Dec. 27, 1960 A. G. ROCCHINI ET AL 2,966,029

CORROSION INHIBITED FUELS CONTAINING VANADIUM

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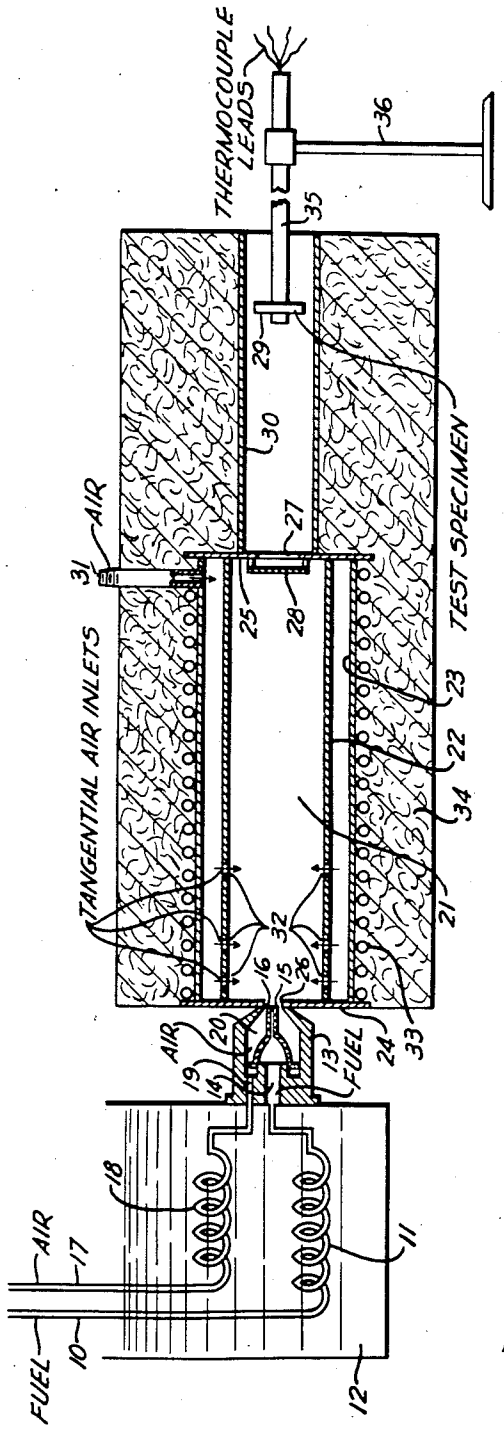


Fig. 1

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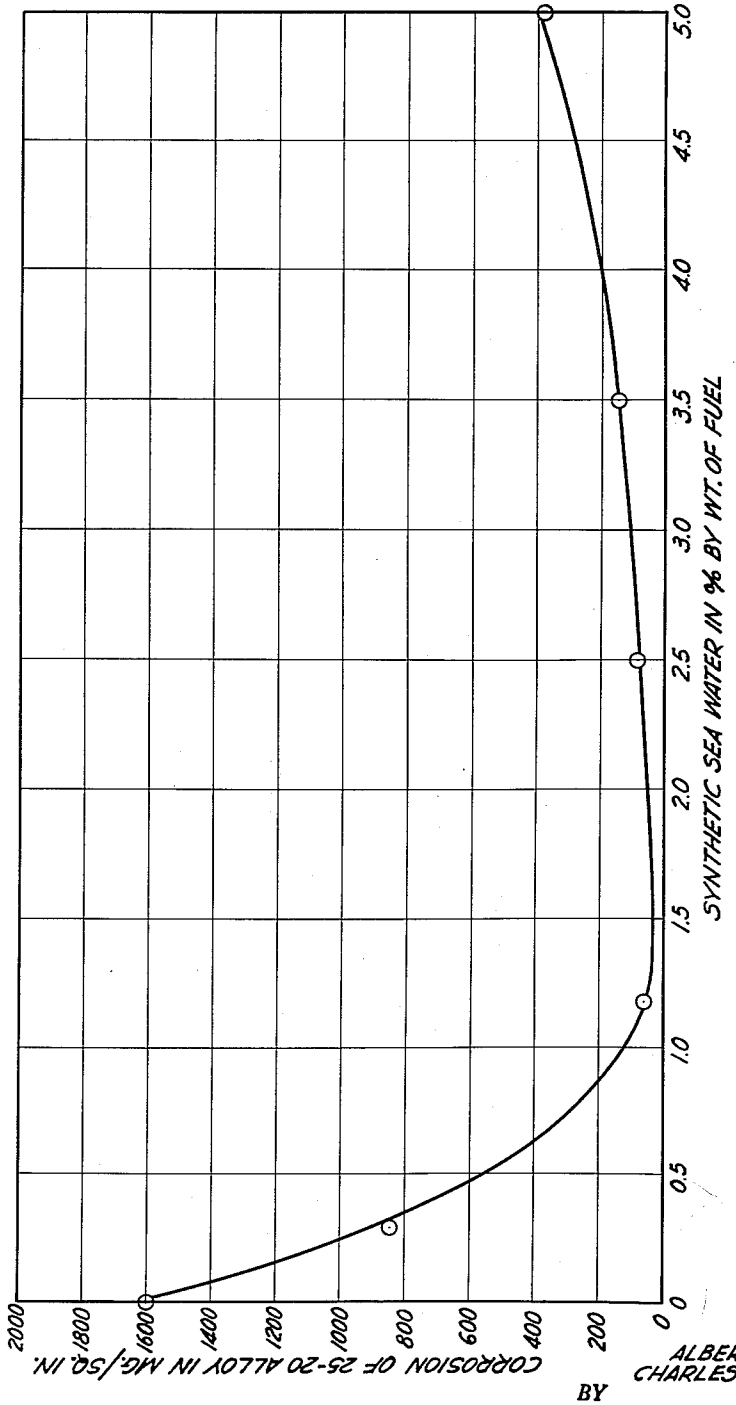


Fig. 2

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CORROSION INHIBITED FUELS CONTAINING VANADIUM

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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 resdiual 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 fuels 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 reducing 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 cooled to ordinary temperatures.

It is to be noted that the corrosion of materials at high temperatures by the hot ash resulting from the combustion of a vanadium-containing residual fuel is to be distinguished from the type of corrosion occurring at atmospheric or slightly elevated temperatures, generally in the presence of air and moisture. Under the latter conditions, an ash containing vanadium oxide has no significant corrosive effect. The corrosion problem described herein may therefore properly be termed a problem of "hot corrosion."

The economic factors involved preclude any extensive treatment of vanadium-containing residual fuels to remove the vanadium therefrom or to mitigate its effects. The vanadium compounds in residual oils are not removed by centrifuging or by the conventional chemical refining treatments.

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, notwithstanding the normally corrosive vanadium content, by incorporating therein a small amount, sufficient to retard the corrosiveness of the ash, of the mixture of salts present in sea water. In the fuel compositions of the invention, corrosion due to the vanadium-containing ash is substantially retarded.

In the accompanying drawings:

Fig. 1 shows an apparatus for testing the corrosivity of residual fuel oil compositions; and

Fig. 2 shows in graphic form the effectiveness of the additive of the invention 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 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 hot 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.

The corrosion retarding additive of the invention is, as has been stated, the mixture of salts present in sea water. The mixture is employed in the dry form as obtained by evaporating sea water to total dryness, or in the form of sea water itself. As stated by H. W. Harvey in "The Chemistry and Fertility of Sea Waters," Cambridge University Press, 1955, page 131, "The sea salts of ocean water, away from any considerable dilution by land drainage, are of almost constant composition. Dittmar's analyses of seventy-seven samples of water collected by H.M.S. Challenger in 1873–6 from all the oceans showed this constancy. Subsequent analyses, in greater detail, bear out Dittmar's very accurate data." On page 1, Harvey states, "Nine kinds of ions constitute 99½% of the salts in solution; these are found in remarkably constant proportion, the one to the other." On page 131, there is given a table of the percentage composition of salts in sea water, as follows:

TABLE I

Percentage composition of salts in ocean water

	Percent		*Percent*
Na^+	30.4	Cl^-	55.2
Mg^{++}	3.7	$SO_4^=$	7.7
Ca^{++}	1.16	Br^-	0.19
K^+	1.1	H_2BO_3	0.07
Sr^{++}	0.04	HCO_3^- and $CO_3^=$	0.35

Minor constituents 0.02–0.03

The total salt content of sea water may vary from about 3.3 to 3.8 percent by weight. This variation in salinity is the chief difference in sea water, the ratio of the salts to each other being practically constant.

When employing in residual fuels the dry mixture of salts present in sea water, it is desirable to use the finely-divided salts. However, the degree to which the salts are subdivided 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 salts 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 dry sea water salts are therefore employed in a particle size range of less than 250 microns, preferably less than 50 microns.

In the practice of the invention with vanadium-containing residual fuel oils, the mixture of salts present in sea water is uniformly blended with the oil in proportion to the vanadium content thereof. This is accomplished by suspending the finely-divided dry salts in the oil, as has been indicated above, or by emulsifying or dispersing a concentrated water solution of the salts or sea water itself 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 additive of the invention is accomplished in several ways. The additive can be suspended or emulsified 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 dry sea water salts or a solution thereof in water 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 uniformly dispersed therein the additive. As still another alternative, particularly with a pitch which is withdrawn in molten form from the processing vessel, the additive 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 additive can be separately fed into the burner as the dry salts or an oil dispersion thereof, a concentrated water solution of the salts, or sea water itself. In any such case, it is preferred to meter the additive 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 additive can be added separately from the fuel either prior to or during combustion itself, or even subsequent to combustion. However it may specifically be added, whether in admixture with or separately from the fuel, the additive is introduced into said plant upstream of the heat resisting metal parts to be protected from corrosion.

The mixture of salts present in sea water is employed in a small amount with respect to the vanadium-containing residual fuel, sufficient to retard the corrosiveness of the ash. Although the exact amount of salts to use will vary in accordance with the vanadium content of the specific residual fuel employed, as will be understood by those skilled in the art, in general a reduction in corrosivity is already observed with as little as about 0.25 atom weight of the sodium present in the mixture of salts per atom weight of vanadium in the residual fuel. Corrosivity is substantially reduced when an amount of additive is employed yielding about 1 to 5 atoms of sodium per atom of vanadium in the residual fuel, and is minimized in the range of about 1.5 to about 4 atoms of sodium per atom of vanadium. Increasing amounts of additive yielding up to about 7 atoms of sodium per atom of vanadium, while still exercising a substantial corrosion retarding effect, are not as effective. Although the amounts of additive have been expressed herein in terms of the sodium content thereof, it will be understood that the additive is not simply a sodium additive but contains the entire mixture of salts present in sea water. Since the ratio of the amounts of salts to each other in sea water is practically constant, the characterization of the amount of sodium to employ is sufficient to characterize the amount of the entire additive. The necessity for using as the additive the mixture of salts present in sea water is emphasized by the fact that sodium chloride itself is substantially ineffective in retarding vanadium corrosion, as will be shown in detail hereinafter.

The following specific examples are further illustrative of the invention. In each of the examples, the additive is employed in the form of sea water made up in accordance with the composition and preparation for "synthetic sea water" shown in ASTM Test D665–54 published in "ASTM Standards on Petroleum Products and Lubricants," November 1954, by The American Society for Testing Materials, Philadelphia, Pa. The composition is as follows:

TABLE II

Salt:	Grams per liter
NaCl	24.54
$MgCl_2 \cdot 6H_2O$	11.10
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.69
$NaHCO_3$	0.20
KBr	0.10
H_3BO_3	0.03
$SrCl_2 \cdot 6H_2O$	0.04
NaF	0.003

The sea water is first mixed in a one-gallon Waring Blendor with a portion of the fuel to be tested to form an emulsified concentrate of sea water in the residual fuel oil. This concentrate is then stirred in the desired proportion into additional residual fuel oil to yield the desired amount of additive in the final fuel oil composition. A series of residual fuel oil compositions employing varying amounts of additive and three different residual fuel oils of varying vanadium content are made up and tested under conditions of burning residual fuel oils in a gas turbine. Identical tests are run on the three residual fuel oils containing no additive. In the testing the apparatus shown in Fig. 1 is employed. As shown in Fig. 1, 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 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 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.

The compounded and uncompounded residual fuel oils are tested 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. The three residual oils employed as base fuels have the following inspection:

TABLE III

	Fuel A	Fuel B	Fuel C
Gravity, °API	20.6	19.6	21.4
Viscosity, Furol, Sec.:			
77° F	74.3	76.7	67.6
122° F	25.4	24.0	21.5
Flash, OC, °F	255	200	175
Fire, OC, °F	295	210	195
Sulfur, B, percent	1.6	1.53	1.6
Ash, percent	0.04	0.04	0.04
Vanadium, p.p.m. of oil	182	150	166
Sodium, p.p.m. of oil	2	1	3

The following table shows the make-up and the reduction in corrosion and deposits obtained with various compounded residual fuel oil compositions employing Fuel A, supra, and the sea water of Table II:

TABLE IV

	Fuel A (Blank)	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Amount of Sea Water:						
Percent by Wt. of Fuel	0	0.3	1.2	2.5	3.5	5.0
Atom Ratio, Na:V	0	0.4:1	1.6:1	3.35:1	4.7:1	6.7:1
Corrosion, Wt. Loss of Specimen, Mg./Sq. In.	1,600	840	60	95	150	376
Reduction in Corrosion Due to Additive, Percent		47	96	94	91	76
Deposits on Specimen, Mg./Sq. In.	530	480	200	230	186	325
Texture of Deposits	Heavy Scale	Black Powder	Black Powder	Black Powder	Black Powder	Black Powder

The data on corrosion shown in the above table is plotted against the amount of sea water additive employed and the curve obtained is shown in Fig. 2. It will be seen from the curve that a reduction in corrosivity is obtained even with small amounts of the mixture of salts present in sea water. The corrosivity is at a minimum at an amount of sea water of about 1.2 percent by weight and shows no substantial rise until an amount of sea water in excess of about 3 percent is employed. These amounts of sea water correspond to an atom ratio of the sodium in the sea water to the vanadium in Fuel A of about 1.5:1 to 4:1. With increasing amounts of sea water the reduction in corrosivity is not as marked, although a substantial improvement is shown over the base oil containing no sea water.

Similar results are obtained when using sea water as an additive to reduce the corrosivity of Fuel B, supra. This is shown in the following table:

TABLE V

	Fuel B (Blank)	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Amount of Sea Water:					
Percent by Wt. of Fuel	0	0.173	0.515	1.24	2.5
Atom Ratio, Na:V	0	0.28:1	0.84:1	2.02:1	4.08:1
Corrosion, Wt. Loss of Specimen, Mg./Sq. In.	830	226	203	31	57
Reduction in Corrosion Due to Additive, Percent		73	76	96	93
Deposits on Specimen, Mg./Sq. In.	325	160	192	225	190
Texture of Deposits	Black Powder	Black Powder	Black Powder	Black Powder	Black Powder

Since, as shown in Tables I and II, supra, the major constituent in sea water is sodium chloride, it might have been expected that sodium chloride itself would also be effective as a corrosion retarding additive to residual fuels containing corrosive amounts of vanadium. Surprisingly, however, this is not the case. Two residual fuel oil compositions are made up using Fuel C, supra, as the base fuel and employing as the additive the sea water of Table II in the one instance and a substantially saturated sodium chloride solution in water in the other. The two compositions and the base fuel are then tested in the apparatus described in Fig. 1 in the same manner as the Fuel A and Fuel B compositions previously described. The results are shown in the following table:

TABLE VI

	Fuel C (Blank)	Fuel C With Sea Water	Fuel C With Sodium Chloride
Amount of Sea Water:			
Percent by Wt. of Fuel	0	0.3	----------
Atom Ratio, Na:V	0	0.42:1	----------
Amount of Sodium Chloride:			
Percent by Wt. of Fuel (Dry Basis)	0	----------	0.02
Atom Ratio, Na:V	0	----------	1:1
Corrosion, Wt. Loss of Specimen, Mg./Sq. In.	992	460	715
Reduction in Corrosion Due to Additive, Percent	----------	54	28
Deposits on Specimen, Mg./Sq. In.	319	145	87
Texture of Deposits	Black Scale	Black Scale	Black Scale

It is apparent from the foregoing data that sodium chloride itself is substantially ineffective in preventing corrosion induced by vanadium-containing corrosive residual fuels. Thus, notwithstanding that in the sodium chloride test more additive is employed, as is reflected in an atom ratio of sodium to vanadium of more than twice that of the sea water test, the sea water resulted in almost twice as much a reduction in corrosion as did the sodium chloride.

The following example is illustrative of the use of the additive of the invention with solid residual fuels.

EXAMPLE 10

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 with stirring 0.2 percent by weight of finely powdered dry salts obtained by the total evaporation of sea water. Upon cooling and solidification, grind the mixture to about 150 mesh. The resulting fuel has an atom ratio, Na:V, of 2:1.

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

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

The preceding description clearly demonstrates the effectiveness of the sea water additive of the invention in reducing the corrosivity of vanadium-containing residual fuels.

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 major amount of a residual petroleum fuel yielding a corrosive vanadium-containing ash upon combustion and a small amount of the mixture of salts present in sea water sufficient to yield from about 1.5 to about 4 atoms of the sodium in said salts per atom of the vanadium in said fuel.

2. A fuel composition comprising a major amount of a residual petroleum fuel oil yielding a corrosive vanadium-containing ash upon combustion and a small amount of sea water sufficient to yield from about 1.5 to about 4 atoms of the sodium in said sea water per atom of the vanadium in said fuel oil.

3. 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 the combustion of said oil, the method of reducing said corrosion which comprises introducing into said plant upstream of said parts a small amount of the mixture of salts present in sea water sufficient to yield about 1.5 to about 4 atoms of the sodium in said salts per atom of the vanadium in said fuel oil.

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