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(54) Title: METHOD FOR REDUCING PARTICULATE EMISSIONS FROM A DIESEL ENGINE WITH ORGANOMETALLIC PLATINUM GROUP METAL COORDINATION COMPOSITION

(57) Abstract

The invention presented relates to a method for regenerating a diesel engine particulate trap. Specifically, the invention involves providing a diesel engine having associated therewith a diesel engine particulate trap which collects particulates from the exhaust of the diesel engine; and firing the diesel engine with a diesel fuel having admixed therein an additive which comprises a fuel soluble, organometallic platinum group metal coordination composition.

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DESCRIPTION

"Method For Reducing Particulate Emissions From A Diesel Engine With Organometallic Platinum Group Metal Coordination Composition"

Related Applications

This application is a continuation-in-part of copending and commonly assigned U.S. Patent Application having Serial No. 07/794,329 entitled "Method for Reducing Emissions From or Increasing the Utilizable Energy of Fuel for Powering Internal Combustion Engines", filed in the names of Epperly, Sprague, Kelso, and Bowers, on November 12, 1991, which in turn is a continuation of U.S. Patent Application Serial No. 07/291,245, filed December 28, 1988, now abandoned, the disclosures of each of which are hereby incorporated by reference.

Technical Field

The present invention relates to a method which is effective at reducing the particulate emissions from a diesel engine, especially a diesel engine having a particulate trap associated therewith.

Diesel engine particulate traps generally comprise an apparatus which is mounted in the exhaust stream of the engine and which "traps" or collects the particulates

flowing in the exhaust stream to prevent their emission to the atmosphere. Diesel engine particulate traps are typically formed of a material such as a ceramic or metal which is shaped such that particulates flowing through the effluent strike the trap surfaces and are collected thereon.

In terms of the emission of gaseous pollutants, the diesel engine is believed to be at least on a par with a gasoline engine equipped with a catalytic converter. In fact, considering the better fuel economy of a diesel engine, carbon dioxide emissions are considerably less than that of a gasoline engine. Likewise, the emission of hydrocarbons, which are a major component of smog, are substantially less than the hydrocarbon emissions from a gasoline engine. The emission of particulates, though, is much higher in diesel engines than in gasoline engines. Accordingly, because diesel particulates are felt by some to be a possible health hazard, practically all manufacturers of diesel engines for passenger vehicles are installing or developing diesel engine particulate trap systems.

One of the principal drawbacks to the use of a diesel engine particulate trap is that as particulates collect on the trap, the pressure drop across the trap increases, eventually leading to inefficiencies in engine operation.

In order to reduce particulate buildup on the trap, it is desired that the particulates are combusted or "burned off" the trap in order to free the surface thereof for further collection of particulates. Temperatures of at least about 600°C are believed to be required to combust the particulates and, thus, regenerate the trap. Since a four-stroke diesel engine

produces an exhaust which operates at an average temperature between about 400°C and 500°C, and which only occasionally reaches temperatures in excess of 600°C, the exhaust temperature is too low to lead to trap regeneration. A two-stroke diesel engine produces an exhaust which is at an even lower temperature, and which rarely exceeds 600°C, making trap regeneration even less likely.

In some proposed systems, a heating element which raises the temperature at the trap to a temperature in excess of 600°C has been suggested. Such heat assisted traps (for instance, traps referred to as "Donaldson traps") are effective at combusting the particulates collected on the trap, but the energy required to raise the trap temperature to the desired level is a major drawback.

What is desired, therefore, is a system whereby the ignition temperature of diesel engine particulates can be lowered in an effective and economic manner.

Background Art

The problem of diesel engine particulate trap regeneration has been addressed in the past, albeit in an unsatisfactory manner. For instance, Müller, Wiedemann, Preuss, and Schädlich, in "Diesel Particulate Filter System With Additive Supported Regeneration", ATZ Automobiltechnische Zeitschrift 91 (1989), discuss the regeneration of a diesel engine particulate trap by the addition of an additive to the fuel which will assist in the regeneration of a particulate trap. Among the additives discussed are copper, nickel, and cobalt, which are dismissed as being environmentally hazardous, and

iron, which is indicated as the additive of choice. Unfortunately, the system of Müller, Wiedemann, Preuss, and Schädlich requires the installation of a separate additive tank in the vehicle to provide the additive to the fuel. This, of course, would lead to problems in terms of retrofit, as well as complications in the operation of the fuel system of the vehicle.

In "Assessment of Diesel Particulate Control - Direct and Catalytic Oxidation", Society of Automotive Engineers (SAE) Paper No. 81 0112, 1981, Murphy, Hillenbrand, Trayser, and Wasser have reported that the addition of catalyst metal to diesel fuel can increase the burning rate of trapped particulates. Unfortunately, catalyst metals of Murphy, Hillenbrand, Trayser, and Wasser are metal chlorides, including platinum chlorides. The use of halogens in platinum compounds has generally been found to be undesirable because the halogen can lead to premature vaporization of the catalyst metal compound, reducing its effectiveness.

The Murphy et al. study noted above found that the use of platinum can lower the ignition temperature of diesel particulates to the range of about 430°C to about 450°C. In the case of a four-stroke engine, the lowering of the ignition temperature for the particulates may be sufficient to regenerate the trap even without any additional heat input. In the case of a two-stroke engine, although the lowering of the ignition temperature might not be sufficient by itself to regenerate the trap, the required additional heat input to do so would be substantially less. Unfortunately, an economical and effective means for supplying a platinum compound to the engine is not taught by the study.

In a unique application of catalytic technology described in International Publication No. WO 86/03492 and U.S. Patent 4,892,562, Bowers and Sprague teach the preparation of diesel fuels containing fuel soluble platinum group metal compounds at levels of from 0.01 to 1.0 parts per million (ppm). Epperly and Sprague disclose a further advance in the field in U.S. Patent 5,034,020.

Although various systems which are suggested as being effective at the regeneration of diesel engine particulate traps have been put forward by the prior art, there has still not been disclosed an effective way of providing an additive to the trap which will reduce the ignition temperature of the particulates without the need for a separate additive reservoir on the vehicle or the use of halogenated compounds.

Disclosure of Invention

The present invention relates to a method for reducing emission of particulates from a diesel engine by facilitating the regeneration of a diesel engine particulate trap. The inventive method involves providing a diesel engine having associated therewith a diesel engine particulate trap and applying to the fuel certain platinum group metal compounds which are directly soluble in the diesel fuel. For the purposes of this description, all parts per million figures are on a weight to volume basis, i.e., grams/million cubic centimeters (which can also be expressed as milligrams/liter), and percentages are given by weight, unless otherwise indicated.

Detailed Description of the Preferred Embodiment

The method of the present invention relates to the combustion of fuels in diesel engines, by which is meant an engine capable of being run on "diesel fuel" which can itself be defined as fuel oil No. 2 or No. 4 petroleum distillates or No. 6 residual fuel of volatility and cetane number characteristics effective for the purpose of fueling a wide range of internal combustion engines.

In a first aspect of the present invention, a diesel engine is provided having associated therewith a diesel engine particulate trap. By this is meant a diesel engine particulate trap is disposed such that the exhaust stream from the engine passes therethrough. Generally, a diesel engine particulate trap is disposed on the tailpipe of the vehicle in which the diesel engine is located, downstream from the exhaust manifold.

Suitable diesel traps are known to the skilled artisan and generally comprise an apparatus designed to trap or collect particulates which are present in the exhaust stream of the diesel engine. Such a trap can be made of any suitable material such as a ceramic (for instance, a cordierite ceramic material), glass fibers, or metals. In addition, the trap can be coated with a catalytic material to facilitate regeneration.

Since flow resistance to the exhaust increases in proportion to the efficiency of the diesel trap at collecting particulates, a compromise must be made between trap efficiency and exhaust back pressure. One type of diesel engine particulate trap which is found to be effective at trapping particulates while still an acceptable compromise in terms of back pressure created

are traps available under the tradenames Dieselfilter or EX 51 100/17 from Corning Glass Corporation of Corning, New York.

More specifically, a suitable diesel engine particulate trap consists of a gas permeable material, such as a ceramic. The trap is formed such that it has at least two (and generally several) parallel gas channels longitudinally arranged in a honeycomb-type structure extending between what can be referred to as an upstream, or engine-side, face and a downstream, or exhaust-side, face. Each passage is plugged at one of its faces such that alternate faces of adjacent passages are plugged. In this way, exhaust entering the trap through a passage at its unplugged upstream face must pass through a wall into an adjacent passage in order to exit the trap from its unplugged downstream face. Particulates in the exhaust are then trapped or collected on the wall. Such a trap is described, for instance, in U.S. Patent 4,568,357 to Simon, the disclosure of which is incorporated herein by reference.

The particulate trap used in the method of the present invention can be one which is self regenerating, that is, trapped particulates are ignited by heat derived from the engine, usually from the hot exhaust gasses themselves. As noted, a four-cycle engine only sometimes provides sufficient exhaust heat to regenerate the trap, whereas two-cycle engines rarely provide sufficient heat.

Another type of trap arrangement which can be used involves the use of a Donaldson trap which involves the addition of an auxiliary heating coil used to bring the trap particulates to ignition by triggering ignition at programmed times in the engine operation cycle. As

discussed above, although a Donaldson trap can be effective at regenerating a particulate trap, the expenditure of energy makes the use of a Donaldson trap inefficient.

In order to heat the particulates collected on the trap to their ignition-temperature, a glow plug or auxiliary burner can be provided, advantageously in contact with the upstream face of the trap. The glow plug or burner can be activated intermittently, such as in response to back pressure increase, elapsed time, or other suitable parameters to ignite the particulates. The use of such means is similarly inefficient.

Often, when heat assisted traps are employed, a two trap system is utilized. In such a system, two particulate traps are arranged in parallel. After a specified period of engine operation during which the exhaust is passed through one of the traps, such as between 1 and 2 hours, the system shifts so that the exhaust is passed through the other. During its period of inactivity, regeneration of the inactive trap can occur.

A second aspect of the claimed invention involves admixing with the diesel fuel used to fire the diesel engine an additive comprising a diesel fuel soluble organometallic platinum group metal coordination composition, to function as an ignition temperature reducer. The additive can also function to replenish catalyst metal coated on the trap surfaces.

The additive composition should be temperature stable, and it should be substantially free of phosphorus, arsenic, antimony, or halides.

Advantageously, the additive also has a partition ratio sufficient to maintain significant preferential solubility in the fuel in order to effectively enhance combustion.

The organic nature of the composition provides solubility in diesel fuel thereby facilitating the introduction of the additive into the combustion chamber of a diesel engine. Without such solubility, much of the additive would precipitate in the fuel tank or fuel lines of the diesel engine prior to introduction into its combustion chamber.

Temperature stability of the additive is very important in practical and operational terms. In a commercial setting, a fuel additive is packaged and then can often sit on a store shelf or in a delivery truck for extended periods of time during which the additive can be exposed to great variations in temperature. If the breakdown temperature of the additive is not sufficiently high (i.e., if the additive is not temperature stable at the temperatures to which is is expected to be exposed), then the packaged additive will quickly break down and become virtually useless.

Moreover, breakdown of the additive after mixing with the fuel will render the additive insoluble in the fuel, since the solubility is provided by the organic functional groups. Such loss of solubility will cause the additive to precipitate and not reach the combustion chamber, as discussed above. This becomes important when the additive is mixed into the fuel in advance of the fuel being provided to the fuel system of the engine (as opposed to a separate additive reservoir on the vehicle, with mixing occurring immediately prior to combustion),

as desired.

Typically, the breakdown temperature of the additive should be at least about 40°C, preferably at least about 50°C in order to protect against most temperatures to which it can be expected to be exposed. In some circumstances, it will be necessary that the breakdown temperature be no lower than about 75°C.

In general, the additive comprises the platinum group metal composition as well as a solvent therefor, as will be discussed in more detail below. The organic nature of the platinum group metal composition helps to maintain the composition in solution in the solvent, thereby preventing "plating out" of the platinum group metal composition in the packaging medium.

As noted, the additive of the present invention should be substantially free from objectionable functional groups such as phosphorus, arsenic, antimony, and, especially, halogens (i.e., they should not contain a substantial amount of such functional groups) which have significant disadvantages like "poisoning" or otherwise reducing the effectiveness of the platinum group metal composition catalyst. Halogens have the additional undesirable effect of rendering a platinum group metal more volatile, leading to reduction of the amount of platinum group metal in the combustion chamber and engine system.

A substantial amount of such functional groups is considered an amount effective to significantly reduce the effectiveness of the catalyst. Preferably, the purified platinum group metal additive composition contains no more than about 500 ppm (on a weight per

weight basis) of phosphorus, arsenic, antimony, or halogens, more preferably no more than about 250 ppm. Most preferably, the additive contains no phosphorus, arsenic, antimony, or halogens.

Such objectionable functional groups can be minimized in several ways. The platinum group metal composition can be prepared in a process which utilizes precursors or reactant compositions having a minimum of such functional groups; or the additive can be purified after preparation. Many such methods of purification are known to the skilled artisan.

One preferred method of purifying the platinum group metal additive to remove halogens is a process utilizing silver salts having non-halide anions which are harmless as compared to the halogens being replaced and involves reacting them with the platinum group metal compound, whereby the halogens in the composition are replaced by the anion of the silver salt (which can be any silver salts of carboxylic acids, such as silver benzoate, or silver nitrate) and the resulting composition is free of halogens, plus a silver halide is produced.

For instance, a slurry or solution in a polar solvent such as acetone or an alcohol and water of silver nitrate or silver benzoate can be prepared and reacted with the platinum group metal composition. The resultant platinum group metal composition is a benzoate or nitrate salt with silver halide also being produced. This process can be expected to reduce the halogen content of a sample by about 50%, and even up to about 90% and higher.

The relative solubility of the additive in the diesel fuel and water is also important since there is often a

substantial amount of water admixed in with fuel. This relative solubility is referred to as the partition ratio and can be expressed as the ratio of the amount in milligrams per liter of composition which is present in the fuel to the amount which is present in the water. This can most easily be determined in a 100 milliliter (ml) sample which is 90% fuel and 10% water. By determining the amount of composition in the fuel and the amount in the water, the partition ratio can be readily determined.

The preferential solubility of the additive in fuel as compared to water can be critical because if a substantial amount of the additive is dissolved in the water which may be present, the overall effectiveness of the additive is proportionally reduced. This partition ratio should be at least about 25 and is most preferably greater than about 50.

In order to reduce the water susceptibility of the platinum group metal composition, it is especially desired that the composition have at least one platinum group metal-to-carbon covalent bond. A platinum group metal-to-oxygen or platinum group metal-to-nitrogen bond can be acceptable, but there must also be at least one metal to carbon bond.

Platinum group metals include platinum, palladium, rhodium, ruthenium, osmium, and iridium. Compounds including platinum, palladium, and rhodium, especially compounds of platinum alone or possibly in combination with rhodium compounds are preferred in the practice of this invention since the vapor pressure of these metals is sufficiently high to facilitate the desired regeneration effect.

Specific suitable compounds according to the present invention include those platinum group metal-containing compositions selected from the group consisting of

a) a composition of the general formula

$$L^1MR^1R^2$$

wherein L^1 is either a single cyclic polyolefin or nitrogenous bidentate ligand or a pair of nitrogenous or acetylenic monodentate ligands, preferably cyclooctadienyl; M is a platinum group metal, especially platinum itself; and R^1 and R^2 are each, independently, substituted or unsubstituted lower alkyl (e.g., 1-5 carbons) benzyl, nitrobenzyl, aryl, cyclopentadiene or pentamethyl cyclopentadiene, preferably benzyl, methyl and/or phenyl;

b) a composition of the general formula

$$L^2M^1R^3$$

wherein L^2 is either a single cyclic polyolefin or nitrogenous bidentate ligand or a pair of nitrogenous or acetylenic monodentate ligands; M^1 is a platinum group metal, especially rhodium or iridium; and R^3 is cyclopentadiene or pentamethyl cyclopentadiene;

c) a composition of the general formula

$$L^3M^2(C_4R^4{}_4)$$

wherein L^3 is either a single cyclic polyolefin or nitrogenous bidentate ligand or a pair of nitrogenous monodentate ligands; M^2 is platinum, palladium,

rhodium, or iridium; and R^4 is $COOR^5$, wherein R^5 is hydrogen or alkyl having from 1 to 10 carbons, preferably methyl;

d) a composition of the general formula

$$L^4M^3(COOR^6)_2$$

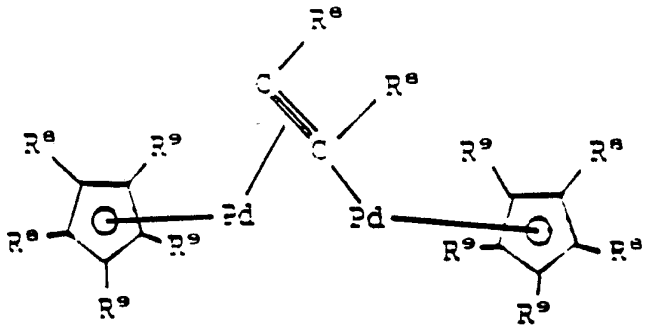
or a dimer thereof, wherein L^4 is a non-nitrogenous cyclic polyolefin ligand, preferably cyclooctadiene or pentamethyl cyclopentadiene; M^3 is platinum or iridium; and R^6 is benzyl, aryl, or alkyl, preferably having 4 or more carbons, most preferably phenyl;

e) a composition comprising a reaction product of $[L^5RhX]_2$ and R^7MgX wherein L^5 is a non-nitrogenous cyclic polyolefin ligand, preferably cyclooctadiene or pentamethyl cyclopentadiene; R^7 is methyl, benzyl, aryl, cyclopentadiene or pentamethyl cyclopentadiene, preferably benzyl or phenyl, and X is a halide. Although presently uncharacterized, it is believed that this reaction product assumes the formula L^5RhR^7.

Functional groups which are especially preferred for use as ligands L^1 through L^3 are neutral bidentate ligands such as cyclopentadiene, cyclooctadiene, pentamethyl cyclopentadiene, cyclooctatetrene, norbornadiene, o-toluidine, o-phenantholine, and bipyridine. Most preferred among monodenate ligands is pyridine.

Also useful in the present invention are

f) palladium acetylene complexes having the general formula



wherein R^8 is aryl or alkyl; and R^9 is aryl;

g) metal allyl complexes having the general formula

$$M^4(C_3H_5)_3 \text{ or}$$

$$M^4(C_3H_5\text{-}R^{10})_2$$

wherein M^4 is platinum group metal, especially rhodium or iridium; and R^{10} is hydrogen, aryl, or alkyl;

h) platinum (IV) compositions having the general formula

$$R_3^{11}PtR^{12}$$

wherein R^{11} is aryl, alkyl or mixtures thereof; and R^{12} is hydroxyl (-OH), acetylacetonate ($-CH_3(COCH_3)_2$), cyclopentadiene or pentamethyl cyclopentadiene (exemplary of which is trimethyl platinum hydroxide); and

i) a composition of the general formula

$$L^6M^5R^{13}$$

wherein L^6 is substituted or unsubstituted butadiene or cyclohexadiene; M^5 is rhodium or iridium; and R^{13} is cyclopentadiene or pentamethyl cyclopentadiene (exemplary of which are butadiene rhodium cyclopentadiene and butadiene iridium cyclopentadiene.

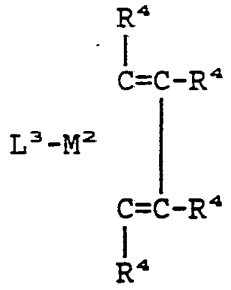
The synthesis of the preferred compounds is relatively straightforward, with the most care being taken to avoid "contamination" of the product by the objectionable functional groups discussed above. For instance, the most preferred synthetic route for production of the compounds of the formula $L^1MR^1R^2$ is by reacting commercially available platinum halides with the desired neutral ligand (except the pyridine derivative which can be added by displacement after the fact) and then reacting with a Grignard reagent having the formula R_2MgX, where X is a halide (and where the desired R^1 and R^2 in the end product are the same functional group). Where the R^1 and R^2 functional groups are desired to be different, a straightforward substitution reaction can then be run.

Exemplary of compounds suitable for use in the present invention and prepared in this manner are dipyridine platinum dibenzyl; bipyridine platinum dibenzyl; dipyridine palladium diethyl; cyclooctadiene platinum dimethyl; cyclooctadiene platinum diphenyl; cyclooctadiene platinum dibenzyl; cyclooctadiene platinum dinitrobenzyl; cyclooctadiene platinum methyl cyclopentadiene; norbornadiene platinum di-cyclopentadiene; dimethyl platinum cyclooctatetrene (which often assumes the formula dimethyl platinum cyclooctatetrene platinum dimethyl); and cyclooctadiene osmium bis (cyclopentadiene).

The compounds of the formula $L^2M^1R^3$ are prepared along a similar pathway, as are the reaction products of $[L^5RhX]_2$ and R^6MgX, with the exception that the starting materials have only one R functional group and are, with respect to $L^2M^1R^3$, L^2RhR^3 or L^2IrR^3. Exemplary of suitable compounds of the formula $L^2M^1R^3$ are cyclooctadiene rhodium cyclopentadiene; cyclooctadiene rhodium pentamethyl cyclopentadiene; norbornadiene rhodium pentamethyl cyclopentadiene; cyclooctadiene iridium cyclopentadiene; cyclooctadiene iridium pentamethyl cyclopentadiene; norbornadiene iridium cyclopentadiene; and norbornadiene iridium pentamethyl cyclopentadiene. Exemplary of compounds which can function as the precursors for the reaction product can include cyclooctadiene rhodium chloride dimer and benzyl magnesium chloride.

Advantageously, in the Grignard-type syntheses, the Grignard reagent can be replaced by one having the formula R_2Z where Z is commonly Na, Li, K, or Tl. This is especially preferred since the halides which are present in a Grignard reagent are eliminated, providing less halides in the final product and also advantageously producing a higher yield of the desired product.

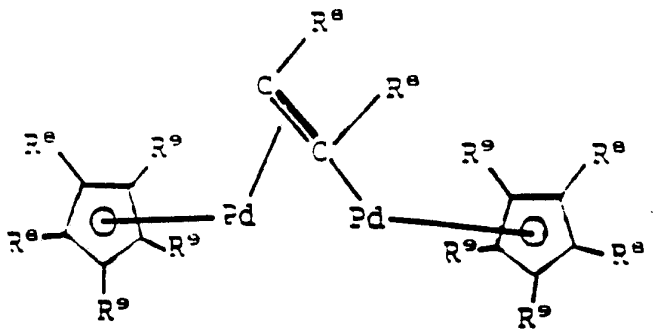
The preparation of compositions of the formula $L^3M^2(C_4R^4_4)$ is also straightforward and proceeds by reacting M^2(dibenyilidine acetone)$_2$ with dimethylacetylene dicarboxylate in acetone and then adding the L^3 ligand. Exemplary of suitable compounds according this formula, which has the structure



is tetrakis (methoxy carbonyl) palladia cyclopentadiene (wherein L^3 is cyclopentadiene, M^2 is palladium, and R^4 is $COOH_3$).

The compositions of the formula $L^4M^3(COOR^5)_2$ can be prepared by reacting $L^4M^3X_2$, where X is a halide and a silver carboxylate such as silver benzoate. This composition can form a dimer, especially when M^3 is platinum. Exemplary of suitable compounds having the general formula $L^4M^3(COOR^5)_2$ are cyclooctadiene platinum dibenzoate dimer; and pentamethyl cyclopentadiene iridium dibenzoate.

The most preferred synthetic route for production of the noted acetylene compounds is by reacting the trimeric palladium salt of a carboxylic acid ($[Pd(OOCR^6)_2]_3$), where R^6 is alkyl such as methyl or ethyl, or aryl such as phenyl, like palladium acetate, propionate or benzoate, with a substituted acetylene, such as diphenylacetylene or methylphenylacetylene, in the presence of a polar solvent, such as an alcohol like methanol (CH_3OH). For example, when the reactants are palladium acetate and diphenylacetylene, the product is u-diphenylacetylene bis(^{5} pentaphenyl cyclopentadiene) dipalladium, which has the general formula



where R^8 and R^9 are each phenyl.

The disclosed metal allyl compositions can be prepared by reacting commercially available platinum group metal halides, such as $RhCl_3$ or $IrCl_3$, with an allyl Grignard reagent, such as C_3H_5MgBr, in a 3:1 molar ratio to produce the desired metal allyl, such as bis (phenyl allyl) palladium, and MgBrCl.

The platinum (IV) compositions can be prepared, for instance, by reacting $R_3^{10}PtX$, where R^{10} is aryl or alkyl, such as phenyl, benzyl or methyl or mixtures and X is a halide, with NaR^{11}, where R^{11} is cyclopentadiene or pentamethyl cyclopentadiene.

Reaction of the $R_3^{12}PtX$ complex with aqueous acetone solutions containing a silver compound such as Ag_2O results in a product where R^{12} is hydroxyl. Alternatively, treatment of the $R_3^{12}PtX$ complex with a solution of acetylacetone in alcoholic potassium hydroxide results in a product where R^{12} is acetyl acetonate.

The compounds of the formula $L^6M^5R^{13}$ can be prepared by reacting commercially available metal halides with butadiene and cyclohexadienes and then reacting with a Grignard reagent having the formula $R_{13}MgX$, where X

is a halide.

The additive will be added to the fuel in an amount effective to reduce the ignition temperature of trapped particulates to below about 500°C, more preferably below about 450°C. To do so, the additive must be intimately mixed with particulates present in the exhaust and/or collected in the trap. Advantageously, the additive is mixed with the particulates such that the additive comprises at least about 0.001%, more preferably at least about 0.010%, and most preferably, at least about 0.1% by weight of the mixed particulates/additive.

Typically, in order to provide sufficient additive, the platinum group metal compound will supply an amount of the platinum group metal within a range of about 0.01 to 1.0 parts of the platinum group metal per one million parts of fuel (ppm w/v) in order to "build up" sufficient platinum group metal over time, for instance, between about 40 and 100 hours of operation. A more preferred range is from about 0.05 to 0.5 ppm and, most preferably, the platinum group metal will be supplied at a level of from about 0.10 to 0.30 ppm on the same basis.

Alternatively, the additive can be provided at a ratio so as to provide a sufficient level of catalyst metal in a relatively short period of time, i.e., under about 10 hours, more preferably under about 5 hours. Effective levels to do so can range up to about 30 ppm, more advantageously, about 15 to about 25 ppm. These levels should be provided for about 0.5 to about 10 hours. Maintenance amounts of from about 0.1 to about 1.0 ppm can then be provided, to maintain superior activity.

The additive composition will preferably include a solvent which is soluble in the fuel, preferably acyl nitrate. The fuel additive compositions may also contain other additives, such as detergents, antioxidants, and cetane improvers which are known as beneficial to engine performance, but the use of such is not an essential feature of the invention.

The total amount of solvent and other additives used will depend on the dosage of platinum group metal composition required and on what is a convenient concentration to handle relative to the amount of fuel to be treated. Typically, solvent (plus other like additive) volumes of about 0.1 to about 40.0 liters/gram of platinum are acceptable.

It has suprisingly been found that the use of the platinum group metal additives discussed above will reduce the ignition temperature of the trapped particulates to a level whereby self-regeneration of a particulate trap, especially in a four-cycle diesel engine may occur. Even if self-regeneration cannot completely occur, i.e., in a four-cycle engine which is not operating hot enough or in a two-cycle engine, the use of the described additives will reduce the temperature to which an auxiliary heat source is required to raise the diesel engine particulate trap, thereby increasing the efficiency of the use of the auxiliary heat source. In this way, significant improvements in the use of a diesel engine particulate trap are obtained, without the art accepted tradeoff of substantially increased back pressure caused by clogging of the trap by collected particulates.

The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention, and it is not intended to detail all of those obvious modifications and variations of it which will become apparent to the skilled worker upon reading this description. It is intended, however, that all such obvious modifications and variations be included within the scope of the present invention which is defined by the following claims.

Claims

1. A method for regenerating a diesel engine particulate trap comprising

a) providing a diesel engine having associated therewith a diesel engine particulate trap which collects particulates from the exhaust of the diesel engine; and

b) firing the diesel engine with a diesel fuel having admixed therein an additive which comprises a fuel soluble, organometallic platinum group metal coordination composition, wherein said composition

I) is resistant to breakdown under ambient temperatures;

II) is substantially free of phosphorus, arsenic, antimony, or halogens; and

III) has a partition ratio sufficient to maintain preferential solubility in the fuel.

2. The method of claim 1, wherein said diesel engine particulate trap is made of ceramic, metal, glass fibers, or mixtures thereof.

3. The method of claim 1, wherein said diesel engine particulate trap further comprises an auxiliary heater to raise the temperature of the diesel engine particulate trap at programmed times in the engine operation cycle.

4. The method of claim 1, wherein said composition has a breakdown temperature of at least about 50°C.

5. The method of claim 1, wherein the partition ratio of said composition is at least about 25.

6. The method of claim 5, wherein said composition has

at least one platinum group metal to carbon covalent bond.

7. The method of claim 1, wherein said composition is selected from the group consisting of

a) a composition of the general formula

$$L^1M^1R^2$$

wherein L^1 is either a single cyclic polyolefin or nitrogenous bidentate ligand or a pair of nitrogenous or acetylenic monodentate ligands; M is a platinum group metal; and R^1 and R^2 are each, independently, substituted or unsubstituted lower alkyl, benzyl, nitrobenzyl, aryl, cyclooctadiene or pentamethyl cyclopentadiene;

b) a composition of the general formula

$$L^2M^1R^3$$

wherein L^2 is either a single cyclic polyolefin or nitrogenous bidentate ligand or a pair of nitrogenous or acetylenic monodentate ligands; M^1 is a platinum group metal; and R^3 is cyclooctadiene or pentamethyl cyclopentadiene;

c) a composition of the general formula

$$L^3M^2(C_4R^4_4)$$

wherein L^3 is either a single cyclic polyolefin or nitrogenous bidentate ligand or a pair of nitrogenous monodentate ligands; M^2 is platinum, palladium, rhodium or iridium; and R^4 is $COOR^5$, wherein R^5 is hydrogen or alkyl having from 1 to 10 carbons;

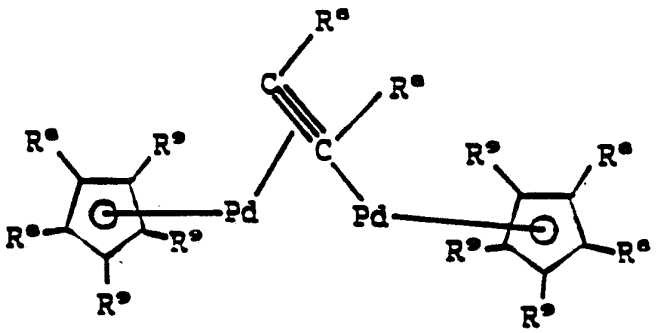
d) a composition of the general formula

$L^4M^3(COOR^6)_2$

or a dimer thereof, wherein L^4 is a non-nitrogenous cyclic polyolefin ligand; M^3 is platinum or iridium; and R^6 is alkyl; and

e) a composition comprising the reaction product of L^5RhX and R^7MgX wherein L^7 is a non-nitrogenous cyclic polyolefin ligand; R^6 is methyl, benzyl, aryl, cyclooctadiene or pentamethyl cyclopentadiene; and X is a halide,

f) palladium acetylene complexes having the general formula



wherein R^8 is aryl or alkyl; and R^9 is aryl;

g) metal allyl complexes;

h) platinum (IV) compositions having the general formula

$R_3^{10}PtR^{11}$

wherein R^{10} is aryl, alkyl or mixtures thereof; and R^{11} is hydroxyl, acetylacetonate, cyclopentadiene or pentamethyl cyclopentadiene; and

i) a composition of the general formula

$L^6M^5R^{13}$

wherein L^6 is substituted or unsubstituted butadiene or cyclohexadiene; M^5 is rhodium or iridium; and R^{13} is cyclopentadiene or pentamethyl cyclopentadiene, wherein said platinum group metal compound is provided in an amount effective to supply from 0.01 to 1.0 parts per million of platinum group metal per part of fuel.

8. The method of claim 7, wherein L^1, L^2, and L^3 are selected from the group consisting of cyclopentadiene, cyclooctadiene, pentamethyl cyclopentadiene, cyclooctatetrene, o-phenantholine, o-toluidine, norbornadiene, pyridine, and bipyridine.

9. The method of claim 7, wherein L^4 and L^5 are selected from the group consisting of cyclooctadiene and pentamethyl cyclopentadiene.

10. The method of claim 7, wherein said additive further comprises a fuel-soluble solvent for said composition.

11. The method of claim 10, wherein the fuel is diesel fuel and said solvent is octyl nitrate.

12. The method of claim 7, wherein R^1 and R^3 are phenyl or lower alkyl, R^2 is phenyl and R^4 is cyclopentadiene.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US92/10819

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C10L 1/30; C07F 15/00
US CL :44/358,359,361,368;556/32,136,137
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/358, 359, 361, 368; 55/32, 136, 137

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 3,328,400 (SHAPIRO ET AL) 27 JUNE 1967 (See col. 2, lines 15-41)	1-12
Y	US,A, 4,207,078 (SWEENEY ET AL) 10 JUNE 1980 (ALL)	1-12
Y	US,A, 2,086,775 (LYONS ET AL) 13 JULY 1937 (See page 2, col. 1, lines 56-col. 2, lines 1-10	1-12

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 25 FEBRUARY 1993	Date of mailing of the international search report 22 MAR 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer MARGARET B. MEDLEY Telephone No. (703) 308-2518

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10819

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 2,151,432 (LYONS ET AL) 21 MARCH 1939 (See pate 1, col. 1, lines 41 & and page 2, col. 1)	1-12
Y	US,A, 4,295,816 (ROBINSON) 20 OCTOBER 1981 (Col. 5)	1-12
Y	DE,A, 2,500,683 (BRANTL) 15 JULY 1976 Abstract	1-12
Y	US,A, 4,568,357 (SIMON) 04 FEBRUARY 1986 (ALL)	1-12
Y	US,A, 4,787,969 (BRAID) 29 NOVEMBER 1988 (Abstract and col. 3, line 20 to col. 5, lines 1-end)	1-12
Y	BELLUCO, Organmetallic and Coordination Chemistry of Plaltinum, Academic Press, N.Y. pages 221,222,226,232,295-297,441-2,449,454 and 455 i (1974)	7-12
Y	Deganello, Transition Metal complexes or Cyclic Polyolefins, Academic Press, NY, pages 97-100,102,277-8,281-3,288-291, (1979)	7-12
Y	Dickson, Organometallic Chemistry of Rhodium and Rhodium and Iridium, Academic Press, NY, pages 167 167-169,178-180,198-200,220-226,248,258-260,264,271, and 277 (1983)	7-12
Y	Matilis, The Organic Chemistry of Palladium, Academic Press, NY, pages 68,70,76,77,83,93,102,103,136,158,165,202-204,228,242,249,257-8 (1971)	7-12