

1

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REDUCING THE CORROSIVITY OF VANADIUM-CONTAINING OILS

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This invention relates to a method for preventing the corrosivity of vanadium-containing oils and more particularly relates to a method for preventing the tendency of fuel oils containing vanadium to produce, when burned, an ash which will corrode boiler tubes and boiler tube supports and cause slagging of fire bricks.

Residual fuel oils contain very small amounts of metals such as vanadium, calcium, iron, nickel, molybdenum, sodium, etc. Some of these elements are introduced during the refining of the oils. Others are present in the original crude either in fine suspension or in the form of soluble organic compounds. When the oil is burned in industrial installations these metals are transformed into oxides which are generally partly blown out of the stacks and partly remain as flue dust. When this flue dust contains vanadium and is deposited on the surface of the boiler tubes or the fire brick walls, corrosion and/or slagging results. The extent of this corrosion and slagging is a function of the melting point of the dust and its content of free vanadium pentoxide remaining in excess depending on the metal content of the oil. This oxide melts at 690° C. and is extremely corrosive, attacking every metal, even platinum and silica when in the molten state. Furthermore, vanadium pentoxide, due to its relatively low melting point will be projected in droplets which will remain liquid (particularly in small installations with restricted-size combustion chambers) and will collect additional dust particles.

It has now been found that the corrosive effect of this vanadium pentoxide may be eliminated or at least greatly reduced by the addition to the oil, prior to burning, of an oil soluble metal compound which will combine with the vanadium pentoxide and form a vanadate of sufficiently high melting point that it will not be melted during the combustion of the oil. The minimum melting point which such a vanadate should possess is above 1600° F. since the temperature reached in the combustion of fuel oil does not quite reach that high. The only vanadates which have been found to possess fusion points as high as 1600° F. are iron, nickel and aluminum meta vanadates. The nickel and aluminum vanadates are particularly efficient since both have melting points above 2000° F. However, the use of nickel is preferred since the addition of aluminum salts may cause gelling of the fuel oil.

Among the oil soluble metal compounds which are suitable are the metal derivatives of acids such as naphthenic acids and fatty acids, phenolates, salts of alkylated phenol sulfides such as di-isobutyl phenol sulfide, salicylates, salts of thiophosphorus acid esters such as dialauryl, thiophosphoric acid, chelates such as the metal derivatives of compounds having difunctional groups, for example diamine and diketo compounds of the type of pentane-dione.

The metal compounds may be added to the oil at any time prior to combustion and in approximately the stoichiometric proportions necessary to form the corresponding meta vanadate. The exact amount depends

2

upon the metal but may easily be calculated from the amount of vanadium pentoxide present in the oil which is usually from 0.0001 to 0.05%. This amounts to between 0.00001 and 0.005% for aluminum, between 0.00002 and 0.01% for iron, and between 0.00002 and .01% for nickel, calculated as the metal. The actual amount of metal compound added will also depend upon the presence of naturally occurring nickel or iron salts in the oil. If these are appreciable, the amount added to combine with the vanadium would be correspondingly less.

Although the addition agents of the present invention may be added to any fuel oil, they are especially adapted for use in conjunction with residual or bunker fuels. These fuels have gravities in the range from 1° to 15° API and furol viscosities at 122° F. in the range from 25 seconds to 300 seconds. From what has been said, therefore, in a specific embodiment of the invention the nickel derivative of naphthenic acid may be employed in a vanadium-containing residual fuel in an amount such that the nickel will be present in the fuel in a proportion sufficient to form nickel meta vanadate with the vanadium.

In order to more fully illustrate the present invention, the following examples are given:

Example 1

The vanadates of aluminum, nickel, iron and magnesium were prepared and the melting point of each was obtained with the following results:

Compound:	Melting point, ° F.
Aluminum vanadate	2100
Ferric vanadate	1615-1630
Nickel vanadate	2000+
Magnesium vanadate	1290-1330

The nickel vanadate was analyzed and found to contain 39.2% vanadium and 25.2% nickel. The vanadium content corresponds very closely to the theoretical for nickel meta vanadate ($\text{Ni}(\text{VO}_3)_2$) but the nickel content is 10% too high, due probably to occluded salts. Since the vanadium pentoxide content of fuel oil varies from 0.0001 to 0.05%, the addition of 0.00002 to 0.01% nickel will be necessary to form the theoretical amount of nickel meta vanadate.

Example 2

A sample of a Venezuela fuel oil ash containing 25% vanadium was found to have a melting point between 1500 and 1550° F. Sufficient anhydrous sodium sulfate was added to this ash to make the sodium content about 11%. The melting point of this material was found to be between 1200 and 1300° F. Sufficient nickel oxide (19.4%) was added to combine with the vanadium present and the melting point was found to have increased to between 1850 and 1950° F.

The nature of the present invention having been thus fully set forth and specific examples of the same given, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. A fuel composition comprising a major amount of a residual fuel oil yielding a corrosive vanadium containing ash upon combustion, and a minor amount, sufficient to retard the corrosiveness of said ash of an oil-soluble metal compound selected from the group consisting of the oil-soluble compounds of iron, aluminum, and nickel, said fuel oil composition in the absence of said metal compound normally yielding a corrosive vanadium containing ash upon combustion.

2. A liquid fuel composition adapted to be burned at substantially atmospheric pressure without corroding the equipment comprising a residual fuel oil containing vana-

3

dium and an oil-soluble metal compound selected from the group consisting of the oil-soluble compounds of iron, aluminum and nickel, said metal compound being present in the amount required to react substantially stoichiometrically with the vanadium upon combustion of the fuel oil to form a meta vanadate of the metal.

3. Composition as defined in claim 2 in which the metal compound is an oil-soluble nickel compound.

4. Composition as defined in claim 2 in which the metal compound is an oil-soluble iron compound.

5. Composition as defined in claim 2 in which the metal compound is an oil-soluble aluminum compound.

6. Composition as defined in claim 3 in which the amount of nickel compound added, calculated as nickel, is between 0.00002 and 0.01% of the residual fuel.

7. Composition as defined in claim 4 in which the amount of iron compound added, calculated as iron, is between 0.00002 and 0.01% of the residual fuel.

8. Composition as defined in claim 5 in which the amount of aluminum compound added, calculated as aluminum is between 0.00001 and 0.005% of the residual fuel.

9. A liquid fuel oil composition adapted to be burned at substantially atmospheric pressure without corroding the equipment comprising a residual fuel oil containing vanadium to which is added a substantially stoichiometric

4

amount of an oil-soluble nickel salt of a high molecular weight fatty acid which will react with the vanadium pentoxide to form a vanadate of the metal melting above 1600° F.

10. A liquid fuel oil composition adapted to be burned at substantially atmospheric pressure without corroding the equipment comprising a residual fuel oil containing vanadium to which is added a substantially stoichiometric amount of an oil-soluble nickel naphthenate which will react with the vanadium pentoxide to form a vanadate of the metal melting above 1600° F.

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