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RESIDUAL FUEL

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This invention pertains to a method for reducing the corrosiveness of ash produced by the combustion of residual type hydrocarbon fuels. It further pertains to improved residual fuel compositions which form substantially non-corrosive ash when they are burned. The invention is more particularly concerned with a composition comprising calcium, barium or magnesium complex salts wherein these salts are present in a stable suspensable form in the residual fuel.

Residual fuels derived from petroleum find wide use in marine and stationary steam power plants where the high B. t. u. content and low cost of such fuels make them very attractive economically. These fuels may be the residual products or blends thereof, obtained from refining operations such as the distillation of crudes, the flashing or distillation of cracked products and redistillation operations. They may consist of either virgin or cracked hydrocarbons. 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 thus apparent that residual fuels may contain distillate fractions as well as residues but in general they consist primarily of residual material.

Residual fuel oils are also known in the trade as bunker fuel oils. They are characterized roughly as boiling above 400° F. The United States Department of Commerce recognizes two grades of residual fuel (No. 5 and No. 6) in its classification system for petroleum fuels. 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, as for example, up to 0.10% by weight or more. It is this grade with which this invention is primarily concerned. The No. 6 or bunker fuel grade has a gravity range of about 9° to 15° A. P. I., a viscosity range of about 30 to 300 at 122° F. (Saybolt Furo), a minimum flash point of 150° F. and a Conradson carbon residue of at least 0.5%.

This invention is concerned primarily with the ash present in residual or bunker fuel oils. The amount and type of ash formed by a residual fuel oil during combustion vary primarily with the ash content and the origin of the crude oil from which it was derived. Crude oils when burned may form up to about 3% by weight of ash and the ash-forming constituents are concentrated almost entirely in the residua by refining operations performed on the crudes. Residual fuels, as such, however, generally contain less than 0.10% by weight of ash.

Chemical analyses of fuel oil ash reveal that a wide variety of chemical constituents may be found. Among these are silicon, aluminum, lead, copper, iron, calcium, magnesium, nickel, vanadium, molybdenum, and tungsten. Of primary interest however, is the vanadium content which may be up to 30%, calculated as V_2O_5 , by weight of an ash.

The vanadium content of ash derived from domestic

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crude oils will vary in general from about 0 to 20% V_2O_5 . Residual fuel oils obtained from Middle East crudes produce ash with vanadium contents of 14 to 45%, while in the case of South American crudes, the value may be as high as 80%. At the present time it is not known exactly what chemical forms or compounds of vanadium actually exist in these oils.

The amount of ash in a residual fuel oil, and in particular, its vanadium content (generally expressed in the results of chemical analysis, as vanadium pentoxide content), has recently become a matter of great importance. This is particularly true in the power generation field where the vanadium contained in the fuels employed has been found to cause extensive corrosion in power equipment that operates at high temperatures. Examples of such high temperature equipment include the gas turbine, the mercury boiler and extremely high temperature and pressure steam boilers. All of these installations have metal parts which are exposed at temperatures above 1000° F. directly to the gases produced by the combustion of residual fuel. In the case of the boilers, the metallic parts include such items as the boiler tubes and super heater tubes. In the case of the gas turbine, the burner chamber, turbine nozzles, and blading are among the parts subjected to these conditions. In general, extensive corrosion of all of these parts has occurred, particularly when a residual fuel forming an ash of high vanadium content was employed.

In an effort to combat the corrosion described above, stainless steels and other heat resistant alloys have been used in the construction of the parts affected. However, this approach to the problem has not been successful to the extent desired. With this in mind, efforts are now being directed toward improving the quality of the fuels. All of the studies made in this direction have shown conclusively that the corrosion is directly due to combustion products of the vanadium compounds which become a component of the ash formed when the fuel is burned.

When a residual fuel containing vanadium compounds is burned, the vanadium apparently reacts with oxygen to form compounds such as vanadium oxides (e. g. V_2O_5) and vanadates. These materials are carried along with the flue gas and are in contact with and partly deposit on the metal parts of the gas turbines and boilers described earlier. Inasmuch as vanadium pentoxide has a melting point of 1274° F., this material very often is present in its liquid form and has a substantial vapor pressure at the temperatures existing in gas turbine or boiler installations. Experimental work shows that vanadium pentoxide is extremely corrosive toward even the most corrosion-resistant alloy steels at temperatures of 1200° F. and up. It has further been shown that this chemical compound is most corrosive when it is present as a fluid. It appears that vanadium pentoxide or other vanadic acids not only destroy the oxidation-resistant surface layer which normally exists on alloy steels, but it also seems to act as an oxidation catalyst, thereby markedly increasing the rate of corrosion once it has started.

Accordingly, an object of the present invention is to provide vanadium-containing residual fuel oil compositions which when burned will form ash that is substantially non-corrosive toward steel and steel alloys at temperatures of 1000° F. and higher. It is a particular object to provide vanadium-containing, residual fuel oil compositions which when burned in installations such as gas turbines, mercury boilers, high-pressure steam boilers, etc., are virtually non-corrosive toward the ferruginous alloys used therein.

It is known in the art that in gas turbines and boilers the addition of calcium and magnesium compounds to high vanadium content fuels reduces the corrosiveness of vanadium toward metals at high temperatures when these

fuels are burned in high temperature equipment. However, the addition of the calcium or magnesium compounds to the fuels presents other problems. If insoluble compounds such as the oxides, carbonates or acetates are employed, they tend to settle out in storage. On the other hand, soluble compounds such as soaps of high molecular weight acids have low metal content. Thus, they must be employed in relatively high concentrations in order to secure the desired results. However, if large concentrations are used, the flame characteristic is adversely affected. Furthermore, these soluble high molecular weight soaps are relatively expensive.

The present invention avoids these difficulties by utilizing a complex soap of a low molecular weight monobasic carboxylic acid and a high molecular weight monobasic carboxylic acid. Desirable low molecular weight acids are acetic acid or other COOH acids having from 1 to 5 carbon atoms, as for example, formic, propionic, crotonic, acrylic, and the like. Satisfactory high molecular weight acids are preferably those of C₁₆ to C₂₂ chain length; for example, stearic acid, oleic acid, hydrogenated fish oil acids, and other acids of the types used in the manufacture of greases.

The weight percentage of the low molecular weight acid in the complex soap should be in the range from 10% to 80% by weight, preferably in the range from 50% to 80% by weight, while the percentage of the high molecular weight acid should be in the range from 90% to 20%, preferably in the range from 50% to 20% by weight. In general, these ranges correspond to mol ratios of low to high molecular weight acids of 0.5/1 to 40/1. Mol ratios higher than 5/1, preferably 7/1 or higher, are definitely preferred, since these are used in lower concentrations in the fuel and have less effect on flame pattern. These complex soaps are formed at elevated temperatures. They are also preferably formed in the presence of a mineral oil, as for example, one having a gravity in the range from about 19° to 22° API. Actually, the residual fuel, if high enough flash, can be employed as the soap diluent in the concentrate.

Example I

A typical satisfactory composition for use in accordance with the present invention is as follows:

Ingredients	Percent Weight
Glacial Acetic acid	¹ 10.00
Stearic or other high molecular weight acid ¹	¹ 5.00
Calcium hydroxide ²	¹ 7.30
Mineral Oil (Vis. @ 210° F.) (55 S.U.S.)	¹ 77.70

¹ Actually employed hydrogenated fish oil acids of predominantly C₁₈ chain length.

² Hydrated lime of high calcium content.

³ Approximately 10:1 Mol ratio.

The method of preparation is to mix the hydrogenated fish oil acids and $\frac{2}{3}$ volume of the mineral oil diluent. The temperature of the mixture is raised to about 150° F., and the acetic acid added. Immediately thereafter a slurry of hydrated lime in the balance of the mineral oil is added to the mixture. The temperature is then raised to about 250° to 300° F., and the water driven off. The temperature is then raised to 450° or 500° F., where the mass becomes solid and the complex forms.

Heating is discontinued and the mass stirred while cooling to 200° F. The product is a smooth unctuous solid material. This additive may be stored or blended directly into the residual fuel while warm. Homogenization of the blended fuel results in a product of excellent dispersion; however, this step is not necessary. Similarly, as above, other metal additives of a complex nature and high metal content may be formed from barium, strontium, zinc, magnesium or mixtures as desired for specific purposes or for economical reasons.

The above product containing 3.95 wt. percent calcium

was added to a bunker fuel oil to obtain a composition containing about 0.105 wt. percent calcium. The mixture contained 292 p. p. m. of vanadium and 1044 p. p. m. of calcium, the Ca/V ratio being 2.75. The mixture was passed through a Manton-Gaulin homogenizer. The resultant fuel was very stable, showing no separation on storage for 17 days at 150° F. In an accelerated settling test, 100 milliliters of the fuel were placed in a centrifuge tube and heated to about 115° F. and centrifuged for five minutes at 1500 R. P. M. The top 50 mls. portion was removed by syphon and submitted for analysis along with the remaining 50 mls. The analytical data are as follows:

[Bunker fuel + 2.73% calcium stearate/acetate complex product.]		
	Centrifuge Sample	
	Top (50 mls.)	Bottom (50 mls.)
Ash, Total, percent (800° C.)	¹ 0.41 (0.42)	0.36
Ca, percent	¹ 0.12 (0.11)	0.10

¹ Duplicate determination.

The data show the calcium to be well distributed and suspended in the fuel. Also, the amount of calcium in the fuel is in good agreement with the amount added (0.105%).

The invention is broadly concerned with the preparation of stable dispersions of high metal content soaps in residual fuels with no tendency toward settling out, even under severe conditions. This is secured by placing the metal in the fuel as a complex metal soap. While one method of preparation has been disclosed, it is within the scope of the present invention to include these complex soaps by any manner of manufacture whatsoever. The process is intended to cover the addition of the above components, high molecular weight acid, low molecular weight acid and hydrated lime directly to the fuel or to its components in its processing or while in storage at temperatures between about 250° to 550° F. Acids such as acetic acid, formic acid and the like, in combination with fatty acids such as palmitic, oleic, stearic and the like are contemplated.

The amount of metal added to the fuel as the complex soap is usually from about 0.02 to about 0.5 wt. percent. In the case of calcium, from 0.04 to 0.2 wt. percent will generally be sufficient to suppress corrosion by most residual fuels. Corrosion by vanadium is particularly suppressed when the atomic ratio of added metal to vanadium is in the range from 1/1 to 5/1, preferably 2/1 to 3/1. Although the invention is especially useful as regards vanadium-induced corrosion, it can be applied to fuels of relatively low vanadium content in order to secure other advantages such as a reduction in stock solids.

What is claimed is:

- An improved residual hydrocarbon fuel containing vanadium as an impurity, said fuel having dissolved therein from about 0.02% to about 0.5% by weight of a metal selected from the group consisting of calcium, barium, and magnesium, said metal being in the form of a complex soap obtained by the saponification of a low molecular weight monobasic carboxylic acid containing from 1 to 5 carbon atoms and a high molecular weight monobasic carboxylic acid containing from 16 to 22 carbon atoms, said complex soap consisting of from about 10 to 80% by weight of the soap of said low molecular weight acid and from about 90 to 20% by weight of the soap of the said high molecular weight acid.
- The composition of claim 1 wherein sufficient complex soap is present to secure an atomic ratio of said metal selected from the group consisting of calcium, barium and magnesium to vanadium of from about 1:1 to 5:1.

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3. The composition of claim 1 wherein said metal is calcium.

4. The composition of claim 1 wherein said metal is barium.

5. The composition of claim 1 wherein said metal is magnesium.

6. The composition of claim 1 wherein said low molecular weight monobasic carboxylic acid is acetic acid and said high molecular weight monobasic carboxylic acid is stearic acid.

7. The composition according to claim 1 wherein said complex soap is obtained by the saponification of a mixture of glacial acetic acid and hydrogenated fish oil acids with hydrated lime.

8. The composition of claim 1 wherein said complex 15

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soap consists of from about 50 to 80% by weight of the soap of said low molecular weight acid and from about 50 to 20% by weight of the soap of said high molecular weight acid.

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