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(54) **Method for reducing combustion chamber deposit flaking**

(57) A method reduces combustion chamber deposit flaking and spark ignited internal combustion engines. The method includes supplying a fuel having an additive that includes a metal-containing compound to a spark ignited internal combustion engine. The metal-containing compound is supplied in an amount effective

to reduce combustion chamber deposit flaking. In one example, the metal is manganese and the additive compound is MMT. The reduction or elimination of combustion chamber deposit flaking means a reduction in cold start emissions from the engine.

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Description

[0001] The present invention is directed to a method of reducing combustion chamber deposit flaking, and consequently, reducing cold start emissions. The method includes combustion of a fuel having a fuel additive containing a metallic compound. In one example, the metallic compound is a manganese-containing compound.

Background

[0002] Spark ignited internal combustion engines (carbureted, port fuel injection "PFI", multiple point injection "MPI", direct-injection gasoline "DIG", etc.) accumulate combustion chamber deposits (CCD) during operation. This deposit is a result of both inefficient combustion of the fuel during the power stroke, and thermal polymerization reactions of certain fuel components to give high molecular weight material that does not burn very well. The deposit layers both on cylinder head surfaces inside the combustion chamber and on piston tops. The piston top deposit in particular is fuel and moisture sensitive, and tends to curl and slough off when the deposit is fuel wetted and/or exposed to moisture. The symptoms of this flaking manifest themselves during cold start cranking when the combustion charge blows the sloughed off deposit from the combustion chamber and into the exhaust valve seats. The deposit flakes thus lodged in this new location wedge in the sealing band of the exhaust valves and prevent the tight sealing necessary to contain the fuel / air combustion charge during the compression stroke, thus inhibiting ignition and necessitating extended engine cranking periods to dislodge the deposit so that the engine can fire up normally. During this cranking, instead of the combustion charge being contained in the cylinder for the subsequent spark ignition, the combustion charge is prematurely expelled into the exhaust system and loads the catalytic converter with raw fuel. Some of this raw fuel escapes out of the exhaust aftertreatment system and may contribute to cold start hydrocarbon "HC" emissions. Also, when the engine does finally fire up, the subsequent hot combustion gases ignite this raw fuel. The ensuing vigorous combustion of raw fuel in the exhaust system may melt the catalytic converter due to the excessively high temperatures generated by this burn, and seriously damage the exhaust aftertreatment system.

[0003] The symptoms of CCD flaking have only recently been observed with the advent of advanced emissions control strategies aimed at lowering hydrocarbon emissions at cold start. The reasons for all these changes resulted from the discovery that a significant portion of total vehicular hydrocarbon emissions were generated during the initial 90 seconds it takes conventional, under the floor three-way catalytic converters to light off during cold start. Therefore, shortening this time interval became of paramount importance. Government environmental regulators also recognized this fact and mandated that vehicle manufacturers develop an on board diagnostic system (OBD) to monitor the emissions control system in a manner that would minimize hydrocarbon emissions to the environment, and this system be under warranty to ensure that it performed its intended task for the duration of the specified warranty period.

[0004] The emission control changes being made have resulted in cold start difficulties ascribed to the higher fueling rates during cold start causing combustion chamber deposits to flake off and become lodged in the exhaust valve sealing band area, thereby preventing a good seal during compression and hence leading to misfires. The OBD system detects this immediately because of the subsequent elevated hydrocarbon emissions due to unburned fuel, and illuminates the malfunction indicator light (MIL) on the dashboard, necessitating a visit to the dealership for corrective repairs. Cold start difficulties due to CCD flaking tend to occur mainly in higher displacement engines with more cylinders (6, 8, and 10 cylinder engines) because in these bigger engines the cranking rate is lower, and it takes longer to blow the flaked deposits away from the exhaust valves.

[0005] One way to deal with the cold start problem caused by CCD flaking is to not drive the vehicle a short distance under light load, thereby leaving the chamber to soak for extended periods of time. Another way to get around this problem is to simply continue cranking to blow away the offending deposit flakes, and on start up, rev up the engine for an additional thirty seconds to clean out the rest of the flaking deposit. However, this method inadvertently leads to very high levels of hydrocarbon emissions and may cause the OBD MIL to illuminate.

Description

[0006] Combustion chamber deposit (CCD) flaking has been discovered to be reduced and even eliminated with the use of a fuel additive containing a metallic compound. In one example, a manganese-containing compound, MMT, completely suppresses CCD flaking.

[0007] A method of reducing combustion chamber deposit flaking in or of reducing cold start emissions from spark ignited internal combustion engines that experience combustion chamber deposits comprises the steps of supplying a fuel comprising an additive that includes a metal-containing compound to a spark ignited internal combustion engine, wherein the metal-containing compound is supplied in an amount effective to reduce combustion chamber deposit flaking.

[0008] The metal-containing compound may be a compound containing one or more of the following metals: man-

ganese, platinum, palladium, rhodium, iron, cerium, copper, nickel, silver, cobalt and molybdenum, and mixtures thereof. An example of a manganese compound is described in detail herein, but other metal-containing additives may be used. In each alternative, the metal compound in the fuel is combusted in a spark ignited internal combustion engine. Use of the metal - containing additive reduces or eliminates CCD flaking.

[0009] The fuels and additives herein are adapted to be combusted in any spark ignited internal combustion engine. Specific engines that will benefit include those having carbureted systems, port fuel injection systems, multi point injection systems, and direct injection gasoline systems. Also, turbocharged and supercharged versions of the foregoing will benefit. Other engines having advanced emissions controls, including for example exhaust gas recirculation, will benefit. Additionally, Otto cycle and two-stroke internal combustion engines will benefit.

[0010] The unleaded or unleaded gasoline bases in the present fuel composition are conventional motor fuel distillates boiling in the general range of about 70°F to 440°F. They include substantially all grades of unleaded gasoline presently being employed in spark ignition internal combustion engines. Generally they contain both straight runs and cracked stock, with or without alkylated hydrocarbons, reformed hydrocarbons and the like. Such gasolines can be prepared from saturated hydrocarbons, e.g., straight stocks, alkylation products and the like, with detergents, antioxidants, dispersants, metal deactivators, rust inhibitors, multi-functional additives, demulsifiers, fluidizer oils, antiicing, combustion catalysts, corrosion inhibitors, emulsifiers, surfactants, solvents or other similar and known additives. It is contemplated that in certain circumstances these additives may be included in concentrations above normal levels.

[0011] Generally, the base gasoline will be a blend of stocks obtained from several refinery processes. The final blend may also contain hydrocarbons made by other procedures such as alkylates made by the reaction of C₄ olefins and butanes using an acid catalyst such as sulfuric acid or hydrofluoric acid, and aromatics made from a reformer.

[0012] The motor gasoline bases used in formulating the fuel blends of this invention generally have initial boiling points ranging from about 70°F to about 100°F and final boiling points ranging from about 420°F to about 440°F as measured by the standard ASTM distillation procedure (ASTM D-86). Intermediate gasoline fractions boil away at temperatures within these extremes.

[0013] It is also desirable to utilize base gasolines having a low sulfur content as the oxides of sulfur tend to contribute to the irritating and choking characteristics of smog and other forms of atmospheric pollution. Fuel sulfur also contributes significantly to the poisoning of exhaust aftertreatment catalysts. To the extent it is economically feasible, the base gasolines should contain not more than about 100 ppm of sulfur in the form of conventional sulfur-containing impurities. Another alternative includes fuels in which the sulfur content is no more than about 30 ppm.

[0014] The gasoline bases which this invention employs should be lead-free or substantially lead-free. However, the gasoline may contain antiknock quantities of other agents such as cyclopentadienyl nickel nitrosyl, N-methyl aniline, oxygenates, and the like. Antiknock promoters such as 2,4 pentanedione may also be included. On certain occasions it will be desirable for the gasoline to contain supplemental valve and valve seat recession protectants. Nonlimiting examples include; boron oxides, bismuth oxides, ceramic bonded CaF₂, iron phosphate, tricresylphosphate, phosphorus and sodium based additives and the like. The fuel may further contain antioxidants such as 2,6 di-tert-butylphenol, 2,6-di-tert-butyl-p-cresol, phenylenediamines such as N-N'-di-sec-butyl-p-phenylenediamine, N-isopropylphenylenediamine, and the like. Likewise, the gasoline may contain dyes, metal deactivators, or other additives recognized to serve some useful purpose. The descriptive characteristics of one common base gasoline is given as follows. Obviously many other standard and specialized gasolines can be used in Applicants' fuel blend.

CHARACTERISTICS OF GASOLINES	
API Gravity (@ 60 F)	50 - 70
Reid Vapor Pressure, EPA, (psi)	6 - 8
Sulfur (ppm)	0 - 500
Research Octane	85 - 120
Motor Octane	75 - 90
R+M/2	87-110
Oxygenates (%)	0 - 30
Aromatics (%)	0 - 50
Olefins (%)	0 - 30
Paraffins (%)	30 - 100

ASTM Distillation Vol % Evaporate	Temp., F.
IBP	70 - 100

(continued)

ASTM Distillation Vol % Evaporate	Temp., F.
5	100 - 130
10	120-140
15	140 - 160
20	150 - 170
30	170 - 190
40	190 - 210
50	200 - 220
60	220 - 240
70	240 - 260
80	280 - 300
90	340 - 370
95	380 - 400
EP	420 - 440

[0015] One metal that may be used includes elemental and ionic manganese, precursors thereof, and mixtures of metal compounds including manganese. These manganese compounds may be either inorganic or organic. Also effective is the generation, liberation or production *in situ* of manganese or manganese ions.

[0016] Inorganic metallic compounds in an example can include by example and without limitation fluorides, chlorides, bromides, iodides, oxides, nitrates, sulfates, phosphates, nitrides, hydrides, hydroxides, carbonates and mixtures thereof. Metal sulfates and phosphates will be operative and may, in certain fuels and combustion applications, not present unacceptable additional sulfur and phosphorus combustion byproducts. Organometallic compounds in an example include alcohols, aldehydes, ketones, esters, anhydrides, sulfonates, phosphonates, chelates, phenates, crown ethers, carboxylic acids, amides, acetyl acetonates, and mixtures thereof.

[0017] Exemplary manganese containing organometallic compounds are manganese tricarbonyl compounds. Such compounds are taught, for example, in US Patent Nos. 4,568,357; 4,674,447; 5,113,803; 5,599,357; 5,944,858 and European Patent No. 466 512 B1.

[0018] Suitable manganese tricarbonyl compounds which can be used include cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tert-butylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and the like, including mixtures of two or more such compounds. In one alternative are the cyclopentadienyl manganese tricarbonyls which are liquid at room temperature such as methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, liquid mixtures of cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl, mixtures of methylcyclopentadienyl manganese tricarbonyl and ethylcyclopentadienyl manganese tricarbonyl, etc.

[0019] Preparation of such compounds is described in the literature, for example, U.S. Pat. No. 2,818,417, the disclosure of which is incorporated herein in its entirety.

[0020] When formulating additives to be used in the methods herein, the metal-containing compound must be employed in amounts sufficient to reduce or eliminate CCD flaking in the spark ignited internal combustion engine. The amounts will vary according to the particular metal or mixture of metals and metal-containing compounds. In the example of a manganese-containing compound, the amount of manganese added can be about 1 to about 50 mg manganese per liter.

[0021] The metal-containing compounds are believed to act as both a free radical sink and a combustion catalyst. As a radical sink, the compounds may be inhibiting radical initiated fuel polymerization reactions hence limiting contribution to hydrocarbonaceous CCD by this route. As a combustion catalyst, the manganese, for instance, catalytically participates in the CCD removal mechanism by promoting carbon oxidation at lower temperatures.

[0022] The term "cold start emissions" refers to and is defined herein in accordance with the industry definition. The industry recognized definition of cold-start emissions can be found in the FTP-75 (Federal Test Procedure). Details of the test procedure are described in the Code of Federal Regulations (CFR 40, Part 86). Briefly, the test procedure consists of the following three phases: 1) Cold-start, 2) Transient, and 3) Hot-start. The FTP-75 emissions cycle sim-

ulates 11.04 miles (17.77 km) distance of travel in a time of 1874 seconds at an average speed of 21.2 mph (34.1 km/h). Before the test, the vehicle is conditioned overnight at 25 +/- 5 C to assure cold start conditions. The cold start is initiated followed by the transient phase. Then the vehicle is shut down for a hot soak of 10 minutes before being restarted to perform the hot phase. The emissions from each phase are collected in a separate Teflon bag for each test phase, and analyzed. Quantities of each emission component (HC, CO, CO₂, NO_x, etc) are expressed in g/mile (g/km) for each phase. For hydrocarbon emissions (HC) the cold-start phase is the most important because it contributes 80 - 90% of the total from the three phases.

Examples

[0023] Fuels that included and did not include a metal-containing compound were compared in an engine test. Manganese in MMT® was the additive used at a treat rate 8.25 mg. of manganese per liter of fuel.

[0024] The vehicle used in this study was a Dodge Intrepid with a six cylinder engine. It was operated for 3000 miles on the test cycle described below while fueled with non additized CITGO RUL gasoline. At the end of the test the engine was dismantled and rated for CCD flaking according to a procedure adapted from that published by Gautam T. Kalghatgi in the SAE Paper Series 2002-01-2833. Then the test was repeated with the additive treated fuel.

Test Procedure: CCD Flaking Test on the Dodge Intrepid

[0025]

Ethyl Test Outline:	
Vehicle	Chrysler Dodge Intrepid
Fuel	CITGO Regular Unleaded
Test # 1	Without MMT Additive
Test # 2	With MMT Additive
Cycle	IVD Chassis Dyno Cycle (Average 45 mph) Two shifts per day (about 600 miles) Soak overnight End test at a cumulative 3000 miles:

At End of Test:

[0026]

1. Dismantle engine as per regular IVD/CCD test
2. Measure deposit thickness on both the head and pistons using the template
3. Spray piston tops with soap water (1 drop of liquid household detergent per 100 mL water) using a house plant water sprayer
4. After 3 hours photograph piston tops and note extent of flaking
5. Spray piston tops again and leave overnight.
6. Photograph piston tops and note extend of flaking
7. Remove flaked deposit by vacuum and weigh
8. Photograph piston tops
9. Measure thickness of remaining deposit using the template
10. Scrape and total piston top deposit
11. Complete IVD and CCD determination on head.

By the term "average" it is meant the average of deposit amounts on the six valves or the six piston tops, or the six cylinder head locations corresponding to the six pistons.

Table 1:

The Manganese Containing Additive Inhibited CCD Flaking			
Additive	Flaked Amount of CCD (milligrams)	Total Engine CCD (milligrams)	Engine IVD (milligrams)
No	89.4	783.4	312.2

Table 1: (continued)

The Manganese Containing Additive Inhibited CCD Flaking			
Additive	Flaked Amount of CCD (milligrams)	Total Engine CCD (milligrams)	Engine IVD (milligrams)
Yes	0	688.9	305.9

[0027] As is evident from this test example, the use of the specific metal-containing additive noted completely eliminated flaking of combustion chamber deposits. In other words, no CCD flaked off when the additive was used. Other metal-containing additives known to be radical sinks (anti-knocks) and/or combustion improvers such as those that enhance carbon burnout at lower temperatures may be used, and the treat rate of any additive may be varied. By changing the selection of additive and/or the treat rate of the additive, the amount of reduction in flaking may be controlled. It is believed that, in the case of a manganese-containing additive, a treat rate of about two mg. of manganese per liter of fuel will achieve up to about a 50% reduction in CCD flaking.

[0028] Given the discovered absence of CCD flaking, it should be evident that a more complete combustion occurs, especially during the cold start period of engine operation. There were no flakes to block the sealing of the exhaust valves. Therefore, less raw fuel is allowed to pass through the cylinder and into the exhaust system. Accordingly, cold start emissions of hydrocarbons should be reduced by use of the additive in spark ignited internal combustion engines that experience combustion chamber deposits.

[0029] It is to be understood that the reactants and components referred to by chemical name anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., base fuel, solvent, etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together either in performing a desired chemical reaction (such as formation of the organometallic compound) or in forming a desired composition (such as an additive concentrate or additized fuel blend). It will also be recognized that the additive components can be added or blended into or with the base fuels individually per se and/or as components used in forming preformed additive combinations and/or sub-combinations. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, components or ingredient as it existed at the time just before it was first blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that the substance, components or ingredient may have lost its original identity through a chemical reaction or transformation during the course of such blending or mixing operations or immediately thereafter is thus wholly immaterial for an accurate understanding and appreciation of this disclosure and the claims thereof.

[0030] At numerous places throughout this specification, reference has been made to a number of U.S. Patents, published foreign patent applications and published technical papers. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0031] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims and the equivalents thereof permitted as a matter of law.

[0032] Patentee does not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part of the invention under the doctrine of equivalents.

Claims

1. A method of reducing combustion chamber deposit flaking in spark ignited internal combustion engines that experience combustion chamber deposits comprising the steps of:

supplying a fuel comprising an additive that includes a metal-containing compound to a spark ignited internal combustion engine,
wherein the metal-containing compound is supplied in an amount effective to reduce combustion chamber deposit flaking.

2. A method of reducing cold start emissions from spark-ignited internal combustion engines that experience combustion chamber deposits comprising the steps of:

supplying a fuel comprising an additive that includes a metal-containing compound to a spark ignited internal combustion engine;
wherein the metal-containing compound is supplied in an amount effective to reduce cold start emissions.

3. A method as described in claim 1 or 2, wherein the metal-containing compound comprises a metal selected from the group consisting of manganese, platinum, palladium, rhodium, iron, cerium, copper, nickel, silver, cobalt, and molybdenum, and mixtures thereof.

4. A method as described in claim 3, wherein the metal-containing compound comprises a manganese compound.

5. The method described in claim 4, wherein the manganese-containing compound is an inorganic manganese compound.

6. The method described in claim 5, wherein the inorganic manganese compound is selected from the group consisting of fluorides, chlorides, bromides, iodides, oxides, nitrates, sulfates, phosphates, nitrides, hydrides, hydroxides carbonates and mixtures thereof.

7. The method described in claim 4, wherein the manganese-containing compound is an organometallic compound.

8. The method described in claim 7, wherein the organometallic compound is selected from groups where the ligands on the metal consist of alcohols, aldehydes, ketones, esters, anhydrides, sulfonates, phosphonates, chelates, phenates, crown ethers, carboxylic acids, amides, acetyl acetonates and mixtures thereof.

9. The method described in claim 4, wherein the manganese-containing compound comprises about 1 to about 50 mgMn/liter of the fuel.

10. The method described in claim 7, wherein the organometallic compound comprises methylcyclopentadienyl manganese tricarbonyl.

11. The method described in claim 4, wherein the manganese-containing compound is selected from the following group:

cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tert-butylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and the like, including mixtures of two or more such compounds.

12. A method as described in claim 1 or 2, where the fuel contains less than about 30 ppm of sulfur.

13. The method as described in claim 1 or 2, wherein the spark ignited internal combustion engine comprises a fuel injection or fuel delivery system selected from the group consisting of the following:

carbureted systems, port fuel injection system, multi point injection system, and direct injection gasoline system.

14. The method as described in claim 1 or 2, wherein the fuel comprises regular, unleaded gasoline.

15. The method as described in claim 1 or 2, wherein the engine comprises six or more cylinders.