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[54] **REDUCING DEPOSITS AND SMOKE FROM JET FUELS WITH ADDITIVES INCORPORATING AN AMMONIUM SALT**

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[58] **Field of Search** 44/51, 68, 71, 72, 76

[56] **References Cited**

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[57] **ABSTRACT**

Smoke and ash deposit formation in commercial and military jet engines and power plants is minimized by inclusion in the fuel of an additive comprising oil-soluble salts of a transition metal, such as manganese or iron, and an alkaline earth metal together with an oil-soluble ammonium salt. A preferred additive comprises methylcyclopentadienyl manganese tricarbonyl and calcium alkylphenol sulfide in amounts to provide a manganese/calcium weight ratio about 5/1. Dosage of the mixed metals is preferably within the range from 200 to 600 ppm. with dosage of ammonium ion within the range from 10 to 100 ppm.

12 Claims, No Drawings

REDUCING DEPOSITS AND SMOKE FROM JET FUELS WITH ADDITIVES INCORPORATING AN AMMONIUM SALT

BACKGROUND

Jet engines for aircraft and for "peak power" electric plants frequently have black smoke in their exhaust gases. For commercial aircraft the smoke is a serious air pollutant as well as a cause of visibility restrictions over large airports at times when the wind velocity is low. For military aircraft the smoke trail presents a combat disadvantage in that planes are visible to anti-aircraft weaponry at much greater distances than otherwise. For peak power electric plants, usually located in heavily populated areas, the smoke presents a serious pollution problem.

It is well known that certain transition metal compounds, when added to the jet fuel, inhibit or materially reduce smoke formation. Such compounds must be soluble in the jet fuel. One particularly effective oil-soluble transition metal compound is methylcyclopentadienyl manganese tricarbonyl, available from the Ethyl Corporation under the designation CI-2. Another similarly effective additive is tertiary amyl ferrocene, available from the Arapahoe Chemical Company. Use of such metallic additives has been limited, especially in aircraft engines, because of ash deposits which adhere to engine surfaces, including spray ports in jet engine afterburners. Engine distress due to the metallic ash deposits severly limits engine life and makes frequent overhaul necessary.

The smoke problem may also be overcome by installation of specially designed combustors within the jet engine assembly. Aside from their expense, these combustors are effective only for certain flow configurations which are difficult to maintain. A further disadvantage is a significant loss of maximum power when the combustors are operating, amounting to as much as 15 percent of the horsepower otherwise available.

Accordingly, there exists a need for an improved additive, for inclusion in the jet fuel, capable of minimizing the existing smoke emission problem found with all jet engine power plants while also minimizing the problem of ash deposits within the engine system and particularly for avoiding plugging of spray bars located in jet engine afterburners.

SUMMARY OF THE INVENTION

One object of our invention is to provide an improved additive for fuels employed in jet engine power plants, capable of inhibiting the formation of visible smoke and minimizing the deposition of ash on engine parts.

A further object of our invention is to provide a jet fuel composition having improved combustion properties and a lesser tendency to deposit inorganic residues on metallic engine surfaces, including spray ports in jet engine afterburners.

Another object of this invention is to increase the useful life of jet engines and to increase the time span between required engine overhauls.

Another object of this invention is to enhance the utility of metallic additives, capable of eliminating or reducing the visible smoke content of jet engine exhaust gases, by modifying these additives to minimize their tendency to cause excessive ash deposits to form on metallic engine surfaces and thereby drastically shorten engine life.

These objects are accomplished in our invention by providing an additive package, suitable for inclusion in jet fuels, and jet fuels containing such an additive package, whereby the smoking tendency of jet fuels is substantially reduced or eliminated while also minimizing the harmful side-effects of ash deposition on metal surfaces, usually associated with smoke inhibitors.

An oil-soluble transition metal compound, effective as a smoke-inhibiting additive, is modified and improved by inclusion of an oil-soluble compound of a secondary metal selected from among the alkaline earths. The secondary metal compound may also be in a basic, or alkaline, form. The additive components should be present in amounts sufficient to provide a weight ratio of transition metal to alkaline earth metal within the range from 67/33 to 95/5. The dosage of the jet fuel with the additive package should provide a total metals content within the range from 200 to 600 w.p.p.m. Additionally, an oil-soluble ammonium salt is present in an amount to provide from 10 to 100 w.p.p.m. ammonium ion.

DESCRIPTION OF THE INVENTION

This invention relates to jet fuel additives and to jet fuels containing these additives.

The additives of this invention comprise two oil-soluble metal compounds together with an ammonium compound, the first metal being derived from a transition metal suitable for reducing the smoking tendency of jet fuels during combustion in a jet engine, leading to visible smoke trails from jet aircraft. The second metal compound, derived from an alkaline earth metal, has been surprisingly discovered to impart additional smoke inhibition power to the transition metal compound and additionally to greatly reduce the formation of ash deposits on the metallic surfaces within the jet engine assembly. The presence of the second metallic compound of this invention has also surprisingly contributed to enhanced fuel stability at operating engine temperature and to fuel storage stability at near ambient temperatures in either the presence or absence of light. Reduction of ash deposits and particularly plugging of spray ports in jet engine afterburners has been surprisingly additionally enhanced by the further inclusion of an oil-soluble ammonium ion-affording compound such as an ammonium salt soluble in the jet fuel.

Suitable transition metal compounds for use in the additives of this invention include any oil-soluble compounds of vanadium, chromium, copper, cobalt, manganese, iron and nickel. Preferred transition metals are manganese and iron. Among the suitable oil-soluble compounds of these metals are the coordination compounds such as, for example, methylcyclopentadienyl manganese tricarbonyl (sold by Ethyl Corp. as CI-2) and tertiary amyl ferrocene (available from Arapahoe Chemical Co.). Such compounds may be employed in jet fuels in amounts sufficient to provide a transition metal content within the range from about 130 to about 570 w.p.p.m. When this is done the combustion of the jet fuel is improved so that visible smoke in the exhaust gas is greatly reduced or nearly eliminated. However, such transition metal additives have been limited in their use because of engine distress caused by the deposition of an inorganic ash, comprising metal oxides, on the surface of the engine internals.

Suitable alkaline earth metal compounds, for minimizing the ash deposition problem and surprisingly further improving smoke inhibition, include any oil-soluble compounds of the alkaline earth metals, especially those of magnesium, calcium and barium. These compounds include carboxylates, petroleum sulfonates, alkyl aryl sulfonates, alkyl phenates or other compounds compatible with the other components of the fuel. A preferred alkaline earth metal is calcium. Especially preferred alkaline earth compounds include magnesium sulfonates prepared with alkyl (C_{20} polypropylene) benzene sulfonic acid, barium nonyl phenol sulfide and calcium nonyl phenol sulfide. The alkaline earth compounds may be either neutral or basic, the alkaline form being prepared by over-basing with the corresponding metal oxide in the presence of carbon dioxide and an amine, such as ethylene diamine, or ammonia, as described in U.S. Pat. Nos. 3,492,230 and 3,524,814. The alkaline earth metal compound is employed in an amount selected to provide a quantity of secondary metal ranging from about 1 to about 35 wt. % of the total metals contained in the additive. Preferably the secondary, or alkaline earth, metal is present in the amount of 5 to 33 wt. % of the total metals, or sufficient to provide a weight ratio of transition to alkaline earth metal within the range from 95/5 to 67/33.

When desired, more than one transition metal compound may be employed together with any desired mixture of alkaline earth metals, limited only by compatibility in the selected jet fuel. Whenever such mixtures are used the weight ratio of transition metal to alkaline earth metal and the additive dosage concentration should conform to the ranges described above for simple combinations.

Suitable ammonium-ion affording compounds, for avoidance of plugging problems in spray bar operation while minimizing the ash deposition problem and improving smoke inhibition by use of the aforesaid metal compound combinations, include any oil-soluble ammonium salts. Such salts may be carboxylates, petroleum sulfonates, alkyl aryl sulfonates or other ammonium-containing or ammonium-affording compounds compatible with the other components of the fuel. Preferred ammonium salts include those prepared with alkyl (C_{20} polypropylene) benzene sulfonic acid, alkenyl (C_{23} polybutenyl) succinic acid and oleic acid. The ammonium salt is employed in an amount selected to provide from about 2 to about 20 wt. % ammonium ion based on the total weight of transition metal and alkaline earth metal. Preferably the ammonium ion is present in the amount of 5 to 10 wt. % based on the total metals. Such dosage of ammonium ion in a jet fuel will usually provide an ammonium ion content within the range from about 10 to about 100 w.p.p.m.

Any conventional commercial or military jet fuel may be improved by inclusion of the additive package of this invention. Such fuels include kerosene, JP-4, JP-5, and the like. These fuels may generally be described as boiling in the range from ambient temperature to 550°F., having an API gravity within the range from 40 to 55, and an aromatics content below about 20 percent. A more complete description of suitable jet fuels may be found in Bureau of Mines, Mineral Industry Survey, 1969.

The metal-containing additive components are suitably provided as a concentrate having a total metals content within the range from 10 to 25 wt. %. The components may be dissolved in any suitable petroleum base stock as a carrier for the concentrate. Such stocks include kerosene, JP-4 or JP-5 jet fuels, heater oil, furnace oil, and light lubricating oil stocks such as 5W grade oil.

The additive concentrate may then be added to a conventional commercial or military jet fuel in sufficient amount to provide a total metals content within the range from about 200 to about 600 ppm., preferably 200 to 500 ppm., and most desirably about 400 to 450 ppm. The corresponding ammonium ion content should be within the range from about 10 to about 100 ppm., preferably 25 to 50 ppm., and most desirably about 40 ppm. While the weight ratio of transition metal to alkaline earth metal may vary from 67/33 to 95/5, it is preferred that the ratio be between 75/25 and 90/10. A particularly preferred additive combination comprises 83 weight parts manganese and 17 weight parts calcium (Mn/Ca = 5/1).

The additive compositions and jet fuels containing them, which comprise the substance of our invention, possess both operational and significant economic value. Smoke is undesirable from both ecological and military viewpoints. Additives heretofore known to reduce smoking problems with jet fuels have in turn created serious economic problems by decreasing the life of the expensive jet engine power plants. The compositions of our invention not only reduce the engine-life problem, by reducing ash deposits, particularly in the critical spray ports in the afterburners, but surprisingly permit substitution of a relatively cheap alkaline earth metal compound for a portion of the required transition metal compound in effecting smoke reduction. Accordingly, the additive compositions and fuels of our invention provide a timely solution to a vexing problem and do so at an economic advantage. An afterburner spraybar includes individual tubes welded into a single unit and contains numerous small (0.025 inches) orifices. A number of these spraybars are circumferentially arranged in the exhaust gas stream. Fuel is pumped rapidly through the spraybars and sprayed into the exhaust gas stream for downstream combustion and subsequently increased engine thrust. There are essentially three fuel stages in an afterburner spraybar:

1. startup: cold fuel (150°–300°F.) is rapidly heated by the extremely hot empty spraybar (heated to 400°–800°F. by the ~ 1250°F. exhaust gas stream).
2. steady state: the cooling effect of rapidly moving fuel stabilizes tube and fuel temperatures.
3. shutdown: the fuel flow is halted and the spraybar drained and rapidly heated by the exhaust gas stream "cooking" any undrained fuel.

In line with the above spraybar-fuel history, the plugging problem appears to be non-combustive and associated with thermal fuel (vapor or liquid phase) decomposition and/or additive deposition from thermal (oxidative) decomposition or fuel evaporation during startup and/or shutdown when the fuel is subjected to abnormal temperature variations.

SPECIFIC EMBODIMENTS OF THE INVENTION

The following examples illustrate, without limitation, the scope of our invention.

EXAMPLE I

Jet fuel compositions were evaluated for combustion properties (soot and ash deposits) in a laboratory burner apparatus. In this evaluation procedure a selected fuel is metered into a vertically-disposed burner fitted with means for controlling air pressure. Centrally above the burner is placed a weighed glass cone, having a truncated base aligned horizontally with the burner tip. A second weighed, truncated glass cone, having a greater maximum circumference than the first cone, is inverted above the first cone. In operation a selected fuel feed rate is set and the air pressure is adjusted so that there is no leakage of fuel at the burner or down the wall of the first cone. This air pressure adjustment is then maintained throughout a series of tests. In operation, deposits collect on the walls of both cones positioned above the burner. After cooling, the cones are weighed to determine the total deposits (soot and ash). The deposits are then collected and burned to determine the residual, or ash, content.

The fuel employed in the following tests was a kerosene boiling within the range from 350° to 550°F. When an oil-soluble manganese compound was present as an additive, Ethyl CI-2 was employed in sufficient amount to provide 200 ppm. metal. When a secondary metal was similarly present, its selected oil-soluble compound was employed in sufficient amount to provide 10 ppm. metal. Total deposits on the lower cone were measured, as set forth in Table I, after burning 50 ml. fuel. Results of two separate series of runs show generally good agreement as to the ability of various metal combinations to reduce deposit formation. Where a secondary metal was employed, the sulfonate salts were C_{20} alkyl benzene sulfonates, overbased with excess metal oxide in the presence of carbon dioxide and either ammonia or ethylene diamine. The phenate salts were either alkaline (calcium) or neutral (barium) C_9 phenolsulfides. The succinate salt was an overbased (or alkaline) C_{23} alkenyl succinate. While all of the additives were effective in reducing deposits, the addition of either 5% calcium or 5% barium to manganese produced a significantly greater reduction in deposits than was realized with manganese alone.

TABLE I

TOTAL DEPOSIT FORMATION

Additive Metals	Run 1 Wt., mg.	Run 1 % Decrease	Run 2 Wt., mg.	Run 2 % Decrease
Base fuel	158	—	72	—
Mn	138	13	63	13
Mn + Ca (Sulfonate)	128	19	59	18
Mn + Ca (Phenate)	116	26	60	17
Mn + Ba (Succinate)	107	33	50	31
Mn + Ba (Phenate)	100	37	48	34

EXAMPLE II

The procedure of Example I was repeated employing the kerosene fuel with manganese present in Ethyl CI-2 and calcium present as the alkaline C_9 alkyl phenol sulfide. Both ash and soot in the total deposit were determined. Results presented in Table II show a distinct improvement in both ash reduction and soot (or smoke) reduction as the amount of calcium relative to manganese is increased up to 20% by weight. Above this optimum level, the effectiveness of calcium diminishes so that little advantage remains at concentrations above 25 percent.

TABLE II

DEPOSIT FORMATION vs. CALCIUM CONCENTRATION

Metals, ppm.			Ash		Soot	
Mn	Ca	%Ca vs. Mn	Wt., mg.	% Decrease	Wt., mg.	% Decrease
0	0	—	—	—	133	0
200	0	0	9	0	110	17
200	10	5	3	67	95	29
200	20	10	2	78	103	22
200	30	15	2	78	105	21
200	40	20	1	89	80	40
200	50	25	2	78	106	20
200	60	30	5	44	125	6

EXAMPLE III

The test procedure of Example II was repeated employing barium as the secondary metal, present as a neutral C_9 alkyl phenol sulfide. The results presented in Table III show the effectiveness of barium in reducing both ash and soot at the 5 wt. % level, based on manganese. Above that concentration a lesser effectiveness is indicated, particularly as regards reduction in soot formation.

TABLE III

DEPOSIT FORMATION vs. BARIUM CONCENTRATION

Metals, ppm.			Ash		Soot	
Mn	Ba	% BA vs. Mn	Wt., mg.	% Decrease	Wt., mg.	% Decrease
0	0	—	—	—	110	0
200	0	0	7.2	0	88	20
200	10	5	2.6	64	67	39
200	20	10	5.5	22	101	8
200	30	15	4.1	43	82	25
200	40	20	4.1	43	91	17
200	50	25	4.8	33	104	5
200	60	30	6.2	14	97	12

EXAMPLE IV

Smoke numbers of selected jet fuels were determined employing a burner rig fitted with a source of air, delivered at 10 atm. pressure, and a duel fuel injection system for switching from regular to test fuels. At a fixed fuel flow rate steady burner conditions were achieved and the exhaust gas was then sampled by tapping the exhaust and passing it through a filter paper until a fixed volume of gas had been filtered. The optical density of the resulting sample spot on the filter paper was then measured and the smoke number calculated. The value reported as the smoke number (S_n) is given by the equation:

$$S_n = 100\ (1 - 10^{(OD_s - OD_w)})$$

where

OD_w = optical density of clean Whatman filter paper, and

OD_s = optical density of sample spot after exhaust sample has passed through.

Because the value of S_n is dependent upon the amount of exhaust gas sampled, the Society of Automative Engineers procedure ARP 1179, for aircraft gas turbine engines, provides for a series of measurements

fitted to a straight line plotting S_n vs. log W/A, where W/A is the weight of fuel per unit area of the sample spot. Finally, the value of S_n is empirically selected as the value read from the chart at the point where W/A is 0.023 lbs./in.^{2} This procedure is repeated at each power (fuel rate) setting. On this basis an S_n value of 25 ± 3 represents threshold visibility. An untreated fuel will have an S_n of 60–70 at low fuel flow rates and a value of 50–60 at high fuel flow rates.

Smoke numbers were determined (employing a full-scale J79-17 jet engine with exhaust gas sampled as set forth above) for JP-4 base fuel (boiling in the range from room temperature to 550°F.) containing various concentrations of manganese (Ethyl CI-2) alone or with calcium (as alkaline alkyl phenol sulfide) in a 5/1 weight ratio. Data presented in Table IV show that the Mn/Ca mixture is as effective as Mn on a total metals basis and that each additive combination provides a minimum smoke number at a concentration of about 400 ppm.

TABLE IV

SMOKE NUMBERS OF Mn and Mn/Ca ADDITIVES

Metals, ppm.	0	112	131	216	445	448	672
Additive	None	Mn	Mn/Ca	Mn/Ca	Mn/Ca	Mn	Mn/Ca
Engine Load, % of Max. R.P.M.							
70	—	28	26	—	26	27	—
80	49	39	36	36	31	31	31
90	53	35	33	31	26	23	25
100	52	33	30	28	25	23	25

EXAMPLE V

An "afterburner spraybar simulator" was constructed, consisting of a glass tube of internal diameter and end constriction similar to an actual spraybar (4 mm OD with internal diameter of 0.13 inches versus 0.14 inches of actual spraybar) inserted snuggly into another glass tube, doubly wound with heating-tape to serve as the simulated exhaust gas stream (heat source). This system was connected to a fuel reservoir and circulating pump and test fuel was cycled through the simulated spraybar. To simulate afterburner operating conditions, the following test procedure was followed:

1. the circulating pump was flushed with 300 mls. each of hexane and acetone and vacuum sucked dry.
2. the test tube (simulated spraybar) was connected to the pump and the system primed with test solution (~ 150–200 grams).
3. the solution was circulated and the heating tape was activated (to raise temperature to a comparative temperature as observed in actual operation).
4. when the reservoir fuel temperature reached 140°–150°F. a 2 minute cycle was run.
5. 2 minute cycle included:
   a. 45 secs. circulating pump operation (whether fuel flows or not). This step simulated start-up, steady state, and shutdown.
   b. 75 secs. non-circulating pump operation. This step simulated exhaust-gas stream heat-up of the "simulated" spraybar.
6. the system was run with the 2 min. cycle until 45 secs. of pump operation was insufficient time to reinstate fuel circulation (plugging).
7. after every fifty 2-minute cycles, a new test fuel reservoir system was inserted.

There was then recorded the number of cycles attained before plugging (45 secs. pump operation insufficient) and the time during each cycle required to initiate fuel recirculation (time the pump is turned on until fuel reflows into reservoir).

The simulator gave essentially the same results as obtained in actual engine tests. Continuous running of kerosene for 24 hours (no 2-minute cycle) under above test conditions produced no deposition in the test tube. Running the 2 minute cycle gave the following results versus actual engine tests:

	SIMULATOR Cycles to Plugging	ACTUAL ENGINE Transients* to Plugging
Kerosene	325 (No signs of plugging)**	Does not plug
Mn	90, 106	80–100
Mn/Ca 5/1	69, 63	60

*On/off operations.
**1 to 2 sec. increase in time to pumping.

The afterburner spraybar simulator was then employed in the evaiuation of various additive compositions for lessening the plugging tendencies of additives such as set forth in the preceding Examples. The tests were conducted as above with a kerosene fuel, corresponding to a JP-4 jet fuel, maintained at a reservoir temperature of 140°–150°F., and pumped through a heating zone to provide an oil at 300°–350°F. in the hottest portion of the cycle. Test results are presented in Table V. Of a variety of surface-active compounds tested, only the ammonium salts were found to be effective in eliminating or materially reducing the plugging tendency of a typical jet fuel doped to minimize smoke problems.

TABLE V

AFTERBURNER SPRAYBAR SIMULATOR TESTS

TEST NUMBER	ADDITIVE COMPOSITION COMPONENT	W.P.P.M.	CYCLES TO PLUGGING
A-1	Mn	490	90, 106
A-2	Mn	430	100
	Ca	21	
A-3	Mn	375	63, 69
	Ca	75	
A-4	Mn	250	69
	Ca	250	
B-1[a]	Detergent A[b]	500	90
B-2	Detergent B[c]	500	79
B-3	Alkenylsuccinic anhydride[d]	400	109

TABLE V-Continued

AFTERBURNER SPRAYBAR SIMULATOR TESTS

TEST NUMBER	ADDITIVE COMPOSITION COMPONENT	W.P.P.M.	CYCLES TO PLUGGING
B-4	Alkenylsuccinic acid[a]	400	153
B-5	Alkenyl succinimide[d]	400	40
B-6	Alkenylsuccinate, diammonium salt[d]	400[e]	300 +
B-7	Alkylbenzene sulfonate, ammonium salt[f]	400[g]	300 +

[a] — All tests in the "B" series include 375 ppm. Mn and 75 ppm Ca (5/1 weight ratio as described in Example IV).
[b] — Commercial amide-imide.
[c] — Commercial Mannich condensation product.
[d] — Alkenyl group is $\overline{C}_{78}$ polybutenyl group.
[e] — Contains 40 w.p.p.m. ammonium ion.
[f] — Alkyl group is $\overline{C}_{30}$ polypropyl group.
[g] — Contains 25 w.p.p.m. ammonium ion.

I claim:

1. An additive composition, suitable for inclusion in jet fuel to inhibit smoke formation and ash deposition, comprising:

a. from 67 to 95 parts by weight of manganese or iron, provided as an oil-soluble metal coordination compound selected from the group consisting of methyl cyclopentadienyl manganese tricarbonyl and tertiary amyl ferrocene;

b. from 5 to 33 parts by weight of an alkaline earth metal, provided as an oil-soluble compound, said metal being selected from the group consisting of magnesium, calcium and barium, and said compound being selected from the group consisting of carboxylates, petroleum sulfonates, alkyl aryl sulfonates, alkyl phenates and alkylphenol sulfides; and

c. from 2 to 20 parts by weight of ammonium ion per 100 parts by weight of total metals from (a) and (b), said ammonium ion being provided as an oil-soluble ammonium salt selected from the group consisting of carboxylates, petroleum sulfonates, alkyl benzene sulfonates and alkenyl succinates.

2. The composition of claim **1** wherein the alkaline earth metal is calcium or barium.

3. The composition of claim **2** wherein the oil-soluble compound of an alkaline earth metal is a calcium alkylphenol sulfide or a barium alkylphenol sulfide.

4. The composition of claim **1** wherein the oil-soluble ammonium salt is an ammonium alkylbenzene sulfonate.

5. The composition of claim **1** wherein the oil-soluble ammonium salt is an ammonium alkenyl succinate.

6. The composition of claim **1** additionally comprising a petroleum base stock, selected from the group consisting of kerosene, jet fuel, heater oil, furnace oil, and light lubricating oil stocks, to provide an additive concentrate having a total metals concentration within the range from 10 to 25 wt. %.

7. A jet fuel composition comprising kerosene and, as a smoke-inhibiting and deposit-reducing additive, an oil-soluble metal coordination compound of manganese or iron and an oil-soluble alkaline earth metal compound together with an oil-soluble ammonium salt in an amount to provide from 200 to 600 p.p.m. total metals together with from 10 to 100 p.p.m. ammonium ion, said metals consisting of 67 to 95 parts by weight of manganese or iron and 5 to 33 parts by weight of an alkaline earth metal; said metal coordination compound being selected from the group consisting of methyl cyclopentadienyl manganese tricarbonyl and tertiary amyl ferrocene; said alkaline earth metal being magnesium, calcium or barium; said alkaline earth metal compound being selected from the group consisting of carboxylates, petroleum sulfonates, alkyl aryl sulfonates, alkyl phenates and alkyl phenol sulfides; and said ammonium ion being provided by an ammonium salt selected from the class consisting of carboxylates, petroleum sulfonates, alkyl benzene sulfonates and alkenyl succinates.

8. The fuel composition of claim **7** wherein the oil-soluble metal compound of manganese is methyl cyclopentadienyl manganese tricarbonyl.

9. The fuel composition of claim **7** wherein the oil-soluble metal compound of iron is tertiary amyl ferrocene.

10. The fuel composition of claim **7** wherein the oil-soluble alkaline earth metal compound is an alkylphenol sulfide of calcium or barium.

11. The fuel composition of claim **7** wherein the oil-soluble ammonium salt is an alkylbenzene sulfonate or an alkenyl succinate.

12. The fuel composition of claim **7** comprising kerosene together with oil-soluble metal compounds and ammonium salts to provide from about 200 to 600 p.p.m. manganese and calcium in a weight ratio manganese/calcium of about 5/1.

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