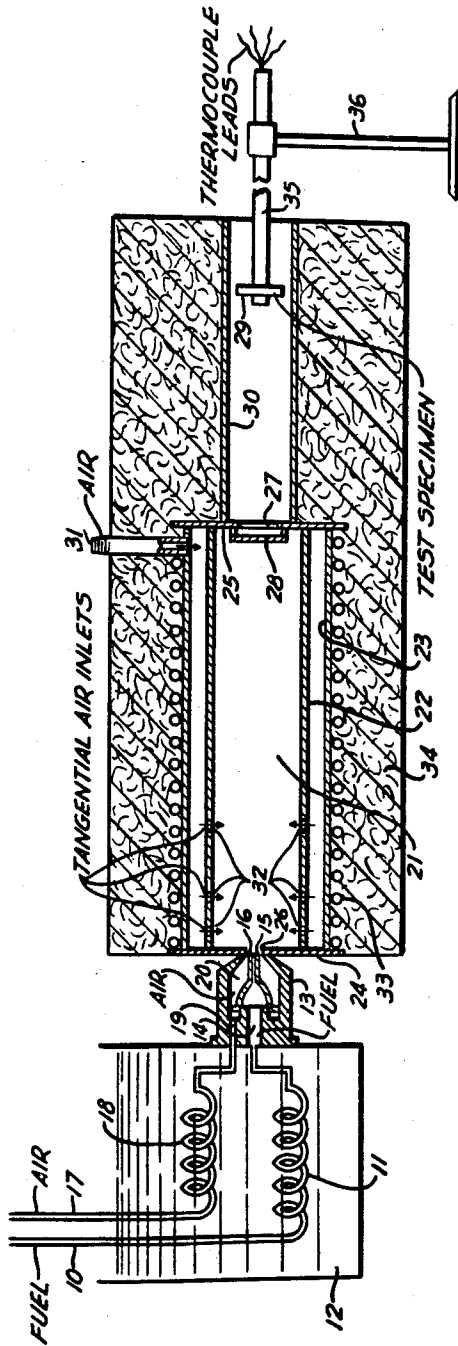


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RESIDUAL FUELS CONTAINING ALKALI METAL COMPOUNDS AS CORROSION RETARDERS

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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.

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

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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 cooled to ordinary temperatures.

It has already been proposed to employ in corrosive residual fuels small amounts of 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 less corrosive by incorporating therein to form a uniform blend, a small, corrosion retarding amount of a mixture, containing two different alkali metals, of any two of the vanadium-free compounds of the alkali metals selected from the group consisting of sodium, potassium and lithium, the mixture of such compounds giving a greater corrosion retarding effect than the individual compounds thereof.

In the accompanying drawing, the single FIGURE shows an apparatus for testing the corrosivity of residual fuel oil compositions.

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 visbreaking 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 contents 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.

Any sodium, potassium and lithium compound, organic or inorganic, which is free from vanadium is used as an additive in accordance with the invention. Such

inorganic compounds as the oxides, hydroxides, acetates, carbonates, silicates, 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 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 acid; (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-octyl phenol)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 sub-division is not critical. One requirement for using a finely-divided material is based upon the desirability of forming a fairly stable dispersion or suspension of the additives when blended with a residual 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 lithium sulfate, sodium and potassium carbonates, 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 in relation to the fuel the amounts of the additives are small, it may be 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. 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.

As has been stated, there is employed in the fuels of the invention a small, corrosion retarding amount of a mixture, containing two different alkali metals, of any two of the vanadium-free compounds of the alkali metals selected from the group consisting of sodium, potassium and lithium. Of the various mixtures, a mixture of sodium and potassium compounds is highly preferred, because the sodium-potassium mixture reduces corrosion to negligible amounts yet requires less total additive for this purpose than lithium-sodium and lithium-potassium mixtures. For example, a sodium-potassium mixture containing about 1 atom weight each of sodium and potassium per atom weight of vanadium in the fuel results in negligible corrosion, whereas the same order of effectiveness is obtained with a lithium-sodium mixture when the mixture contains 3 atom weights of lithium and 1 atom weight of sodium per atom weight of vanadium. With the lithium-potassium mixtures, the lithium content of a mixture containing 1 atom weight of potassium per atom weight of vanadium should be on the order of about 4, 5 or 6 atom weights of lithium per atom weight of vanadium to obtain comparable results. Nevertheless, as compared with the results obtained when using single sodium, potassium or lithium additives, the additive combinations of the invention in the same total additive amount as the single additives are unexpectedly superior.

The following examples are further illustrative of the invention.

EXAMPLE I

With a residual fuel oil uniformly blend 0.11 percent by weight of a wet paste of sodium petroleum naphthenate containing 8 percent by weight of sodium and 0.19 percent by weight of a solution of potassium petroleum naphthenate in naphtha containing 8.1 percent by weight of potassium. The residual fuel oil employed has the following inspection:

Gravity, ° API	20.2
Viscosity, Furol. sec.:	
77° F.	65.2
122° F.	22.0
Flash, OC, ° F.	160
Fire, OC, ° F.	210
Sulfur, B, percent	1.8
Ash, percent	0.04
Vanadium, p.p.m. of oil	203
Sodium, p.p.m. of oil	11

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

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EXAMPLE II

To the same residual fuel oil of Example I, add and uniformly blend 0.5 percent by weight of a solution of lithium petroleum naphthenate in naphtha containing 1.7 percent by weight of lithium and 0.11 percent by weight of a wet paste of sodium petroleum naphthenate containing 8 percent by weight of sodium. The resulting composition has an atom weight ratio of lithium to vanadium of 3:1 and an atom weight ratio of sodium to vanadium of 1:1.

EXAMPLE III

Uniformly blend with the same residual fuel oil of Example I, 0.5 percent by weight of a solution of lithium petroleum naphthenate in naphtha containing 1.7 percent by weight of lithium and 0.19 percent by weight of a solution of potassium petroleum naphthenate in naphtha containing 8.1 percent by weight of potassium. The resulting fuel oil composition has an atom weight ratio of lithium to vanadium of 3:1 and an atom weight ratio of potassium to vanadium of 1:1.

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 0.156 percent by weight of potassium carbonate and 0.06 percent by weight of sodium carbonate. Upon cooling and solidification, grind the mixture to about 150 mesh. The resulting fuel has an atom weight ratio of potassium to vanadium of 1:1 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 the drawing 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 preheated 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

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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 specimen 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 ⅜ 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 the fuel oil compositions similar to those of these examples but containing only one of the additives in varying proportions, and with the un-compounded residual fuel oil of Example I. The same base fuel is used in all the tests. The following table shows the corrosion and deposits obtained.

Table I

	Atom Wt. Ratio, Additive Metal: V	Corrosion, Wt. Loss of Specimen, Mg./Sq. In.	Deposits	
			Amount, Mg./Sq. In.	Nature
Uncompounded Fuel of Ex. I		1430	1151	Hard Scale.
Fuel+Sodium Naphthenate	4:1	99	370	Powdery.
Do.	2:1	112	195	Do.
Fuel+Potassium Naphthenate	4:1	176	232	Do.
Do.	2:1	206	229	Do.
Fuel+Lithium Naphthenate	4:1	192	207	Hard Scale.
Fuel+Potassium Naphthenate+Sodium Naphthenate (Ex. I)	(K:V=1:1)	0	110	Powdery.
Fuel+Lithium Naphthenate+Sodium Naphthenate (Ex. I)	(Li:V=1:1)			
Fuel+Lithium Naphthenate+Sodium Naphthenate (Ex. II)	(Li:V=3:1)	14	140	Do.
Fuel+Lithium Naphthenate+Potassium Naphthenate (Ex. III)	(Li:V=3:1)	142	210	Do.
	(K:V=1:1)			

It will be seen from the preceding table that, although the individual alkali metal additives used alone tend to diminish corrosion, considerable corrosion is still obtained. However, when the additives are employed in combination, corrosion is unexpectedly further reduced. Thus, it will be noted that, in every case where the combined additives are employed, corrosion is reduced from the values obtained with the individual additives in the same concentration as the combined additives. The preceding table makes clear the unexpected effect of the combined additives, particularly the sodium-potassium and sodium-lithium combinations, of minimizing corrosion to negligible amounts. Similar minimizing of corrosion is obtained from the lithium-potassium combinations by increasing the amount of lithium, as has previously been stated.

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 II

	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, a small amount sufficient to retard the corrosiveness of the ash of a mixture, containing two different alkali metals, of any two of the vanadium-free compounds of the alkali metals selected from the group consisting of sodium, potassium and lithium, the amounts of said alkali metal compounds being: (a) about 1 atom weight each of sodium and potassium per atom weight of vanadium in said fuel when said mixture contains said sodium and potassium compounds; (b) about 3 atom weights of lithium and 1 atom weight of sodium per atom weight of vanadium in said fuel when said mixture contains said lithium and sodium compounds; and (c) about 3 to 6 atom weights of lithium and about 1 atom weight of potassium per atom weight of vanadium in said fuel when said mixture contains said lithium and potassium compounds.

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

3. The fuel composition of claim 1, wherein the two alkali metals are sodium and potassium.

4. The fuel composition of claim 1, wherein the two alkali metals are sodium and lithium.

5. The fuel composition of claim 1, wherein the two alkali metals are lithium and potassium.

6. The fuel composition of claim 1, wherein the alkali metal compounds are selected from the class consisting of oil-soluble and oil-dispersible salts of acidic organic compounds.

7. A fuel composition comprising a uniform blend of a major amount of a residual fuel oil yielding a corro-

sive vanadium-containing ash upon combustion, an amount of a vanadium-free sodium compound yielding about 1 atom weight of sodium per atom weight of vanadium in said fuel oil, and an amount of a vanadium-free potassium compound yielding about 1 atom weight of potassium per atom weight of vanadium in said fuel oil.

8. The fuel composition of claim 7, wherein the sodium and potassium compounds are naphthenates.

9. A fuel composition comprising a uniform blend of a major amount of a residual fuel oil yielding a corrosive vanadium-containing ash upon combustion, an amount of a vanadium-free lithium compound yielding about 3 atom weights of lithium per atom weight of vanadium in said fuel oil, and an amount of a vanadium-free sodium compound yielding about 1 atom weight of sodium per atom weight of vanadium in said fuel oil.

10. The fuel composition of claim 9, wherein the lithium and sodium compounds are naphthenates.

11. A fuel composition comprising a uniform blend of a major amount of a residual fuel oil yielding a corrosive vanadium-containing ash upon combustion, an amount of a vanadium-free lithium compound yielding about 3 to 6 atom weights of lithium per atom weight of vanadium in said fuel oil, and an amount of a vanadium-free potassium compound yielding about 1 atom weight of potassium per atom weight of vanadium in said fuel oil.

12. The fuel composition of claim 11, wherein the lithium and potassium compounds are naphthenates.

13. 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 sufficient to retard the corrosiveness of said ash of a mixture, containing two different alkali metals, of any two of the vanadium-free compounds of the alkali metals selected from the group consisting of sodium, potassium and lithium, the amounts of said alkali metal compounds being: (a) about 1 atom weight each of sodium and potassium per atom weight of vanadium in said fuel when said mixture contains said sodium and potassium compounds; (b) about 3 atom weights of lithium and 1 atom weight of sodium per atom weight of vanadium in said fuel when said mixture contains said lithium and sodium compounds; and (c) about 3 to 6 atom weights of lithium and about 1 atom weight of potassium per atom weight of vanadium in said fuel when said mixture contains said lithium and potassium compounds.

14. The method of claim 13, wherein the two alkali metals are sodium and potassium.

15. The method of claim 13, wherein the two alkali metals are sodium and lithium.

16. The method of claim 13, wherein the two alkali metals are lithium and potassium.

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