

[54] **REDUCING DEPOSITS AND SMOKE FROM JET FUELS**

[75] Inventors: **Roger William Watson**, Batavia;  
**John Henry Udelhofen**, Glenwood;  
**Joseph Stephan Strukl**, Hickory Hills, all of Ill.

[73] Assignee: **Standard Oil Company**, Chicago, Ill.

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*Primary Examiner*—Winston A. Douglas

*Assistant Examiner*—W. J. Shine

*Attorney, Agent, or Firm*—Philip Hill; Arthur G. Gilkes; William T. McClain

[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. A preferred additive comprises methylcyclopentadienyl manganese tricarbonyl and calcium alkylphenol sulfide in amounts to provide a manganese/calcium weight ratio about 5/1. The calcium salt may be in an alkaline form derived by over-basing with calcium oxide and carbon dioxide.

**4 Claims, No Drawings**

# REDUCING DEPOSITS AND SMOKE FROM JET FUELS

## 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. Engine distress due to the metallic ash deposits severely 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.

## 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.

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 sub-

stantially 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 10 to 600 p.p.m.

## 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, the first 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.

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 10 to about 600 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<sub>20</sub> polypropylene) benzene sulfonic acid, barium nonyl phenol sulfide and calcium monyl 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. percent of the transition metal contained in the additive. Preferably the secondary, or alkaline earth, metal is present in the amount of 5 to 30 wt. percent of the transition metal.

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.

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. percent. 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 10 to about 600 p.p.m., preferably 200 to 500 p.p.m., and most desirably about 400 p.p.m. 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. More preferably, the transition metal should be manganese and the alkaline earth metal should be calcium, with the respective metals being present in a weight ratio between 80/20 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, 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.

## 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 p.p.m. metal. When a secondary metal was similarly present, its selected oil-soluble compound was employed in sufficient amount to provide 10 p.p.m. 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<sub>20</sub> 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<sub>9</sub> phenol-sulfides. The succinate salt was an overbased (or alkaline) C<sub>23</sub> alkanyl succinate. While all of the additives were effective in reducing deposits, the addition of either 5 percent calcium or 5 percent barium to manganese produced a significantly greater reduction in deposits than was realized with manganese alone.

TABLE I

Additive metals	TOTAL DEPOSIT FORMATION			
	Run 1		Run 2	
	Wt., mg.	% Decrease	Wt., mg.	% Decrease
Base fuel	158	—	72	—
Mn	138	13	63	13
Mn + Mg (Sulfonate)	140	11	68	7
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 as 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 percent 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, p.p.m.		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 procedure of Examples I and II was repeated employing magnesium as the secondary metal, present as an alkaline  $C_{20}$  polypropylene benzene sulfonate. Results presented in Table III show that use of about 5–10 percent magnesium with manganese provides good reduction in both ash and soot but further increase in the magnesium content provides control of ash deposit but is ineffective in controlling soot formation.

TABLE III

DEPOSIT FORMATION vs. MAGNESIUM CONCENTRATION							
Metals, p.p.m.		Ash		Soot			
Mn	Mg	% Mg vs. Mn	Wt.,mg.	%Decrease	Wt.,mg.	%Decrease	
0	0	—	—	—	120	0	
200	0	0	7.2	0	89	25	
200	10	5	1.6	78	89	25	
200	20	10	2.0	72	98	18	
200	30	15	1.7	76	106	12	
200	40	20	1.6	78	111	9	
200	50	25	2.0	72	120	0	
200	60	30	2.4	66	131	11*	

\*Increase in soot deposit

## EXAMPLE IV

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

TABLE IV

DEPOSIT FORMATION vs. BARIUM CONCENTRATION							
Metals, p.p.m.		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	

TABLE IV-Continued

DEPOSIT FORMATION vs. BARIUM CONCENTRATION							
Metals, p.p.m.		Ash		Soot			
Mn	Ba	% Ba vs. Mn	Wt.,mg.	%Decrease	Wt.,mg.	%Decrease	
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 V

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 dual 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:

$$S_n = 100 (1 - 10(OD_w - OD_s))$$

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 Automotive 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<sup>2</sup>. This procedure is repeated at each power (fuel rate) setting. On this basis an  $S_n$  value of  $25 \pm 3$  represents threshold visibility. An untreated fuel will have an  $S_n$  of 60–70 at low fuel flow rates and a value of 50–50 at high fuel flow rates.

Employing a JP-4 jet fuel, boiling in the range from room temperature to 550°F., smoke numbers were measured on fuels containing an oil-soluble compound of either manganese or iron together with an oil-soluble magnesium, calcium or barium compound to provide a secondary metal additive. The manganese additive was Ethyl Cl-2 while the iron additive was Arapahoe tertiary amyl ferrocene. The secondary metal compounds were the same as used previously in Examples II, III and IV. Fuel rates selected were 35 gal. per hour, typical of high-smoke operation and 43 gal. per hour, typical of low-smoke operation. Where a secondary metal was present, the amount was always 5 wt. percent of the primary metal employed. Data presented in Table V indicate the effectiveness of the secondary metals, especially calcium, in lowering the smoke number below the values achieved when using the primary metal alone. Of the two primary metals employed in this series iron generally performed better than manganese, whether alone or in combination with a secondary metal.

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TABLE V

Fuel Rate,gph Primary Metal,p.p.m.	SMOKE NUMBER REDUCTION S <sub>n</sub> by SAE-ARP 1179					
	35			43		
	5	11	22	5	11	22
Additive						
None		(68)			(55)	
Mn	55	31	10	13	14	6
Mn + Mg	50	36	23	14	12	23
Mn + Ca	28	33	—	17	19	—
Mn + Ba	55	32	—	16	18	—
Fe	35	29	27	11	5	13
Fe + Mg	45	32	16	18	9	10
Fe + Ca	34	23	18	11	5	14
Fe + Ba	44	26	17	17	7	14

## EXAMPLE VI

Smoke numbers were determined (employing a full-scale J79-17 jet engine with exhaust gas sampled as in Example V) for JP-4 base fuel 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 VI 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 p.p.m.

TABLE VI

Metals, p.p.m. Additive Engine Load, % of Max R.P.M.	SMOKE NUMBERS OF Mn and Mn/Ca ADDITIVES						
	0	112	131	216	445	448	672
	None	Mn	Mn/Ca	Mn/Ca	Mn/Ca	Mn	Mn/Ca
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 VII

Storage stability tests were conducted at 110°F. (in dark bottles) and at room temperature (in clear bottles), employing Ethyl CI-2 and the secondary metal compounds used in Examples II, III and IV. The concentrations below were tested in kerosene.

Mn, p.p.m.	Secondary Metal, p.p.m.
4000	—
400	200
200	—
200	10
20	—
20	1

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After 6 months storage at 110°F. none of the solutions exhibited any marked color change or precipitation.

At room temperature Ethyl CI-2 gave a brown precipitate upon exposure to light for prolonged periods. The presence of a secondary metal greatly reduced the rate of precipitation.

## EXAMPLE VIII

Thermal stability of fuels consisting of JP-4 jet fuel together with either the Mn or Mn/Ca additive of Example VI was determined by a coker test (modified ASTM D-1660). The results showed greater fuel stability over a broad additive concentration range for the Mn/Ca system. With Mn alone stability continually decreased with increasing additive concentration.

We claim:

1. A composition, suitable as a deposit-reducing and smoke-inhibiting additive for jet fuels, comprising methylcyclopentadienyl manganese tricarbonyl and basic calcium alkylphenol sulfide to provide 80-90 parts by weight manganese and 10-20 parts by weight calcium.

2. The composition of claim 1 comprising about 83 parts manganese and about 17 parts calcium.

3. A jet fuel composition comprising, as a deposit-reducing and smoke-inhibiting additive, a mixture of oil-soluble compounds of manganese and calcium consisting essentially of methylcyclopentadienyl manganese tricarbonyl and basic calcium alkylphenol sulfide in sufficient amount to provide 200-500 p.p.m. total metals, consisting of 80-90 wt. percent manganese and 10-20 wt. percent calcium.

4. The composition of claim 3 containing about 400 p.p.m. total metals, consisting of about 83 wt. percent manganese and 17 wt. percent calcium.

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