

1

3,000,710
MINERAL BASE VANADIUM-CONTAINING RESIDUAL FUEL OIL COMPOSITION AND METHOD OF PREPARATION

James H. Kirk, Dyer, Ind., assignor to Sinclair Refining Company, New York, N.Y., a corporation of Maine
No Drawing. Filed Feb. 16, 1956, Ser. No. 565,786
3 Claims. (Cl. 44-72)

This invention relates to fuels and in particular relates to fuels, and a method of preparation, which are especially useful for steam generating boilers, gas turbine engines and similar equipment.

An especially vexatious problem to the manufacturers and users of steam generating boilers, gas turbine engines and other equipment, where combustion products of the fuel employed are intentionally directed towards various metal parts of the equipment, is attributed to the vanadium content of the residual fuels constituting the source of energy. The problem has two aspects: the first being ash deposits having a high vanadium content, and the second being the corrosion of metal parts resulting from vanadium present in ash deposits. In steam boilers and the like, gases resulting from the combustion of the fuel are directed towards the boiler tubes in a manner whereby the gases strike the tubes and effect a transfer of energy. The petroleum base fuels normally employed for boilers characteristically contain small amounts of vanadium of the order of up to about 300 or more parts per million. During combustion of the fuel, various ashes which contain the vanadium form; these ash materials are carried in the combustion gases to the boiler tube area where at least a part of the ash deposits. In addition to affecting the operating efficiency of the boiler, ash deposits present a serious corrosion problem which materially reduces equipment life since they appear to penetrate the natural oxide film on the metal parts, apparently by means of a fusion phenomenon, and attack the base metal.

Efforts towards solution of this problem have been directed into many avenues and some apparent solutions are disclosed in the patent literature (see British Patents No. 689,579 and No. 697,619). One suggested method involves treatment of the fuel to reduce the vanadium content to a minimum or eliminate it entirely. Such method does not appear to be practical at the present state of technology since it necessitates use of treating methods inherently expensive and, therefore, increases the fuel cost to the point where the expense of the fuel may make further use of residual oil-fired equipment uneconomic. A method which has attained some commercial significance comprises using additives in the fuels to lessen the effect of the vanadium ash. Highly promising additives include various forms of magnesium oxide such as dolomite, epsomite, magnesium naphthenate, and the like. Still other methods have proceeded on the theory that if the vanadium in the fuel could be converted to a form having a boiling point lower than the temperatures existing within the equipment, the vanadium would pass through without depositing as an ash. This method is not known to have obtained any commercial significance.

A fuel composition has now been discovered which greatly lessens corrosion of metal parts due to the vanadium content normally present in the fuel. It has also been discovered that corrosion due to the vanadium content of a fuel base can be minimized by substantially preventing the occurrence of the mechanism whereby such corrosion is effected. A method also has been discovered whereby a residual oil composition containing a high magnesium content is obtained consistently.

Although my invention is not to be limited by theory, it seems that the vanadium values normally contained

2

in the common residual fuels employed as an energy source for steam generating boilers and similar equipment are converted to a form or complexed so that the ash material, resulting upon combustion of the fuel, has a fusion point in excess of that which would normally result in fusion of the ash containing the vanadium values with metal parts. Thus, the vanadium values are converted to a form whereby they pass through the equipment with the combustion gases. In any event, it is known that the resulting fuel contains magnesium in the amounts indicated, that the magnesium is non-filterable when using the ordinary fuel line filter, and that the magnesium does not settle out upon prolonged storage of the product.

The mineral oil base constituting the major constituent of the novel fuel compositions is an article of commerce commonly termed residual oil. Residual oils are customarily obtained as pressure pipe still tars resulting from thermal cracking, as still bottoms from vacuum flashing topped crudes, and bottoms from catalytic cracking operations. Residual oils generally having boiling ranges above 850° F., are liquid at room temperature, and have API gravities of about 1 to 15 or more. Residual oils are derived from various crudes, for example naphthenic, paraffinic and Mid-Continent crudes. As the major portion of the vanadium values in crudes tends to concentrate in residual oil, the residuals generally have vanadium contents, on a weight basis, ranging from about 0.0005 to 0.1 percent.

Compositions constituting the present invention in fuels are composed of residual fuel oil containing the combined magnesium. The form of magnesium which is capable of effecting this combination is magnesium nitrate. The best results can be obtained with the substantially pure form of magnesium nitrate, though other compounds and metals which do not deleteriously affect the invention may be present. In general magnesium should be present in the residual oil in amounts equivalent to at least about three times the amount of vanadium present. Residual oils commonly contain 25 to 300 or more parts of vanadium per million parts of oil and those having a vanadium content of as low as about 5 or 10 parts per million should be treated before they can be used in steam boilers and the like with reasonable safety. Accordingly, the fuel compositions of the present invention will normally contain at least about 25 or 30 to 900 parts or more of combined magnesium per million parts of oil with about 75 to 900 parts of combined magnesium constituting the usual range. It may be desirable to employ excess magnesium as a safety measure though too much of an excess may make the resulting fuel expensive and thereby militate against its use on economic grounds.

Compositions of the present invention can be made by contacting the magnesium nitrate and the residual oil at an elevated temperature. If desired the oil can be first preheated and magnesium nitrate then added, or the components can be mixed at ambient temperatures and heated as a mixture. A particularly advantageous procedure comprises adding the magnesium nitrate to the vacuum still which produces the residual fuel as a bottoms product. In this procedure magnesium nitrate to most advantage is incorporated in the crude, or fraction thereof, entering the still or alternatively the respective materials can be introduced into the still separately. Whether the composition be produced in a still when the residual is produced or by contacting a residual oil and magnesium nitrate in apparatus other than a still, the temperature employed is at least about 212° F. in order to drive off a substantial amount of water introduced or formed in the reaction, and which usually re-

sults in a substantially anhydrous product. A preferred temperature range is about 300 to 900° F. The maximum temperature permissible is determined primarily by the temperature at which excessive cracking and coking of the residual oil occurs and by the availability of pressure equipment. To avoid excessive cracking and the like and to avoid the necessity to employ pressure equipment, it is preferable to limit the upper temperature to the cracking temperature or the boiling point of the residual oil, whichever is lower. Where water is employed, for example by adding the magnesium nitrate to the oil as a water solution, about 1 to 10 parts, and preferably 1 to 3 parts, of water per part of magnesium nitrate are conducive of satisfactory results. I believe the function of the water is that of a reaction initiator and its removal serves to disperse the magnesium throughout the oil.

The invention can be effected by adding magnesium nitrate, and water when desired, to the residual oil in a suitable vessel and applying heat for a time sufficient to result in a substantially anhydrous product. Normally about 10 minutes to two hours or more are required to effect the combination and obtain a dehydrated product. About 0.5 to 15 weight percent of magnesium nitrate, based on the amount of oil used, is employed though smaller or greater quantities can be used so long as the resulting product contains at least the minimum quantity of magnesium specified.

The invention will be described further by means of the following examples.

Example I

The residual oil employed in this example was obtained as bottoms in a vacuum flash distillation of a topped 36° API Wyoming crude oil and typically had the following properties:

API gravity	8.6
Viscosity/210° F. (Furol)	146.9
Viscosity/250° F. (Furol)	49.1
Pour, ° F.	90
Carbon residue, percent	19.87
Ash, percent	0.126
Sulfur, percent	3.28
Metals, percent:	
Magnesium	0.0003
Calcium	0.0015
Barium	0.0038
Nickel	0.0039
Sodium	0.0020
Vanadium	0.0032

About 200 grams of the oil were placed in a beaker and 10 grams of solid magnesium nitrate hexahydrate were added. The mixture was heated slowly for about 30 minutes, a final temperature of about 700° F. being obtained. Upon cooling, the mixture was filtered and the filtrate recovered as product. Analysis of the product disclosed a combined magnesium content of 125 p.p.m.

Example II

About 300 grams of the residual oil of Example I and 3 grams of magnesium nitrate hexahydrate were used in this example. The nitrate was dissolved in water and the resulting solution added dropwise to the oil which was first heated to 400° F. After complete addition of the magnesium nitrate, the mixture was permitted to

cool and was then filtered. Analysis of the product filtrate showed a magnesium concentration of 215 p.p.m.

A test was made which was identical to the procedure of Example II with the exception that the oil was first heated to 700° F. The product resulting contained 96 p.p.m. of magnesium.

A series of runs was conducted with 1000 gram samples of this same oil (of Example I) and 0.415 gram of magnesium oxide (theoretically equivalent to 250 p.p.m. Mg in finished oil). In one run 100 ml. of water were added; in the second run no added water was employed; in the third run no added water was employed and only 0.3 gram of magnesium oxide was added. In each run the maximum temperature reached was 485° F. In all three runs the product contained less than 4.5 p.p.m. of magnesium. Substantially similar runs employing magnesium sulfate and magnesium carbonate gave similar results.

A number of runs analogous to the foregoing were conducted employing magnesium oxide. Occasionally the resulting product contained an adequate magnesium content while in the remaining runs it did not. While I am unable to explain these erratic results with magnesium oxide, my data do show consistent results when employing magnesium nitrate as shown in Examples I and II above.

This application is a continuation-in-part of my co-pending application Serial No. 478,493 filed December 29, 1954, abandoned.

I claim:

1. The method of producing a mineral base vanadium-containing residual fuel oil composition containing magnesium, on a weight basis, in an amount equivalent to at least about three times the amount of vanadium present which comprises contacting at a temperature in excess of about 212° F. to 900° F. and for at least about 10 minutes a vanadium containing residual oil and magnesium nitrate in an amount sufficient to provide at least three parts of magnesium in the resulting product per part of vanadium present, said product being substantially anhydrous and filtering the product.

2. The method of claim 1 wherein said magnesium nitrate is employed as a water solution.

3. A mineral base vanadium-containing residual fuel oil composition containing magnesium in an amount, on a weight basis, equivalent to at least about three times the amount of vanadium present and obtained by contacting a vanadium-containing residual oil with magnesium nitrate at a temperature above about 212° F. to 900° F. and for at least about 10 minutes to give a substantially anhydrous product, and filtering the mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,079,051	Sullivan et al.	May 4, 1937
2,706,149	Brenneman	Apr. 12, 1955
2,781,005	Taylor et al.	Feb. 12, 1957

FOREIGN PATENTS

711,895	Great Britain	July 14, 1954
689,579	Great Britain	Apr. 1, 1953
697,619	Great Britain	Sept. 23, 1953

OTHER REFERENCES

Symposium on Corrosion of Materials at Elevated Temperatures, A.S.T.M. Publication No 108, June 26, 1950, Oil Ash Corrosion of Materials at Elevated Temperatures, by C T. Evans, Jr., pp. 98-102.