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METHOD OF FILTERING A FUEL OIL

James H. Kirk, Dyer, Ind., assignor, by mesne assignments, to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

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

The petroleum materials normally employed as fuel for steam generating boilers, gas turbine engines and similar equipment must be inexpensive if, in the case of steam boilers and the like, they are to compete with alternative fuel such as coal and, in the instance of gas turbine engines, if the engine is to be competitive with other engines as a source of power. A particularly inexpensive petroleum material which has found use for these applications is known as residual stock. Generally, however, residual stock is highly corrosive, since sodium and other impuriities of crudes tend to concentrate in the residuals during conventional refining procedures. For example, residual fuels usually contain some ash which causes corrosion of gas turbine nozzles and buckets in addition to causing deposits to build up in the turbine. Of the various elements in the ash, sodium is one of the most undesirable. Accordingly, a gas turbine manufacturer has specified that the turbine fuel should not contain more than 10 parts per million of sodium and, preferably, not more than 5 parts per million. Treatment of residuals designed to correct the corrosion characteristics, such as desalting and washing, affects the cost of the resulting fuel to an undesirable extent. The instant invention relates to a method for producing a fuel composition from residual stock in an inexpensive and efficacious manner where the resulting fuel contains less than about 10 parts per million of sodium.

I have now discovered a method whereby residual stock can be treated to result in a significantly less corrosive fuel, which is less expensive than prior art methods. The method is effected by passing a dry residual stock through a filter having an average porosity not greater than about 40 microns. Fuels produced in accordance with my method are characterized by significant reduction in sodium content, that is to a sodium content below 10 p.p.m., and hence in the corrosivity they normally would evidence in use. Preferably, I reduce the sodium content to less than about 5 p.p.m. to make it a more acceptable fuel. The residual stock treated by this invention in general contains more than about 5 p.p.m. of sodium since if it contains a substantially lesser amount there is little need for its treatment in meeting the most rigorous specifications now in effect. The feed may contain less than 10 p.p.m. of sodium and in such case the sodium content will be further reduced. The method also removes other contaminants such as lead and iron and the final composition frequently shows better anti-corrosion properties than are attributable solely to sodium removal.

The filtering step of my invention can be effected with a variety of different filter materials. Particularly satisfactory results have been achieved with both sintered glass filters and blotter paper. Regardless of the composition of the filter material employed, effective operation of my method requires that the porosity of the filter material be below a certain limit. Thus, the average filter porosity must be such that materials having a dimension of more than about 40 microns will not pass through the filter; that is, the filter pores must have an average size which is not greater than about 40 microns. The lower limit which can be employed is limited solely by the existence of perceptible porosity and filter rates which are tolerable. I have successfully used filters having a porosity of as little as 4.5 to 5 microns; it is preferred, however, to employ filters of about 10 to 40 micron porosity.

The filter can be employed in any manner desired. Gravity flow can be used but it is more desirable and is preferable to use a common filter press with a pressure head being maintained on the residual stock, for example of from about 20 to 60 p.s.i.g. Other pressures can be employed depending on the choice of the operator and the equipment available. A filter aid can be employed in my process and can be any of the commercially available filter aids so long as they do not deleteriously affect the process. Especially satisfactory filter aids include High Flow and Sil-O-Cel (proprietary products of the Johns-Manville Co.), and generally consist of diatomaceous earth. Generally, from about 0.01 to 1.0 weight percent of the filter aid, based on the residual stock, is slurried with the oil. I prefer to employ about 0.03 to 0.07 weight percent, and particularly 0.05 weight percent.

Fuel materials which can be treated in accordance with my process include materials commonly marketed as heating fuels, gas turbine fuels and the like. In general, these are known as residual fuels and are customarily obtained as pressure pipe still tars resulting from thermal cracking, as still bottoms from vacuum flashing topped crudes, bottoms from catalytic cracking operations and viscosity breaking operations, and the bottoms resulting upon distillation of crudes at atmospheric pressure. Commercial examples include ASTM No. 5 and No. 6 heating fuels. Residual fuels are derived from various crudes, for example, naphthenic, paraffinic, Mid-Continent crudes and others.

The residual stock to be filtered in the manner of my invention must be substantially completely dry. While an absolutely anhydrous state is not essential, it is preferred that no detectable water be present when tested by distillation dryness procedures. Frequently residual stocks are characterized by the degree of dryness necessary for practicing the instant invention due to their source or previous treatment. Where, however, "wet" stocks are to be treated, dehydration to dryness can be effected in any manner desired. Suitable methods include passing the stock through lines containing desiccants, placing desiccants in storage tanks which are employed for stock awaiting treatment, raising the temperature of the stock to above the boiling point of water while agitating to insure escape of the water as steam and similar methods. Preferably, the residual stock is maintained, during filtration, at a temperature of about 212 to 300° F. to aid in securing fairly rapid filtration rates; accordingly, dehydration of "wet" stock by simply raising the temperature and agitating is an especially advantageous and preferred procedure since preheat and dehydration are accomplished simultaneously.

The invention will be described further by means of the following examples. It should be understood that the specific details disclosed are not to be construed as limiting the invention.

A No. 6 residual heating fuel was employed in Examples I and II. The fuel had the following properties.

TABLE I

Physical tests:	
Gravity	7.5
Flash, ° F	290
Furol vis. at 122° F	121
Pour, ° F	35
Sulfur, percent	2.7
Ash, p.p.m	316

Example I

A sample of the No. 6 fuel oil was dehydrated by heating to 250° F. in a vessel while agitating the oil. High Flow filter aid was slurried with the oil in an amount equal to 0.5 pound of filter aid per 100 pounds of oil. The slurry was then filtered in a press using blotter paper having less than 40 micron porosity as the filter. The filtered oil was fortified to substantially the original level with magnesium naphthenate to inhibit against corrosion by vanadium and tested in a gas turbine fuel corrosion burner. Analysis of the fortified sample compared to the unfiltered stock and the corrosion data obtained are:

TABLE II

Metal Analysis	Unfiltered Stock	Filtered and Fortified
Sodium, p.p.m	5.8	3.1
Magnesium	60	85
Vanadium	24.3	26.8
Calcium	10.1	1.4
Aluminum	7.9	1.2
Chromium	5.1	0.3
Iron	17.0	0.5
Lead	14.0	1.4
Corrosion (Gas Turbine Fuel Corrosion Burner—100 hrs.):		
1,400° F., Loss, mgs	210	15
1,600° F., Loss, mgs	130	43

Example II

To demonstrate the effectiveness of the invention with a high sodium fuel, a sample of a No. 6 heating fuel known to have a high sodium content was washed with 5% of a water solution containing 0.7 pound of magnesium sulfate per gallon. After thoroughly mixing at 200° F. the mixture was allowed to settle 48 hours in an oven at 180 to 200° F. and the top layer decanted off. The washed oil was dehydrated by heating to 250° F. with agitation. High Flow filter aid was slurried with the oil in an amount equal to 0.5 pound per 100 pounds of oil. The slurry was then filtered in a press using blotter paper having less than 40 micron porosity as the filter. The filtered oil was fortified with magnesium naphthenate as in Example I. Analysis of the fortified sample compared to the unfiltered stock and the corrosion data obtained are:

TABLE III

Metal Analysis	Before Filtering	After Filtering
Sodium, p.p.m	25	2.7
Magnesium	98	90
Vanadium	31	31
Calcium		2.4
Lead	1.5	0.4
Chromium	0.2	0.16
Iron	18.0	0.4
Aluminum	6	2.0
Copper	2.4	0.1
Corrosion (Gas Turbine Fuel Corrosion Burner—100 hrs.):		
1,400° F., Loss, mgs	98	12
1,500° F., Loss, mgs		23
1,600° F., Loss, mgs	134	102

The corrosion data and the reduction in sodium values as shown in Tables II and III clearly demonstrate the effectiveness of my invention with both regular heating oils and high sodium content heating oils.

Example III

Samples of a No. 6 heating oil were filtered under identical circumstances except for changes in porosity of the filter employed. Effectiveness of the various filters in removal of sodium was noted by analysis of the filtrate. The results are:

TABLE IV

Sintered Glass Filter	Porosity, Microns	Sodium in Filtrate, p.p.m.
Charge Oil		12–15
Coarse	40–60	11
Medium	10–15	3
Fine	4.5–5	1
Coarse precoated with filter aid [1]	<40	2

[1] Johns-Manville High Flow.

From these data it can be observed that the filter having an average porosity exceeding the limit established for my invention was not effective in removing sodium while the filters conforming to the invention reduced the sodium content satisfactorily.

Example IV

A No. 6 heating fuel was filtered with and without a filter aid to demonstrate the value of a filter aid in the process. One-half of the oil was filtered through double sheets blotter paper while the other half was filtered under the same conditions but with the addition of 0.5 pound of High Flow filter aid per 100 pounds of oil. The results obtained are:

TABLE V

Metal Analyses	Charge Oil	Paper Only	Paper + Filter Aid
Sodium, p.p.m	13.5	7	3.0
Magnesium	8.0	5	4.0
Vanadium	22.6	24.2	22.8
Calcium	2.4	6.7	3.0
Aluminum	3.7	1.8	0.9
Iron	20.0	2.0	0.4
Lead	3.5	0.8	1.1

Example V

In other runs employing filter aid and different pressures on the filter press, No. 6 fuel oil containing about 0.054 pounds of High Flow filter aid per 100 pounds of oil (111 grams of High Flow added to 436 pounds of the oil) was filtered using blotter paper with a porosity of less than 40 microns. One run was conducted at a pressure of 60 p.s.i.g. and the other at 20 p.s.i.g. The feed, samples taken from the first few pounds of filtrate and samples of the last few pounds of filtrate for each run were analyzed for sodium content. The data are:

TABLE VI

	Sodium, p.p.m.
Feed	12–15
First filtrate at 20 p.s.i.g.	6
Last filtrate at 20 p.s.i.g.	3
First filtrate at 60 p.s.i.g.	3
Last filtrate at 60 p.s.i.g.	3

From the data of Tables V and VI it is apparent that the use of filter aid is advantageous even in the relatively small amounts employed in Example V.

Example VI

The necessity for employing a dehydrated oil in the process to effectively remove sodium was demonstrated

by filtering samples of an oil containing 0.2 percent water, by distillation, through sintered glass filters before and after dehydration. The results found are:

TABLE VII

Charge Stock	Porosity, Microns	Sodium in Filtrate, p.p.m., 12.5-13.5
Before Dehydration—Filter Type:		
Coarse	40-60	13.5
Medium	10-15	12.5
Fine	4.5-5	(1)
Coarse precoated with High Flow filter aid	<40	13
After Dehydration—Filter Type:		
Fine	4.5-5	4.5
Coarse precoated with High Flow filter aid	<40	7.5

[1] Would not go through filter.

I claim:

1. The method of producing a non-corrosive residual fuel in which magnesium is added to the fuel, the improvement which comprises passing a dry residual oil stock as a slurry containing about 0.01 to 1.0 pound of filter aid per 100 pounds of oil filtered through a filter having an average porosity of not greater than about 40 microns, the resulting residual fuel being decreased in

sodium content, containing less than 10 parts per million of sodium and having substantially reduced corrosive properties.

2. The method of claim 1 wherein said dry residual oil is maintained at a temperature of about 212° F. to 300° F. during filtration.

References Cited in the file of this patent

UNITED STATES PATENTS

2,067,345	Roberts et al.	Jan. 12, 1937
2,174,265	Holt	Sept. 26, 1939
2,179,028	Alton	Nov. 7, 1939
2,296,850	Harrison	Sept. 29, 1942
2,789,695	Winkler et al.	Apr. 23, 1957
2,789,696	Jahnig et al.	Apr. 23, 1957

FOREIGN PATENTS

517,222	Belgium	Feb. 14, 1953

OTHER REFERENCES

"Filtration With Filter-Cel," publication by Celite Products Co. (copyrighted 1923), pages 1 to 11.

"Desalting Crude Oils" (Egloff et al.), Petroleum Technology, May 1938, pp. 19–20.

"Chemical Refining of Petroleum" (Kalichevsky), Reinhold Publishing Co. (New York), page 35 (1942).