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PETROLEUM FUEL COMPOSITION AND PROCESS

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The present invention concerns a process of operating a power plant and an improved petroleum fuel oil composition containing vanadium, and particularly to an improved residual oil composition containing vanadium which has a significantly reduced tendency to corrode ferrous metals at elevated temperatures. More particularly, the instant invention relates to a method of operating and reducing corrosion in a gas turbine plant and to improved water washed residual petroleum oils containing vanadium which have reduced corrosiveness and deposit forming tendencies at temperatures above about 1600° F. This application is a continuation-in-part of Serial No. 24,266, filed April 25, 1960.

The parent application was concerned with hot corrosion problems caused by the presence of vanadium, sodium, and sodium and vanadium in residual fuel oils. This application employed an additive combination of alkaline earth metal oxides and aluminum-silicon clays like kaolin in combination to provide protection from corrosion with reduced deposit formation for both water washed and sodium- and vanadium-containing fuels. Although the previous additives provide adequate protection at the normal operating temperatures of gas turbines, i.e. 1300 up to 1500° F., these additives and other additives of the prior art utterly fail to protect ferrous metals against the catastrophic corrosive effects of vanadium-containing ash at higher temperatures of above 1600° F., especially in the absence of water washing the fuel and without an undesirable increase in deposit formation.

There exists in power plants and in gas turbine plants, in particular, certain "hot spots" such as in areas about the nozzle vanes and in the first stage turbine blades and other areas wherein the temperature exceeds the normal average operating temperatures. Marine and stationary steam power plants and boilers are also subject to areas of elevated temperatures. These hot spots are subjected to exceptionally severe corrosion by the normally corrosive vanadium ash and often reach temperatures of from 1600° F. to 1900° F., e.g. 1700° F. to 1800° F. Future designs of gas turbine plants indicate that even higher operating temperatures are contemplated, and that hot spots of 2000° F. to 2100° F. are possible in the near future. Previous attempts to control corrosion at temperatures of above 1500° F. by the use of greater quantities of additive have been unsuccessful, and usually created new problems of deposit formation and reduced heat exchanger efficiency. The employment of water washed fuels to reduce the sodium content to preferably less than 5 p.p.m., or at least 10 p.p.m., together with prior art additives, has proven uneconomical and of little significant aid.

The present invention concerns the discovery that small amounts of a barium-aluminum silicate combination significantly and unexpectedly reduces hot corrosion at temperatures above 1600° F. The applicant has found that only barium of the alkaline earth metals of magnesium, calcium, and strontium provides this surprising reduction in vanadium corrosion and deposit formation at these elevated temperatures. This reduction in corrosion is not fully understood, but it is believed to be due to the formation of an extremely high melting barium-alumina-silica vanadate complex or composition having the approximate formula $BaO.3V_2O_5.3(Al_2O_3.2SiO_2)$. This high melting barium vanadate compound also has utility as a

catalyst or catalyst support in the oxidation of hydrocarbons such as in the oxidation at high temperatures of auto gaseous exhaust products or the oxidation of o-xylene to phthalic anhydride.

The employment of the magnesium, calcium or strontium members of the alkaline earth family in combination with kaolin apparently forms lower melting vanadates which, although effective at lower temperatures, permit significant corrosion to occur at the elevated temperatures occurring at the turbine hot spots. It has been now discovered that the reduced corrosion is also accompanied by an enhanced reduction in deposit formation when the barium additive is employed within certain concentration limits. The utilization of higher quantities of barium than the defined limits may be employed to control corrosion but with the consequential result of higher deposit formation and a slight shift to reduce corrosion at lower temperatures is encountered to about 1500° F. The instant discovery is particularly suitable with water washed residual fuels, since a barium oxide-kaolin additive in combination with a vanadium-containing fuel comprising less than 10 p.p.m. of sodium allows on combustion the formation of a substantially less corrosive ash, reduced deposit formation and a higher temperature protection corrosive threshold level.

The fuel oils to which this invention is applied comprise those petroleum hydrocarbon fuel oils and blends thereof which, when combusted, yield corrosive vanadium-containing ash. These fuels may be the residual, solid or liquid, petroleum products or blends thereof, obtained from refining operations such as the distillation of crudes, the flashing or distillation of cracked products and redistillation operations, the residue obtained from deep vacuum reduction of asphaltic crudes, the visbreaking of liquid distillation bottoms, coking of distillation bottoms, Athabaska tars and bitumen, and the like. They may consist of either virgin or thermally or catalytically cracked hydrocarbons or both. Inasmuch as the viscosity of a residual fuel is one of its more important properties, it is sometimes necessary, where a particular residuum is too viscous, to dilute it with a low viscosity distillate fraction. It is apparent then that residual fuels may contain distillate fractions as well as residues, but in general they consist primarily of residual material.

The amount and volume of ash in a residual fuel oil and, in particular, its vanadium and sodium content depends in part on the crudes from which it is derived. Thus, the vanadium content of residual fuel oils may vary from 2 to 2,000 or more p.p.m. as is found in Venezuela or Middle Eastern crude, but normally ranges from 5 to 1,000 p.p.m. as found in fuel in domestic use. The vanadium content of ash derived from domestic fuel crude oils varies in general from trace quantities to 20% by weight V_2O_5, while Middle East crudes vary between 14 to 45% and South American crudes may be as high as 80%. The amount of sodium found in the fuel is dependent also on the source, with the sodium content of ash from residual fuels varying from trace amounts up to 95 wt. percent for domestic fuel and up to 50 wt. percent for Midle East and South American fuels. In general, the source of sodium contamination in these fuels is due in part to salt water associated with crude oils, oil soluble sodium compounds in the crude oil, salt water picked up by crude oil during its transportation by tankers, and the like.

The present invention is particularly directed toward residual fuel and blends thereof containing vanadium in which the atomic weight ratio of alkali metals such as sodium to vanadium is 0.3 or less, e.g. 0.1 or less, and to residual fuels containing less than 10 p.p.m. or even 5 p.p.m. or lower of sodium. Water soluble alkali metal salts, such as sodium salts, may be removed from the oil

by centrifuging, filtering, electrostatic precipitation, or other means, but is conventionally accomplished by water washing the oil as described, for example, in the Industrial and Engineering Chemistry, vol. 46, No. 10, pages 2163–2166 (October 1954).

Residual fuel oils are also known in the trade as Bunker C fuel oils. They are characterized roughly as boiling above 400° F. The United States Department of Commerce, in its classification system for petroleum fuels, recognizes two grades of residual fuel, No. 5 and No. 6. The No. 5 grade is essentially a distillate fuel with small amounts of residual materials. It contains relatively little ash-forming material. The No. 6 fuel is usually a true residual fuel containing a substantial amount of ash, up to 0.10% by weight or more, although the total ash from commercial residual fuel oils usually ranges between about 0.02 to 0.2% by weight. It is with this grade or blends thereof that the present invention is primarily concerned, but not restricted thereto. The No. 6 or bunker fuel grade has a gravity range of about 9 to 15° API, a viscosity range of about 30 to 300 seconds (Saybolt Furol) at 122° F., and a minimum flash point of 150° F.

Typical residual fuel inspections are as follows:

TABLE I

Residual Fuel Inspections

	A [1]	B	C
Gravity, ° API	12.6	12.5	15.9
Flash (PM), ° F	180	184	148
Viscosity, Furol, at 122° F	177	172	208.9
Ash, Total, Percent	0.09	0.09	0.19
Ash, H_2O Soluble, Percent	0.02	0.03	0.17
Sulfur, Percent	2.53	2.72	1.54
Water, by distillation, Percent	0.30	0.15	Trace
Sediment, by Hot Filtration, Percent	0.02	0.02	0.17
Metals, Parts Per Million (p.p.m.), by Weight in Fuel:			
Calcium	2.2	3.2	128
Iron	4.3	9.1	24.4
Magnesium	58.0	6.6	13.5
Nickel	54.8	55.3	7.7
Sodium	4.2	54.2	409
Vanadium	400	400	6.0

[1] Fuel A is Fuel B water washed to reduce water soluble salts, e.g. sodium.

The additive employed may comprise a single compound containing a combined form of barium with aluminum silicates or the barium may be added in a single compound in combination with aluminum silicate minerals, rocks, clays, and the like of varying composition and degrees of purity. Whether employed as a single compound or separately, the applicant has found that the higher melting point barium-vanadium complex is only obtained when the alumina silicate exists in a combined form in a ratio of at least about 1/2 of Al_2O_3/SiO_2. The upper limit of Al_2O_3/SiO_2 is not critical and depends upon the level of deposits that can be tolerated, but usually is not more than 1/6, e.g. 1/4. Thus, combinations of barium oxide and barium sulfate with the separate addition of alumina and silica, or the use of mullite

$$3Al_2O_3.2SiO_2$$

failed in crucible tests at 1500° F. and higher temperatures to yield the high melting complex and would not yield sufficient corrosion protection at elevated temperatures.

The additive may comprise a single compound; the only requirement is that the Al_2O_3/SiO_2 combined ratio be at least 1/2. Additional barium in the compound higher than that recommended is not excessively disadvantageous, but may tend to increase deposit formation. Lower levels of barium can be brought up to the desired concentration level by the addition of a barium-containing compound such as BaO, $BaCO_3$, $BaSO_4$, etc. Suitable barium-aluminum silicate compounds include those hydrated and nonhydrated synthetic, artificial and natural zeolites, clays, montmorillonite clays, and the like, wherein barium is chemically combined with aluminum silicates. For example, the barium zeolites may be formed in solution by double decomposition with a barium salt. Suitable single compounds include those having the general formula

$$BaO.xAl_2O_3.ySiO_2.zH_2O$$

where, by way of illustration, x is a number from 1 to 6, y is a number between 2 and 12, and z is a number from 0 to 12, with x, y, z, for example, being 1, 5, and 4, respectively, the only restriction being that the ratio of Al_2O_3/SiO_2 be at least 1/2. The operativeness of the single additive is not affected by the presence or absence of other alkali (Na) and alkaline earth (Mg, Ca) and transition (Fe, Ni) metals and the like in the additive mixture, although economic requirements would indicate that these elements should be held to a minimum level.

Where the barium is separately added or required to increase the barium level, the compound may be any vanadium-free barium-containing compound which at elevated temperatures, e.g. above 1000° F. or even above 1500° F., yields the oxide of barium. Suitable barium compounds would then encompass inorganic and organic barium compounds like the oil soluble barium salts of organic and fatty acids such as barium naphthenates, barium acetate, barium petroleum sulfonates, barium organic chelates such as barium aceto-acetic esters of C_8 oxo alcohols, and inorganic barium salts and oxides of barium such as sulfates, barium hydroxide, barium chloride, barium carbonate, barium oxide, barium phosphate, and the like. The preferred barium additives are barium carbonate and barium oxide due to commercial availability and cost.

The preferred method of combating corrosion is to employ an inorganic barium salt or oxide together with a vanadium-free aluminum silicate clay such as kaolin. Suitable clays encompass those rocks, minerals and clays of varying composition and degrees of purity which are generally characterized as containing Al_2O_3 and SiO_2 in a ratio of at least 1/2 and which are plastic and soft when wet and harden when fired at elevated temperatures. Suitable clays include both hydrated and dehydrated compounds and are represented by compounds and mixtures thereof such as kaolin, halloysite ($Al_2O_3.3SiO_2.2H_2O$), acid clay, china clay, porcelain clay, and other commercial and noncommercial clays. The presence of other alkaline earth or alkali metals in the clays in major or minor amounts or as impurities does not affect the efficacy of the inventive use provided that the requisite concentration levels of barium and Al_2O_3/SiO_2 are maintained. Of course, it is also within the scope of this invention that those aluminum- and silicon-containing organic and inorganic polymers, salts, chelates, and the like may be employed so long as these compounds form the oxides of their metals at temperatures above about 1000° F. or even 1500° F. The upper limit of SiO_2 in clay is not critical, but as with the barium aluminum silicate compounds, the Al_2O_3/SiO_2 ratio can be as high as 1/6, e.g. 1/4 or higher. Suitable and nonlimiting examples of commerical additives and mixtures thereof would include kaolin, acid clay, china clay, porcelain clay, albite, almondite, anorthite, and the like. The economically preferred additive is kaolin, a hydrated alumnia silicate clay, which can be represented by the formula

$$Al_2O_3.2SiO_2.2H_2O$$

The utilization of kaolin alone in vanadium-containing residual fuels gives negligible protection against vanadium corrosion, while the preferred additive mixture of barium oxide and kaolin gives superior results against hot corrosion above 1600° F. and in reduced deposit formation. At temperatures below 1500° F., kaolin fails to react with barium or vanadium and instead decomposes to mullite and SiO_2.

Of course, the additive compounds employed must be substantially vanadium free in order not to themselves contribute to increased corrosion and reduced effective-

ness. Further, alkali metal-containing compounds such as sodium-containing compounds are somewhat undesirable if employed after water washing as they tend to unduly increase the sodium content of the ash and should be controlled by additional kaolin as recited in the parent application. Sodium-containing compounds can be effectively utilized prior to water washing which will remove any excess sodium or other water soluble salts contributed by the additive mixture.

The additives may be incorporated in the oil or in an oil concentrate together with other commonly employed fuel additives, such as rust inhibitors, pour point depressants, sludge inhibitors, etc., either in the form of oil soluble additives or as a dispersed stabilized oil or water mixture or any combination thereof. Additionally, the additives may be injected separately or in combination into the combustion zone of the boiler or gas turbine or upstream of the particular metallic parts, e.g. the first stage turbine blades, or hot spots to be protected or by other methods of direct utilization.

To render corrosive vanadium-containing ash substantially less corrosive and to greatly retard corrosive effects above about 1600° F., and atomic weight ratio of Ba/V/Al+Si of above 0.25/1/0.5 is required, with a range of 0.25/1/0.5 to 3.0/1/5.0 operable and 0.5/1/2.0 to 2.0/1/3.0 particularly suitable. Although greater amounts of barium may be used, an increase in deposit formation is noticed.

EXAMPLE I

Evidence of the beneficial results of the present invention is obtained from both a static oil ash corrosion test and particularly in a pilot gas turbine test unit (GTTU) as shown in Table II and as described in the parent application. Deposit formation is calculated as the weight difference (ΔW_1) between the specimen removed from the unit and the original specimen placed in the unit corrected for corrosion products, i.e.

$$\Delta W_1 - \left(\frac{\text{molecular weight of steel oxide}}{\text{molecular weight of steel}} - 1\right)\Delta W_2$$

where ΔW_2 is the weight difference between the original specimen placed in the unit and the specimen after the deposit and oxide scale has been removed by electrolytic desalting.

TABLE II

Effectiveness of Barium-Alumina Silicates at Elevated Temperatures

Fuel	Additive	Ratio	GTTU Test Data					
			Corrosion, mg./cm.² wt. loss			Deposits, mg./cm.²		
			1,500° F.	1,650° F.	1,700° F.	1,500° F.	1,650° F.	1,700° F.
Fuel A	MgO	3/1 Mg/V	8	40	70	13.5		25
Fuel B	BaO-Kaolin	0.5/1/2 Ba/V/Al+Si	10	28	12	1.5	2	7
	do	1/1/2 Ba/V/Al+Si	10		12			
	do	2/1/2 Ba/V/Al+Si	9	24	11	1.5	2	7
	do	3/1/2 Ba/V/Al+Si		8			25	
	CaO-Kaolin	1/1/1 Ca/V/Al+Si	9.5	35	[1] 55	11.5	18	[1] 22
	do	2/1/1 Ca/V/Al+Si	6.5	20	[1] 30	10.5	16	[1] 20
	None		80	240	[1] 500	2.0	2.5	[1] 3.0

[1] Extrapolated from 1,650° F.

The above data amply demonstrate the unexpected reduction in both corrosion and deposits at elevated temperatures occasioned by the use of the barium-alumina silicate mixture. Thus, at 1500° F., the use of magnesium, barium and calcium yields similar corrosion protection, but as the temperature increases to 1700° F., the other group II-*a* metals permit a three- to fourfold increase in corrosion with increasing deposit formation. The use of no additive allows catastrophic corrosion to take place, while the use of the normal 3/1 Mg/V ratio in a water washed fuel also fails to give adequate protection. At 1700° F., the barium-kaolin additive gives a protection level similar to that at 1500° F., while the deposit formations remain extremely low. As evidenced above, increasing the amount of the barium additive above the economically preferred 0.5/1/2 level has no great advantages. As the barium concentration level increases, the excess barium apparently shifts the formation of the complex to a slightly lower temperature of about 1550° F., but is accompanied by an undesirable increase in deposit formation.

EXAMPLE 2

A residual fuel oil having an outstanding ability to reduce the corrosive effects of vanadium-containing ash at temperatures of from 1700 to 1900° F. is obtained by uniformly blending into a petroleum residual fuel oil having an ash content of about 0.04 wt. percent and containing about 192 parts per million (p.p.m.) of vanadium and about 3 p.p.m. of sodium, a small amount of about 0.014 wt. percent barium carbonate and about 0.12 wt. percent of a halloysite ($Al_2O_3.3SiO_2.2H_2O$).

EXAMPLE 3

A bunker C fuel oil of unexpected and enhanced characteristics is produced by water washing the fuel to obtain less than 5 p.p.m. of sodium, the fuel having about 242 p.p.m. of vanadium, an ash content of 0.12 wt. percent, and a sulfur content of more than 1.5 wt. percent. An additive concentrate comprising a major amount of a heavy fuel oil and a minor amount, e.g. 10 to 50, of a hydrated barium-alumina silicate compound having the approximate formula $BaO.Al_2O_3.5SiO_2.4H_2O$ is dispersed therein by jet milling the additive to about 0.1 to 5.0 microns with 95% less than 1.5 micron and homogenizing the mixture. This additive concentrate is then incorporated into the bunker C oil in an amount to give a Ba/V/Al and Si ratio of about 1/1/2. This fuel oil, when combusted in a gas turbine plant having stainless steel parts comprising about 20 to 30 iron, 25% chromium ore, 20% nickel, about 2.0 manganese and minor traces of other elements, enhances the high temperature corrosion life of these metal parts.

What is claimed is:

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 an additive selected from the group consisting of (1) a mixture of a barium compound which yields the oxide at temperatures above 1000° F. and an aluminum silicate clay, and (2) a barium aluminum silicate wherein the silicates have a ratio of Al_2O_3/SiO_2 of between ½ and ⅙ and said small amount is sufficient to yield a ratio of Ba/V/Al+Si of from 0.25/1/0.5 to 3.0/1/5.0 whereby enhanced corrosion protection is effected at temperatures above about 1600° F.

2. A fuel composition as defined in claim 1 wherein

said residual fuel contains less than 10 parts per million of water soluble alkali metal salts.

3. A fuel composition as defined in claim 1 wherein said barium compound is barium oxide.

4. A fuel composition is defined in claim 1 wherein said barium compound is a hydrated barium oxide aluminum silicate.

5. A fuel composition as defined in claim 1 wherein said barium compound is barium carbonate.

6. A fuel composition as defined in claim 1 wherein said barium compound is barium sulfate.

7. A fuel composition as defined in claim 1 wherein said clay is kaolin.

8. A fuel composition as defined in claim 1 wherein said clay is halloysite.

9. An improved residual petroleum fuel boiling above 400° F. to which has been added an additive mixture of (1) a barium compound which yields the oxide at temperature over 1000° F., and (2) kaolin in an amount sufficient to give a Ba/V/Al+Si ratio of from 0.25/1/0.5 to about 2.0/1/3.0 whereby enhanced corrosion protection is effected at temperatures between 1600° F. and 1900° F.

10. A fuel as defined in claim 9 wherein said fuel contains less than 10 parts per million of sodium.

11. A fuel as defined in claim 9 wherein said ratio of Ba/V/Al+Si is about 0.25/1/2.

12. In a power plant in which a fuel oil containing vanadium is burned and which includes heat resisting ferrous metallic parts exposed to hot combustion gases and liable to be corroded by the corrosive vanadium-containing ash resulting from the combustion, the method of reducing said corrosion which comprises introducing into said plant a small corrosion inhibiting amount of an additive selected from the group consisting of (1) a mixture of a barium compound which yields the oxide at temperatures above 1000° F. and an aluminum silicate clay, and (2) a barium aluminum silicate wherein the silicates have a ratio of Al_2O_3/SiO_2 of between ½ and ⅙ and said small amount is sufficient to yield a ratio of Ba/V/Al+Si of from 0.25/1/0.5 to 3.0/1/5.0 whereby enhanced corrosion protection is effected at temperatures above about 1600° F.

13. A process as defined in claim 12 wherein said power plant is a gas turbine and said additive mixture is introduced upstream of said metal parts.

14. A process as defined in claim 12 wherein said additive mixture is incorporated into the fuel oil burned in said plant.

15. A process as defined in claim 12 wherein said additive mixture is injected into the combustion zone of said plant.

16. In a gas turbine plant in which a residual fuel oil containing vanadium is burned and which includes heat resisting ferrous metallic parts exposed to hot combustion gases and liable to be corroded by the corrosive vanadium-containing ash resulting from said combustion, the method of reducing said corrosion which comprises incorporating in the fuel oil to be burned in said gas turbine a small amount of an additive mixture comprising (1) a barium compound selected from the group consisting of barium hydroxide, barium oxide, barium carbonate, and barium sulfate and (2) kaolin in an amount sufficient to give a Ba/V/Al+Si ratio of from 0.25/1/0.5 to about 2.0/1/3.0 whereby enhanced corrosion protection is effected at temperatures between 1600° F. and 1900° F.

17. A process as defined in claim 16 wherein said residual fuel has been water washed to reduce the sodium content to less than 10 parts per million.

18. A fuel composition as defined in claim 9 wherein said barium compound is barium oxide.

19. A fuel composition as defined in claim 9 wherein said barium compound is barium carbonate.

20. A process as defined in claim 16 wherein said barium compound is barium oxide.

21. A process as defined in claim 16 wherein said barium compound is barium carbonate.

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