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FUEL OILS

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This invention relates to vanadium-containing fuel oils. More particularly, it is concerned with rendering non-corrosive those residual fuel oils 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 at elevated temperatures and attacks such parts as boiler tubes, hangers, turbine blades, etc. 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 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 cheap residual fuels in gas turbines is the corrosiveness induced by those residual fuels containing sufficient amounts of vanadium to cause corrosion problems. 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 problem, 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. All of these factors appear to militate against the extensive use of residual fuel oils for gas turbines.

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

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 oil 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 fuel oils to remove the vanadium therefrom or to mitigate its effects. This is due in large part to the fact that the vanadium is apparently bonded into organic macro-molecules which behave much like asphaltenes. The vanadium compounds in residual oils are therefore not removed by centrifuging or by the conventional chemical refining treatments.

I have now discovered that residual fuel oils containing vanadium in an amount sufficient to yield a corrosive vanadium-containing ash upon combustion can be rendered non-corrosive, notwithstanding the normally corrosive vanadium content, by incorporating in the fuel oil a small amount, sufficient to retard the corrosiveness of said ash, of an oil-soluble or oil-dispersible organic silicon compound. In accordance with my invention, residual fuel oils thus prepared exhibit a substantial retardation or elimination of "hot corrosion."

While I do not desire to be bound by any theory as to the action taking place, it is my present belief that the organic silicon compound reacts during combustion of the fuel oil with the vanadium component thereof to form a stable, high-melting, relatively non-corrosive vanadium compound which is not decomposed to vanadium oxide under the conditions of combustion. It is my further belief that this reaction takes place prior to the time any substantial amount of vanadium oxide ash comes into contact with the parts of the equipment otherwise corrosively affected. In any event, I have demonstrated that the addition of an oil-soluble or oil-dispersible organic silicon compound to a residual type petroleum fuel oil normally yielding a corrosive vanadium-containing ash completely changes the character of the ash from a hard, adherent, slag-like deposit to a loose, light, fluffy powder which is easily blown out by the combustion draft in a turbine, furnace or boiler, or which falls to the floor of a furnace or boiler. I have also demonstrated that the addition of the organic silicon compound eliminates or materially retards the corrosion normally obtained from the ash of a residual type fuel oil containing substantial amounts of vanadium.

The type of residual fuel oils to which my 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 vis-breaking 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 0.12 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 oil-soluble or oil-dispersible organic silicon compounds used in accordance with my invention are themselves well known in the art. They include such materials as the organosilanes, i. e., derivatives of the silanes, Si_nH_{2n+2}, in which one or more of the hydrogen atoms are replaced by hydrocarbon or substituted hydrocarbon radicals, for example:

Tetrapropyl silane
Tetraphenyl silane
Tripropyl, amyl silane
Tripropyl, chloroamyl silane
Dimethyl, dihydroxymethyl silane
Hexapropyl disilane
Triisobutyl silane, etc.

A particularly suitable class of organic silicon compounds is the organosiloxanes, which includes such types of compounds as $R_3SiOSiR_3$, $R_3SiO(SiR_2O)_nSiR_3$, $(R_2SiO)_n$, etc. This class includes, for example, the liquid "silicone" polymers such as dimethyl silicone, methyl phenyl silicone, etc., also known as methylpolysiloxanes and methylphenylpolysiloxanes. Other suitable classes of organic silicon compounds include: (1) the organosilanols, $R_nSi(OH)_{4-n}$, examples of which are ethylpropylphenyl silanol, tripropyl silanol, triisoamyl silanol, phenylbenzylsilane diol, etc.; (2) the silicate esters and their polymers, e. g., tetramethyl orthosilicate, tetraethyl orthosilicate, the higher secondary alkyl orthosilicates, tetraphenyl orthosilicate, glycol orthosilicate, etc.; (3) the silazanes, R_3SiNH_2, $R_3SiNHSiR_3$, etc. containing the linkage —N—Si—C—; (4) the aminosilanes, as shown in U. S. Patent 2,566,363, e. g., $(RO)_2Si(NH_2)_2$, di-tertiarybutoxydiaminosilane, including hydrolysis produits and polymers thereof; and (5) the di- or tri-hydrocarbonoxysilanes, e. g., alkoxy- and aroxysilanes of the type $R_nSi(OR')_{4-n}$, hexaalkoxydisilanes, etc.

The above-described organic silicon compounds are liquids or solids. Both liquid and solid materials are readily dissolved or dispersed in the vanadium-containing residual fuel oils. The requirement for oil-solubility or dispersibility of the organic silicon compounds is to insure uniform blending of the compounds throughout the body of the fuel oil to which they are added. It would obviously be undesirable for the bulk of the additive to be concentrated in a small portion of the fuel oil while the remainder of the oil contained little or no additive. The requirement for uniform blending of the organic silicon compounds is therefore satisfied by the use of oil-soluble or oil-dispersible compounds. As will be apparent to those skilled in the art, the distinction between oil-solubility and oil-dispersibility is a matter of degree, it being sufficient for the purposes of this invention that a fairly stable dispersion of the dispersible additives be obtained, or that redispersion of a settled additive can be easily accomplished by simple agitation.

In the practice of my invention, therefore, the organic silicon compound can be admixed with the vanadium-containing residual fuel oil to form a solution or a relatively stable suspension or dispersion; if any settling takes place, redispersion can be satisfactorily accomplished by simple agitation. Alternatively, the additive can be separately fed to the fuel oil line just prior to the burner, or even directly into the flame. In such instances, the organic silicon compound is preferably employed as a concentrated solution or dispersion in a naphtha or heavy fuel oil and is metered into the combustion device in the proportions required.

As I have stated, the oil-soluble or oil-dispersible organic silicon compound is employed in a minor amount with respect to the vanadium-containing fuel oil, sufficient to retard the corrosiveness of the ash from the fuel oil. It is desirable to employ such an amount of the additive as to result in at least about one atom weight of the silicon therein per atom weight of the vanadium in the fuel oil. Preferably, the atom weight ratio of the silicon to the vanadium is 2:1. While larger amounts of the organic silicon compounds can be used, it is ordinarily unnecessary to exceed an atom weight ratio of silicon to vanadium of 3:1.

The following specific examples are further illustrative of my invention.

Example 1.—In 99.8 parts by weight of a No. 6 residual fuel having a vanadium content of 305 parts per million, as vanadium, there was dispersed 0.2 part of the liquid dimethyl silicone polymer known as D. C. Fluid 200. A similar dispersion was prepared in the identical proportions, but using the aminosilane known as "Sylon." This aminosilane is disclosed in Example I of U. S. Patent No. 2,566,363. Two hundred (200) gram portions of each of the dispersions were then placed in 4" diameter 18–8 stainless steel dishes. The dishes were heated until the fire temperature of the oil had been reached and the oil ignited. After the oil had burned itself out, the dishes containing the residue from the ignition were placed in a muffle furnace and heated for 14 days at 1350° F. At the end of this time, the dishes were allowed to cool slowly and the nature of the ash was determined by inspection. The ash was then removed from the dishes, the dishes wiped clean with steel wool, and the bottoms and the walls of the dishes were examined for corrosion in the form of etching or pitting. The following table shows the results obtained, the identical residual fuel oil without the addition of metal having been run for purposes of comparison.

Additive	Nature of Ash	Corrosion
None	Hard and crusty	Heavy corrosion with deep pitting.
D. C. Fluid 200	Light and fluffy	No pitting.
Sylon	do	Do.

Example 2.—In order to demonstrate the corrosiveness of a residual fuel oil ash containing high amounts of vanadium and to demonstrate the corrosion inhibiting effects of the additives of this invention, the following tests were performed. An Eastern Venezuela No. 6 fuel oil was fired at 1600° F. to obtain an ash having a vanadium content, determined by analysis, of 36.75 percent. Strips of 1/16 inch thick 19–9 DL stainless steel sheet were cleaned by sand blasting in order to insure clean and uniform surfaces. The strips were then roasted in contact with the vanadium-containing ash for seven days in an electrically heated muffle furnace held at 1350° F. At the end of seven days' heating the specimens were allowed to cool and were then examined for corrosion. Tests were made on the ash alone and on ash containing the additives disclosed herein. In order to insure complete removal of all organic or carboniferous material, the ash was roasted for two hours at 1350° F. prior to being employed in the tests. In cases where an additive compound was also employed, it was added to the ash and well mixed prior to this preliminary heating. The additives were employed in amounts of 10 percent weight of their mixture with the ash. The following table shows the results obtained.

Additive	Appearance of Metal After Test
None	Very heavy corrosion with large area of metal eaten away.
D. C. Fluid 200	Very light etching; no pitting.
Sylon	Very light pitting.

As is apparent from the preceding description, the use of the additives of my invention strikingly changes the character of a vanadium-containing ash to a light and fluffy powdery material, and substantially reduces the corrosiveness of the ash.

I claim:

1. A fuel oil composition comprising a major amount of a residual fuel oil yielding a corrosive vanadium-con-

taining ash upon combustion, and a small amount, sufficient to retard the corrosiveness of said ash, of a compound selected from the class consisting of oil-soluble and oil-dispersible organic silicon compounds.

2. The composition of claim 1, wherein said organic silicon compound is selected from the class consisting of organosilanes, organosiloxanes, organosilanols, silicate esters, and aminosilanes.

3. The composition of claim 1, wherein said organic silicon compound is employed in an amount sufficient to yield at least about 1 atom weight of silicon per atom weight of vanadium in said oil.

4. The composition of claim 1, wherein said organic silicon compound is an aminosilane.

5. The composition of claim 1, wherein said organic silicon compound is a siloxane.

6. The composition of claim 5, wherein said siloxane is a liquid dimethyl silicone polymer.

7. A fuel oil composition comprising a major amount of a residual fuel oil yielding a corrosive vanadium-containing ash upon combustion, and a small amount, sufficient to retard the corrosiveness of said ash of a compound selected from the class consisting of oil-soluble and oil-dispersible silicate esters.

8. The composition of claim 7, wherein said silicate ester is tetraethyl orthosilicate.

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