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VANADIUM-CONTAINING PETROLEUM FUELS MODIFIED WITH THORIUM AND ALKALI METAL ADDITIVES

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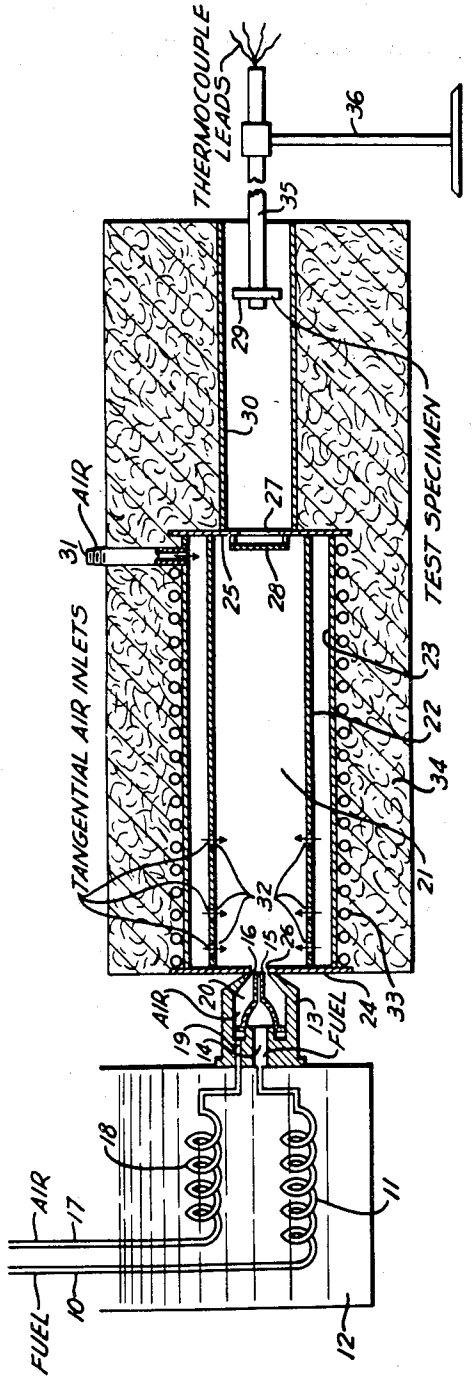
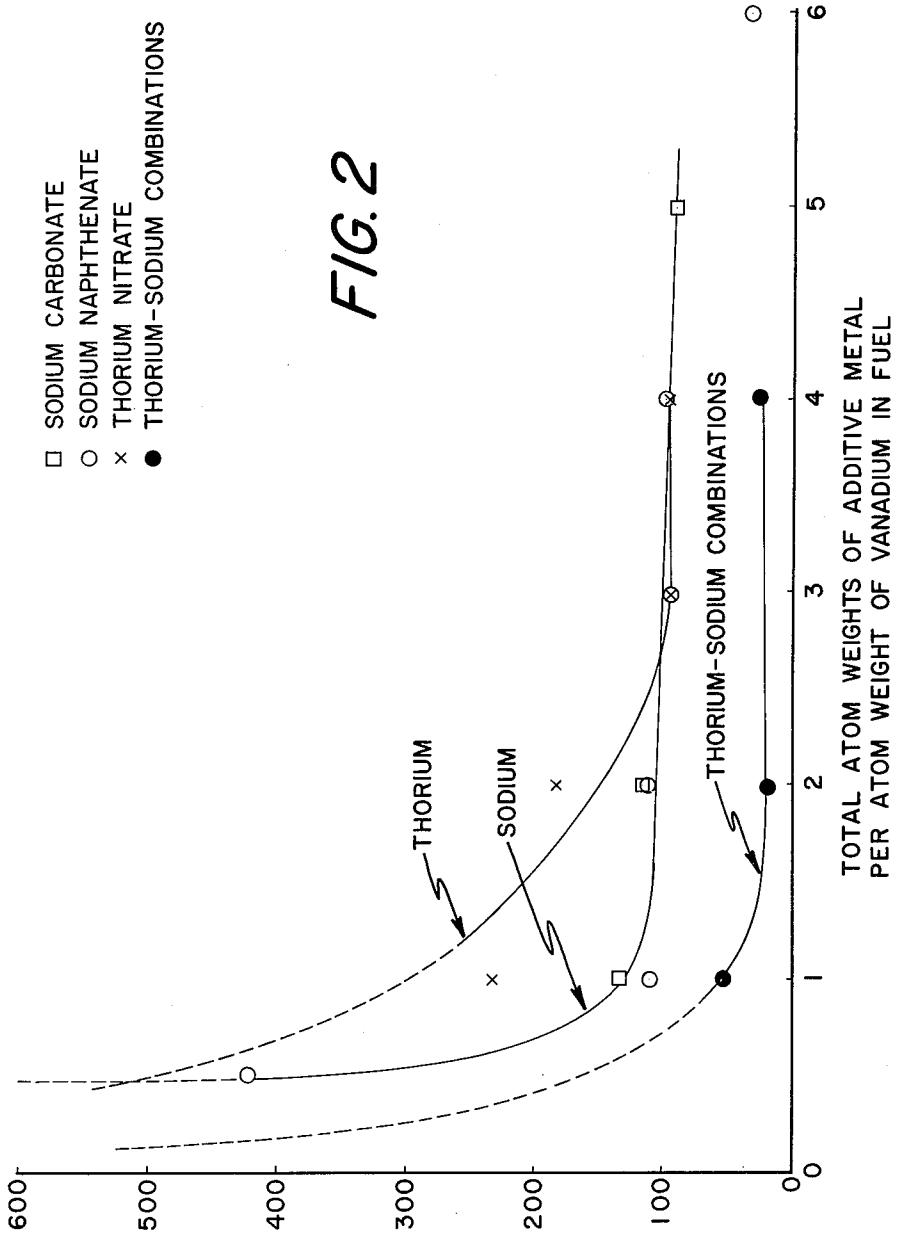


Fig. 1

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FIG. 2



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VANADIUM-CONTAINING PETROLEUM FUELS MODIFIED WITH THORIUM AND ALKALI METAL ADDITIVES

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This invention relates to vanadium-containing petroleum fuels. More particularly, it is concerned with rendering non-corrosive those residual fuels which contain such an amount of vanadium as normally to yield a corrosive vanadium-containing ash upon combustion.

This application is a continuation-in-part of our prior copending application, Serial No. 701,846, filed December 10, 1957, now abandoned, and assigned to the same assignee as the present application.

It has been observed that when a residual type fuel oil containing substantial amounts of vanadium is burned in furnaces, boilers and gas turbines, the ash resulting from combustion of the fuel oil is highly corrosive to materials of construction at elevated temperatures and attacks such parts as boiler tubes, hangers, turbine blades, and the like. These effects are particularly noticeable in gas turbines. Large gas turbines show promise of becoming an important type of industrial prime mover. However, economic considerations based on the efficiency of the gas turbine dictate the use of a fuel for this purpose which is cheaper than a distillate diesel fuel; otherwise, other forms of power such as diesel engines become competitive with gas turbines.

One of the main problems arising in the use of residual fuel oils in gas turbines is the corrosiveness induced by those residual fuels containing sufficient amounts of vanadium to cause corrosion. Where no vanadium is present or the amount of vanadium is small, no appreciable corrosion is encountered. While many residual fuel oils as normally obtained in the refinery contain so little vanadium, or none, as to present no corrosion problems, such non-corrosive fuel oils are not always available at the point where the oil is to be used. In such instance, the cost of transportation of the non-corrosive oil to the point of use is often prohibitive, and the residual oil loses its competitive advantage. These factors appear to militate against the extensive use of residual fuel oils for gas turbines. Aside from corrosion, the formation of deposits upon the burning of a residual fuel in a gas turbine may result in unbalance of the turbine blades, clogging of openings and reduced thermal efficiency of the turbine.

Substantially identical problems are encountered when using a solid residual petroleum fuel containing substantial amounts of vanadium. These fuels are petroleum residues obtained by known methods of petroleum refining such as deep vacuum reduction of asphaltic crudes to obtain solid residues, visbreaking of liquid distillation bottoms followed by distillation to obtain solid residues, coking of liquid distillation bottoms, and the like. The solid residues thus obtained are known variously as petroleum pitches or cokes and find use as fuels. Since the vanadium content of the original crude oil tends to concentrate in the residual fractions, and since the processing of the residual fractions to solid residues results in further concentration of the vanadium in the solid residues, the vanadium corrosion problem tends to be intensified in using the solid residues as fuel.

The vanadium-containing ash present in the hot flue gas obtained from the burning of a residual fuel containing substantial amounts of vanadium compounds causes "catastrophic" corrosion of the turbine blades and other metal parts in a gas turbine. The corrosive nature of the ash appears to be due to its vanadium oxide content. Certain inorganic compounds of vanadium, such as vanadium oxide (V_2O_5), which are formed on combustion of a residual fuel oil containing vanadium compounds, vigorously attack various metals, their alloys, and other materials at the elevated temperatures encountered in the combustion gases, the rate of attack becoming progressively more severe as the temperature is increased. The vanadium-containing ash forms deposits on the parts affected and corrosively reacts with them. It is a hard, adherent material when colled to ordinary temperatures.

It has already been proposed to employ in corrosive residual fuels certain metal compounds to mitigate the vanadium corrosion. Such compounds are of varying effectiveness and it has not always been possible to reduce vanadium induced corrosion to a minimum amount.

It has now been discovered that residual petroleum fuels containing vanadium in an amount sufficient to yield a corrosive vanadium-containing ash upon combustion can be rendered substantially non-corrosive by incorporating therein to form a uniform blend a small amount of a vanadium-free thorium compound sufficient to yield about 0.5 to 2 atom weights of thorium per atom weight of vanadium in said fuel, and a small amount of a vanadium-free alkali metal compound sufficient to yield about 0.5 to 2 atom weights of alkali metal per atom weight of vanadium, the total amount of thorium and alkali metal thus ranging from about 1 atom weight to 4 atom weights per atom weight of vanadium. In the fuel compositions of the invention the coaction of the two additive compounds is such that corrosion is reduced to negligible amounts.

In the accompanying drawings, the FIGURE 1 shows an apparatus for testing the corrosivity of residual fuel oil compositions and FIGURE 2 shows in graphic form the individual effects and combined effects of certain of the described additives in retarding corrosion.

The type of residual fuel oils to which the invention is directed is exemplified by No. 5, No. 6 and Bunker "C" fuel oils which contain a sufficient amount of vanadium to form a corrosive ash upon combustion. These are residual type fuel oils obtained from petroleum by methods known to the art. For example, residual fuel oils are obtained as liquid residua by the conventional distillation of total crudes, by atmospheric and vacuum reduction of total crudes, by the thermal cracking of topped crudes, by visbraking heavy petroleum residua, and other conventional treatments of heavy petroleum oils. Residua thus obtained are sometimes diluted with distillate fuel oil stocks, known as "cutter" stocks, and the invention also includes residual fuel oils so obtained, provided that such oils contain sufficient vanadium normally to exhibit the corrosion characteristics described herein. It should be understood that distillate fuel oils themselves contain either no vanadium or such small amounts as to present no problem of corrosion. The total ash from commercial residual fuel oils usually ranges from about 0.02 to 0.2 percent by weight. The vanadium pentoxide (V_2O_5) content of such ashes ranges from zero to trace amounts up to about 5 percent by weight for low vanadium stocks, exhibiting no significant vanadium corrosion problem, to as much as 85 percent by weight for some of the high vanadium stocks, exhibiting severe corrosion.

The type of vanadium-containing solid residual fuels to which the invention is directed is exemplified by the coke obtained in known manner by the delayed thermal coking or fluidized coking of topped or reduced crude oils and by the pitches obtained in known manner by the deep vacuum reduction of asphaltic crudes to obtain solid residues. These materials have ash content of the

order of 0.18 percent by weight, more or less, and contain corrosive amounts of vanadium when prepared from stocks containing substantial amounts of vanadium. A typical pitch exhibiting corrosive characteristics upon combustion had a softening point of 347° F. and a vanadium content, as vanadium, of 578 parts per million.

In accordance with the invention, any thorium compound, organic or inorganic, which is free from vanadium, is used as the thorium additive of the invention. Similarly, any organic or inorganic vanadium-free alkali metal compound is employed. The alkali metals include sodium, potassium, lithium, cesium and rubidium; sodium and potassium compounds are preferred. Such inorganic alkali metal and thorium compounds as the oxides, hydroxides, acetates, carbonates, oxalates, sulfates, nitrates, halides, and the like are successfully employed. In this connection, the mixture of salts present in sea water, as disclosed in our copending application, Serial No. 654,812, filed April 24, 1957, now U.S. Patent 2,966,029, comprises a suitable alkali metal compound.

The organic compounds of thorium and the alkali metals include the oil-soluble and oil-dispersible salts of acidic organic compounds such as: (1) the fatty acids, e.g., valeric, caproic, 2-ethylhexanoic, oleic, palmitic, stearic, linoleic, tall oil, and the like; (2) alkylaryl sulfonic acids, e.g., oil-soluble petroleum sulfonic acids and dodecylbenzene sulfonic acid; (3) long chain alkyl-sulfuric acids, e.g., lauryl sulfuric acids; (4) petroleum naphthenic acids; (5) rosin and hydrogenated rosin; (6) alkyl phenols, e.g., iso-octyl phenol, t-butylphenol and the like; (7) alkylphenol sulfides, e.g., bis(iso-octylphenol)monosulfide, bis(t-butylphenol) disulfide, and the like; (8) the acids obtained by the oxidation of petroleum waxes and other petroleum fractions; and (9) oil-soluble phenol-formaldehyde resins, e.g., the Amberols, such as t-butylphenol-formaldehyde resin, and the like. Since the salts or soaps of such acidic organic compounds as the fatty acids, naphthenic acids and rosins are relatively inexpensive and are easily prepared, these are preferred materials for the organic additives.

When employing in residual fuels the inorganic additives of the invention, it is desirable to use finely-divided materials. However, the degree of subdivision is not critical. One requirement for using a finely-divided material is based upon the desirability of forming a fairly stable dispersion or suspenion of the additive when blended with a reidual fuel oil. Furthermore, the more finely-divided materials are more efficient in forming uniform blends and rendering non-corrosive the relatively small amounts of vanadium in a residual fuel, whether the fuel be solid or liquid. The inorganic additives are therefore employed in a particle size range of less than 250 microns, preferably less than 50 microns. However, where the inorganic additives are water-soluble, for example, in the case of thorium nitrate, sodium carbonate, and the like, it is not necessary to employ finely-divided materials since, if desired, the additives can be dissolved in water to form a more or less concentrated solution and the water solution emulsified in the fuel.

The organic additives of the invention are oil-soluble or oil-dispersible and are therefore readily blended with residual fuels to form uniform blends. Since on a weight basis to the fuel, the amounts of the additives are small, it is desirable to prepare concentrated solutions or dispersions of the organic additives in a naphtha, kerosene or gas oil for convenience in compounding.

In the practice of the invention with vanadium-containing residual fuel oils, the mixture of additives is uniformly blended with the oil in the disclosed proportions. This is accomplished by suspending the finely-divided dry additives in the oil, emulsifying or dispersing a concentrated water solution of the water-soluble inorganic additives in the oil, or dissolving or dispersing the organic additives in the oil. If desired, suitable surface active agents, such as sorbitan monooleate and monolaurate and the ethylene oxide condensation products thereof, glycerol monooleate, and the like, which promote the stability of the suspensions or emulsions can be employed.

In the practice of the invention with the solid residual fuels, incorporation of the additives of the invention is accomplished in several ways. The additives can be suspended, emulsified or dissolved in the liquid vanadium-containing residual stocks or crude oil stocks from which the solid residual fuels of the invention are derived, and the mixture can then be subjected to the refining process which will produce the solid fuel. For example, in the production of a pitch by the deep vacuum reduction of an asphaltic crude oil, the additives or a concentrate thereof are slurried with the oil in proportion to the vanadium content thereof, and the whole subjected to deep vacuum reduction to obtain a pitch containing the additives uniformly dispersed therein. As still another alternative, particularly with a pitch which is withdrawn in molten form from the processing vessel, the additives can be mixed with the molten pitch and the mixture allowed to solidify after which it is ground to the desired size.

In the case of either liquid or solid residual fuels, the additives can be separately fed into the burner as concentrated solutions or dispersions. In such a case, it is preferred to meter the additives into the fuel line just prior to the combustion zone. In a gas turbine plant where the heat resisting metallic parts are exposed to hot combustion gases at temperatures of the order of 1200° F. and above, the additives can be added separately from the fuel either prior to or during combustion itself, or even subsequent to combustion. However they may specifically be added, whether in admixture with or separately from the fuel, the additives are introduced into said plant upstream of the heat resisting metal parts to be protected from corrosion.

It is a characteristic feature of the invention that the use of both the thorium and alkali metal additives in the proportions described and claimed results in an unexpectedly greater reduction in corrosion to lower, substantially minimal amounts than can be obtained by using either the thorium or alkali metal additives singly in the same total additive content. This unexpected coaction is obtained when the amounts of the alkali metal and thorium additives are each in the range of about 0.5 to 2 atom weights per atom weight of vanadium in the fuel, the total amount of additive thus being in the range of about 1 to 4 atom weights of additive metals per atom weight of vanadium.

The following specific examples are further illustrative of the invention:

EXAMPLE I

With a residual fuel oil uniformly blend 0.18 percent by weight of thorium nitrate and 0.02 percent by weight of sodium carbonate. The residual fuel oil employed has the following inspection:

Gravity: °API	21.4
Viscosity, Furol: sec.:	
77° F.	67.6
122° F.	21.5
Flash, OC: °F.	175
Fire, OC: °F.	195
Sulfur, B: percent	1.6
Ash: percent	0.04
Vanadium: p.p.m. of oil	166
Sodium: p.p.m. of oil	3

The resulting composition has an atom weight ratio of thorium to vanadium of 1:1 and an atom weight ratio of sodium to vanadium of 1:1.

EXAMPLE II

Uniformly blend with a residual fuel oil 0.114 percent by weight of thorium nitrate and 0.012 percent by

weight of sodium carbonate. The residual fuel oil employed has the following inspection:

Gravity: °API	20.2
Viscosity, Furol: sec.:	
77° F.	67.2
122° F.	25.3
Flash, OC: °F.	240
Fire, OC: °F.	250
Sulfur, B: percent	2.1
Ash: percent	0.04
Vanadium: p.p.m. of oil	243
Sodium: p.p.m. of oil	10

The resulting composition has an atom weight ratio of thorium to vanadium of 0.5:1 and an atom weight ratio of sodium to vanadium of 0.5:1.

EXAMPLE III

To the same residual fuel oil of Example II, add and uniformly blend 0.456 percent by weight of thorium nitrate and 0.048 percent by weight of sodium carbonate. The resulting fuel oil composition has an atom weight ratio of thorium to vanadium of 2:1 and an atom weight ratio of sodium to vanadium of 2:1.

EXAMPLE IV

Melt a solid petroleum pitch obtained from the deep vacuum reduction of an asphaltic crude. This pitch has a softening point of 347° F. and a vanadium content of 578 parts per million. While the pitch is in molten form, add and uniformly blend therein 0.6 percent by weight of thorium oxide and 0.08 percent by weight of sodium sulfate. Upon cooling and solidification, grind the mixture to about 150 mesh. The resulting fuel has an atom weight ratio of thorium to vanadium of 2:1 and an atom weight ratio of sodium to vanadium of 1:1.

In order to test the effectiveness of the additives of this invention under conditions of burning residual fuels in a gas turbine, the apparatus shown in FIGURE 1 is employed. As shown therein, the residual oil under test is introduced through line **10** into a heating coil **11** disposed in a tank of water **12** maintained at such temperature that the incoming fuel is preheated to a temperature of approximately 212° F. From the heating coil **11** the preheated oil is passed into an atomizing head designated generally as **13**. The pre-heated oil passes through a passageway **14** into a nozzle **15** which consists of a #26 hypodermic needle of approximately 0.008 inch I.D. and 0.018 inch O.D. The tip of the nozzle is ground square and allowed to project slightly through an orifice **16** of approximately 0.020 inch diameter The orifice is supplied with 65 p.s.i.g. air for atomization of the fuel into the combustion chamber **21**. The air is introduced through line **17**, preheat coil **18** in tank **12**, and air passageways **19** and **20** in the atomizing head **13**. The combustion chamber **21** is made up of two concentric cylinders **22** and **23**, respectively, welded to two end plates **24** and **25**. Cylinder **22** has a diameter of 2 inches and cylinder **23** has a diameter of 3 inches; the length of the cylinders between the end plates is 8½ inches. End plate **24** has a central opening **26** into which the atomizing head is inserted. End plate **25** has a one (1) inch opening **27** covered by a baffle plate **28** mounted in front of it to prevent direct blast of flame on the test speciment **29**. Opening **27** in end plate **25** discharges into a smaller cylinder **30** having a diameter of 1½ inches and a length of 6 inches. The specimen **29** is mounted near the downstream end of the cylinder approximately 1¾ inches from the outlet thereof. Combustion air is introduced by means of air inlet **31** into the annulus between cylinders **22** and **23**, thereby preheating the combustion air, and then through three pairs of 3/16 inch tangential air inlets **32** in the inner cylinder **22**. The first pair of air inlets is spaced ¼ inch from

end plate **24**; the second pair ¾ inch from the first; and the third 3 inches from the second. The additional heating required to bring the combustion products to test temperature is supplied by an electric heating coil **33** surrounding the outer cylinder **23**. The entire combustion assembly is surrounded by suitable insulation **34**. The test specimen **29** is a metal disc one inch in diameter by 0.125 inch thick, with a hole in the center by means of which the specimen is attached to a tube **35** containing thermocouples. The specimen and tube assembly are mounted on a suitable stand **36**.

In conducting a test in the above-described apparatus, a weighed metal specimen is exposed to the combustion products of a residual fuel oil, the specimen being maintained at a selected test temperature of, for example, 1350°, 1450° or 1550° F. by the heat of the combustion products. The test is usually run for a period of 100 hours with the rate of fuel feed being ½ pound per hour and the rate of atomizing air feed being 2 pounds per hour. The combustion air entering through air inlet **31** is fed at 25 pounds per hour. At the end of the test run the specimen is reweighed to determine the weight of deposits and is then descaled with a conventional alkaline descaling salt in molten condition at 475° C. After descaling, the specimen is dipped in 6 N hydrochloric acid containing a conventional pickling inhibitor, and is then washed, dried and weighed. The loss in weight of the specimen after descaling is the corrosion loss.

Tests are conducted in the apparatus just described using a 25—20 stainless steel as the test specimen. The tests are run for 100 hours at a temperature of 1450° F. under the conditions described above. Tests are made with the fuel oil compositions of Examples I, II and III, with fuel oil compositions similar to these examples but containing only one of the additives in varying amounts, and with the uncompounded residual fuel oils of the examples. The following tables show the corrosion and deposits obtained:

Table I

	Corrosion, Wt. Loss of Specimen, Mg./Sq. In.	Deposits, Mg./Sq. In.
Uncompounded Fuel of Example I	992	319
Uncompounded Fuel of Examples II and III	1,143	231

Table II

SODIUM ADDITIVES

	Atom Wt. Ratio, Na:V	Corrosion, Wt. Loss of Specimen, Mg./Sq. In.	Deposits, Mg./Sq. In.
Fuel+Sodium Naphthenate	0.5:1	426	512
Do	1:1	110	237
Fuel+Sodium Carbonate	1:1	133	234
Fuel+Sodium Naphthenate	2:1	112	195
Fuel+Sodium Carbonate	2:1	117	211
Fuel+Sodium Naphthenate	3:1	96	121
Do	4:1	99	370
Fuel+Sodium Carbonate	5:1	91	205
Fuel+Sodium Naphthenate	6:1	34	68

Table III

THORIUM ADDITIVES

	Atom Wt. Ratio, Th:V	Corrosion, Wt. Loss of Specimen, Mg./Sq. In.	Deposits, Mg./Sq. In.
Fuel+Thorium Nitrate	1:1	234	44
Do	2:1	184	91
Do	3:1	95	134
Do	4:1	91	84

Table IV

SODIUM AND THORIUM COMBINATIONS

	Atom Wt. Ratio, Additive Metals:V	Corrosion, Wt. Loss of Specimen, Mg./Sq. In.	Deposits, Mg./Sq. In.
Compounded Fuel of Example I.	Th:V=1:1 / Na:V=1:1	20	209
Compounded Fuel of Example II.	Th:V=0.5:1 / Na:V=0.5:1	51	220
Compounded Fuel of Example III.	Th:V=2:1 / Na:V=2:1	27	154

The corrosion result for each fuel shown in the above tables was plotted against the total additive content for such fuel, separate curves being obtained for the sodium additives alone, the thorium additives alone and the combination of sodium and thorium additives. These curves are shown in FIGURE 2.

It will be seen from the data in the above tables and the curves of FIGURE 2 that, over the entire range of proportions of total additive content of from about 1 to 4 atom weights of additive metal per atom weight of vanadium, the thorium and sodium additive combinations unexpectedly reduce corrosion to a far greater extent than the same concentration of either the thorium or sodium additives alone. Furthermore, the amount of corrosion obtained with the combination of additives tends to approach minimal, substantially negligible amounts. Best results for the thorium and alkali metal additive combinations are obtained in total additive amounts of from 2 to 4 atom weights per atom weight of vanadium in the fuel. While the additive combinations in amounts less than about 1 atom weight of total additive metal per atom weight of vanadium would seem to possess an unexpected superiority over the individual additives at the same concentrations, the amount of corrosion with the combinations at such concentrations would rapidly increase with decreasing additive content.

Similar results to those shown for the thorium nitrate and sodium carbonate are obtained using the other thorium and alkali metal compounds disclosed.

A typical analysis of the 25–20 stainless steel employed in the testing described is shown in the following table in percent by weight:

Table V

	25–20
Cr	25
Ni	20
C	0.08
Mn	2.0
Si	1.5
S	0.03
P	0.04
Fe	Balance

Resort may be had to such modifications and variations as fall within the spirit of the invention and the scope of the appended claims.

We claim:

1. A fuel composition comprising a uniform blend of a major amount of a residual petroleum fuel yielding a corrosive vanadium-containing ash upon combustion, an amount of a vanadium-free thorium compound yielding about 0.5 to 2 atom weights of thorium per atom weight of vanadium in said fuel, and an amount of a vanadium-free alkali metal compound yielding about 0.5 to 2 atom weights of alkali metal per atom weight of vanadium in said fuel, the total amount of thorium and alkali metal ranging from about 1 to 4 atom weights per atom weight of vanadium.

2. The fuel composition of claim 1, wherein the fuel is a solid residual petroleum fuel.

3. A fuel composition comprising a major amount of a residual fuel oil yielding a corrosive vanadium-containing ash upon combustion, an amount of a vanadium-free thorium compound yielding about 0.5 to 2 atom weights of thorium per atom weight of vanadium in said fuel oil and an amount of a vanadium-free sodium compound yielding about 0.5 to 2 atom weights of alkali metal per atom weight of vanadium in said fuel oil, the total amount of thorium and sodium ranging from about 1 to 4 atom weights per atom weight of vanadium.

4. The fuel composition of claim 3, wherein the total amount of thorium and sodium is in the range of 2 to 4 atom weights.

5. The fuel composition of claim 3, wherein the thorium compound is thorium nitrate and the alkali metal compound is sodium carbonate.

6. In a gas turbine plant in which a fuel oil containing vanadium is burned and which includes heat resisting metallic parts exposed to hot combustion gases and liable to be corroded by the corrosive vanadium-containing ash resulting from combustion of said oil, the method of reducing said corrosion which comprises introducing into said plant upstream of said parts a small amount of a vanadium-free mixture of a thorium compound and an alkali metal compound, the amount of said thorium compound yielding about 0.5 to 2 atom weights of thorium per atom weight of vanadium in said fuel, and the amount of alkali metal compound yielding about 0.5 to 2 atom weights of alkali metal per atom weight of vanadium in said fuel, the total amount of thorium and alkali metal ranging from about 1 to 4 atom weights per atom weight of vanadium.

7. The method of claim 6, wherein the alkali metal compound is a sodium compound.

References Cited in the file of this patent

UNITED STATES PATENTS

2,949,008 Rocchini ---------- Aug. 16, 1960

FOREIGN PATENTS

761,378 Great Britain ---------- Nov. 14, 1956
1,113,013 France ---------- Nov. 23, 1955
1,117,896 France ---------- Mar. 5, 1956