specimen in the test solution and was considered to be practically complete after about 15 minutes of warming on the hot plate.

Using this test procedure, a saturated aqueous solution of ethylenediaminetetraacetic acid was found to dissolve the manganese containing deposit very readily. A saturated solution of nitrilo-triacetic acid was also found to be effective.

Similar results are obtained using a 0.001 percent solution of (p-tolylimino)diacetic acid; a 5 percent solution of trimethylenedinitrilotetraethylene phosphoric acid; a two percent solution of a monocalcium salt of ethylene-diaminetetraacetic acid; a one percent solution 3,3'-{2-[bis(carboxymethyl)amino]ethyl} - imino}dipropionic acid; a three percent solution of methylnitrilo-diphosphonic acid; or a 20 percent solution of monopotassium salt of nitrilotriacetic acid, in the test procedure described above.

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 an acidic chelating compound as herein described. 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.

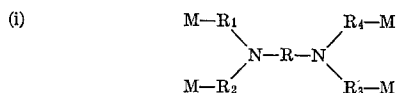
The process of the present invention is described above. It is intended that the present invention be limited only within the lawful scope and extent of the following claims.

I claim:

1. A method of removing manganese containing deposits formed on surfaces of a jet engine from burning a fuel containing a cyclopentadienyl manganese tricarbonyl

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bonyl compound wherein the cyclopentadienyl radical has up to 17 carbon atoms, which comprises treating said surfaces with an aqueous solution of an acidic chelating compound selected from polybasic acids having the formula



and



wherein R, R₁, R₂, R₃, and R₄ are hydrocarbon alkyl groups having from 1 to about 4 carbon atoms, M is selected from



and



L is selected from hydrogen, C₁-C₄ alkyl groups and C₆-C₁₂ aryl groups and n is selected from 0 to 1 and partial salts of the (i) and (ii) type acids.

2. The method of claim 1 wherein the said aqueous

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solution contains from 0.001 percent to about 20 percent by weight of said chelating compound.

3. The method of claim 1 wherein said aqueous solution is a saturated solution.

5 4. The method of claim 2 wherein said chelating compound is ethylenediamine tetraacetic acid.

5. The method of claim 2 wherein said chelating compound is nitrilotriacetic acid.

10 6. The method of claim 3 wherein said chelating compound is ethylenediamine tetraacetic acid.

7. The method of claim 3 wherein said chelating compound is nitrilotriacetic acid.

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