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RESIDUAL FUEL OILS

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This invention relates to improved fuel oils and is concerned more particularly with the prevention of the formation of sediment in residual fuel oils during storage.

Residual fuel oils are normally obtained from heavy tars produced during the cracking of petroleum oils, either thermally or catalytically. These heavy tars are blended to the desired viscosity or gravity with petroleum oils to produce heavy fuels. The fuel oils can vary considerably in various characteristics and may have a viscosity within the range of from about 90 seconds Universal at 100° F. to 300 seconds Furol at 122° F., and an A. P. I. gravity from 0 to 25°. The cracked heavy tars and blends thereof tend to develop sediment or sludge-like materials during storage, which form troublesome deposits in the storage tanks, clog the filters from the tanks or the strainers at the burners, or otherwise impair the efficiency and form deposits on the burner parts. The exact nature of these deposits and sediment has not been determined, nor has the mechanism of their formation been completely established. It appears, however, without intending to be bound by any definite theory as to their formation and structure, that residual fuel oils are colloidal solutions in which asphaltenes are dissolved and dispersed in oil. An equilibrium apparently exists between the dissolved and the dispersed asphaltenes which is affected by several factors, such as the solvent properties of the oil, the amount and kind of protective material in the oil, the character of the asphaltenes, and the sensitivity of the asphaltenes to external factors such as heat, etc. Whatever may be the facts of the make-up of residual fuel oils, it is true that these residual fuel oils possess a tendency to deposit sediment or sludge-like material under certain conditions and that the presence of such sediment seriously interferes with the efficient use, as well as the commercial utilization of residual fuel oil products.

It is an object of this invention to provide an improved residual fuel oil substantially free of sediment. Another object of this invention is to provide a method for preventing the formation of sediment during the storage of residual fuel oils. A further object of this invention is to provide an improved residual fuel oil in which is incorporated a hydrocarbon product capable of preventing substantially the formation of sediment during storage. Other objects and advantages of this invention will become apparent as the description thereof proceeds.

I have discovered that by adding certain aromatic hydrocarbon fractions synthesized from petroleum to a residual fuel oil, the separation of sediment or sludge-like material from the fuel oil is substantially completely eliminated.

A suitable source of such aromatic fractions is the heavy fraction from catalytic hydroforming. The hydroforming process involves contacting heavy naphtha with a catalyst in the presence of hydrogen. Suitable catalysts include oxides of the 6th group metals supported on activated alumina, particularly the oxides of chromium or molybdenum. In carrying out this process the vaporized naphtha can be contacted with a catalyst at a temperature between about 850° F. and about 1050° F., preferably between about 900° F. and about 1000° F., at a pressure of about 50 to about 600 pounds per square inch, preferably 200 to 350 pounds per square inch, and a space velocity of about 0.2 to about 2 volumes of liquid feed per volume of catalyst space per hour, preferably about 0.5 to 1.0 volumes of liquid feed per volume of catalyst space per hour, with an onstream time of about 1 to about 20 hours, preferably about 6 hours. In this "hydroforming" process, from about 1000 to 5000, preferably about 2500 cubic feet of hydrogen-containing gas are used per barrel of stock charged. Although this operation is carried out in the presence of hydrogen, it is actually a dehydrogenation process, since hydrogen is produced during the reaction and may be recycled. This process produces large yields of aromatic hydrocarbons including synthetic aromatic hydrocarbon fractions suitable for my purpose. Products higher boiling than gasoline are separated from the gasoline formed. The fraction has a gravity of from about 8.0° to 13.0° A. P. I., for example 11° A. P. I., and a distillation range of from about 400° F. to about 750° F. or higher. This fraction can be used as such or can be distilled into various fractions of the desired viscosity in order to be utilized most efficiently in blended residual fuel oils.

Another suitable source of a synthetic aromatic hydrocarbon fraction is the cycle stock from the catalytic cracking of gas oils. The cracking operation in the presence of a catalyst appears to convert a substantial amount of the hydrocarbons present to polynuclear aromatic hydrocarbons of relatively high boiling point. Virgin gas oil can be contacted with catalysts at temperatures of from about 800° F. to about 1050° F. and pressures of about atmospheric to about 50 pounds per square inch gauge. As cracking catalysts I can employ various solid refractory materials of the metal oxide type, such as active silica-alumina, silica-magnesia, alumina-zirconia, silica-zirconia-alumina, silica gels promoted with one or more metal oxides adsorbed thereon or admixed therewith, such as for example, magnesia or alumina, acid-treated ben-

tonite, or other acid-treated clays such as Super Filtrol, and other natural and synthetic refractory materials of the solid active metal oxide type, preferably those containing at least active silica or active alumina or both. Fixed bed, moving bed, or powdered catalyst operations can be employed. Low velocity upflow reactors are suitable for use with powdered catalysts. In the fixed bed or moving bed operations, space velocities falling within the range of from about 0.5 to about 6 volumes of oil per apparent volume of catalyst per hous and a catalyst residence or holding time of between about ten minutes and four hours are suitable. When using powdered catalysts, however, space velocities of between about 1 and about 20, for example 5 volumes of oil per volume of catalyst (measured "at rest") per hour, and a holding time of between 0.5 and 60 minutes can be used. It is contemplated that high space velocities will be used with low holding times and low space velocities will be coupled with high holding times to obtain the desired degree of cracking. The products from catalytic cracking are fractionated into light products, heavy products and a residuum, the fraction of heavy products containing the synthetic aromatic hydrocarbon fraction suitable for my purpose. The heavy product fraction is preferably treated to concentrate the synthetic hydrocarbon constituents, preferably by solvent extraction.

Suitable solvents that can be used for the extraction of an aromatic fraction include nitroparaffins, such as nitroethane and nitromethane, mixtures of nitroparaffins with other compounds, such as sulfur dioxide, acetonitrile, ethanol, and other solvents of high specificity. The solvent chosen should have selective solubility for the higher boiling aromatic hydrocarbons to the substantial exclusion of other hydrocarbons, although the solvent may selectively dissolve all of the aromatic hydrocarbons, the higher boiling aromatic hydrocarbons being separated from the monoaromatic hydrocarbons in a subsequent step. In recovering the desired aromatic fraction, the heavy product is contacted, for example, in countercurrent fashion with nitromethane at temperatures within the range of from about 50° F. to about 200° F., preferably at about 80° F. to about 100° F. The solution of solvent and extracted material is separated from the undissolved hydrocarbons and cooled to a temperature below about 80° F., preferably below 60° F., and allowed to separate. A phase separation occurs, less desirable hydrocarbons, mostly unchanged gas oil, being rejected as the raffinate layer and the preferred fraction being recovered with the extract layer, from which it is separated by stripping out the solvent. Other methods and other solvents can be employed for recovering aromatic hydrocarbons, any suitable means being encompassed within this invention.

All of the synthesized aromatic mixtures above described have a specific dispersion greater than 200 and generally greater than 250. The specific dispersion is determined according to the formula

$$\text{Specific dispersion} = \frac{F-C}{d} \times 10^4$$

wherein F is the refractive index based on the hydrogen β spectrum line, C is the refractive index based on the hydrogen α spectrum line, and d is the density of the compound at the temperature at which the refractive indices were obtained. The refractive indices of the F and C lines were determined by a refractometer such as a Pulfrich refractometer, and the density by a Westphal balance or other accurate means.

For comparative purposes, the following table of values for the specific dispersion of various classes of hydrocarbons is offered:

Hydrocarbon	Specific dispersion $\left(\frac{F-C}{d} \times 10^4\right)$
Paraffins and naphthenes	96 to 101
Monoolefins	109 to 135
Diolefins	126 to 145
Mononuclear aromatics	156 to 189
Polynuclear aromatics	Greater than 200

Analysis of my preferred fraction is not easy, due to the complexity of the mixture. The principal constituent appears to be a complex mixture of polynuclear aromatic hydrocarbon derivatives. This aromatic hydrocarbon fraction can replace all or a part of the blending oil in the heavy residual fuel oil mix. Generally speaking, however, we have found that adding only minor amounts of such aromatic fractions to the blend is sufficient to reduce the formation of sediment considerably.

As an example of the improved results obtained by my invention, a fuel oil comprising a blend of heavy tar from thermal cracking and a blending oil in the proportions of 20% tar and 80% blending oil showed 3.6% sediment in seven days at room temperature. A similar blend in which only 5% of the blending oil was replaced by a synthetic aromatic fraction showed 3.2% sediment in the same period of time. The synthetic aromatic fraction was obtained by the solvent extraction of cycle stock from catalytic cracking, using nitromethane as the solvent, as described above, and had a specific dispersion of 264.

A series of storage tests was made using various proportions of tar, blending oil and the synthetic aromatic hydrocarbon fraction. The tar was obtained from a thermal cracking process and had an A. P. I. gravity of 9.2°. The blending oil was a heavy distillate from the cracking of gas oils and had a distillation range of from about 350° F. to about 750° F., with 50% of the distillate distilling up to 592° F. The blending oil was aromatic in nature, having a specific dispersion of about 180. The synthetic aromatic hydrocarbon fraction was obtained from the catalytic hydroforming of a heavy naphtha and had a boiling range of from about 450° F. to 750° F. with 50% distilling up to 490°. It had a specific dispersion of 264. A blend of 20%-tar and 80% blending oil was used as the control, and various portions of the blending oil were replaced with the catalytic hydroforming high-boiling fraction. At the end of seven days storage the following amount of sediment was found in the various samples:

Blend	Per cent sediment
20% tar 80% blending oil	0.6
20% tar 70% blending oil 10% polymer	0.1
20% tar 40% blending oil 40% polymer	0.1
20% tar 20% blending oil 60% polymer	0.1

From the above it is obvious that the addition of 10% of a mixture of aromatic hydrocarbons

derived from petroleum oils by catalytic conversion has materially decreased the amount of sediment formation. Additional amounts of the fraction failed to give additional lowering of the amount of sediment and apparently this amount of sediment is present as such in the initial material and not formed during storage.

It should be pointed out that the blending oil used in these tests was highly aromatic as evidenced by the specific dispersion. The aromatics, however, were evidently predominantly mononuclear in character and did not have the attribute of preventing sediment formation so that the desirability of using our synthetic aromatic hydrocarbon fraction is even more emphasized.

I have also discovered that these synthetic aromatic hydrocarbon fractions have the added advantage of reducing deposits in preheaters. When residual fuel oils are passed through preheaters to elevate the temperature of the oil prior to combustion in the oil burners, it frequently happens that the preheater is coated with a deposit, which retards heat transfer, reduces the capacity of the oil lines, and interferes with oil atomization. It has been found that when even minor amounts of my preferred aromatic hydrocarbon fraction are added to residual fuel oils, that the "heater coating index" is considerably reduced. Heater coating indices are obtained by the Batchelder method and are described in The Refiner, volume 15 (Nov.) 1936, page 485. The Batchelder method measures the amount of benzene-insoluble incrustation which gathers on a polished steel rod immersed in a fuel oil. The rod has an area of 0.115 square foot and is maintained at a temperature of 350° F. The oil sample is placed in a one quart vessel which is cooled externally by a water bath held between 60 and 80° F. The oil is changed every twenty-four hours until a run of ninety-six hours has been completed. At the completion of the testing the rod is withdrawn and the deposit which is formed thereon is washed off with benzol and a stiff brush. The benzol-insoluble material is collected and weighed and the weight thus obtained is the heater coating index.

When a residual fuel oil similar to that above, containing 20% tar and 80% blending oil, was tested by the Batchelder method, 1.261 grams of deposit were obtained, while in a similar blend in which 5% of the blending oil had been replaced with 5% of catalytic hydroforming polymer the deposit was only 0.059 gram. This is an added advantage in employing a synthetic aromatic hydrocarbon mixture in residual fuel oils, since not only is the sediment formation in storage decreased, but the preheater deposits are reduced substantially. Generally speaking, sediment formation and heater deposit stability do not correlate, since one is a storage problem and the other is a heating problem, and it has been found, broadly, that compounds effective for reducing sediment formation may increase or at least do not affect heater deposit formation, while reagents used to prevent heater deposit formation may increase the amount of sediment formation in storage. My synthetic aromatic hydrocarbon fractions are advantageous for the improvement of residual fuel oils from both angles.

Throughout the specification and claims, wherein the term "synthetic aromatic hydrocarbons" is used, it is intended to refer to a fraction or mixture of aromatic hydrocarbons, the fraction or mixture having a specific dispersion above 200 and preferably above about 250, obtained by the catalytic conversion of petroleum oil fractions at conversion temperatures.

I claim:

1. A stable residual fuel oil composition comprising a heavy residual cracked petroleum tar, a distillate petroleum oil and an amount of a fraction consisting substantially entirely of polynuclear aromatic hydrocarbons sufficient to prevent sediment formation during storage, said petroleum tar being one which when blended with said distillate petroleum oil alone in amounts of about 20% tar and about 80% distillate oil would normally tend to form sediment during storage.

2. A stable residual fuel oil composition comprising a heavy residual cracked petroleum tar, a distillate petroleum oil and at least 5% of a fraction consisting predominantly of polynuclear aromatic hydrocarbons sufficient to prevent sediment formation during storage, said petroleum tar being one which when blended with said distillate petroleum oil alone in amounts of about 20% tar and about 80% distillate oil would normally tend to form sediment during storage.

3. A stable residual fuel oil composition comprising a heavy residual cracked petroleum tar, a distillate petroleum oil having a boiling range within the approximate range of 350° F. to 750° F. and a specific dispersion of not more than 180 and an amount of a fraction consisting substantially entirely of polynuclear aromatic hydrocarbons sufficient to prevent sediment formation during storage, said petroleum tar being one which when blended with said distillate petroleum oil alone in amounts of about 20% tar and about 80% distillate oil would normally tend to form sediment during storage.

4. A stable residual fuel oil composition comprising a heavy residual cracked petroleum tar, a distillate petroleum oil and an amount of a fraction consisting substantially entirely of polynuclear aromatic hydrocarbons sufficient to prevent sediment formation during storage, said fraction being obtained as a high boiling fraction from the catalytic hydroforming of naphtha, said petroleum tar being one which when blended with said distillate petroleum oil alone in amounts of about 20% tar and about 80% distillate oil would normally tend to form sediment during storage.

5. A stable residual fuel oil composition comprising a heavy residual cracked petroleum tar, a distillate petroleum oil and an amount of a fraction consisting predominantly of polynuclear aromatic hydrocarbons sufficient to prevent sediment formation during storage, said fraction being obtained as a high boiling fraction from the catalytic hydroforming of naphtha and having a specific dispersion greater than 250, said petroleum tar being one which when blended with said distillate petroleum oil alone in amounts of about 20% tar and about 80% distillate oil would normally tend to form sediment during storage.

6. A stable residual fuel oil composition comprising a heavy residual cracked petroleum tar, a distillate petroleum oil and an amount of a fraction consisting predominantly of polynuclear aromatic hydrocarbons sufficient to prevent sediment formation during storage, said fraction having a boiling range within the approximate limits of 450° F. and 750° F. and a specific dispersion of about 264, said petroleum tar being

one which when blended with said distillate petroleum oil alone in amounts of about 20% tar and about 80% distillate oil would normally tend to form sediment during storage.

7. A stable residual fuel oil composition comprising about 20% of a heavy residual cracked petroleum tar, not more than about 70% of a distillate petroleum oil and not less than 10% of a fraction consisting predominantly of polynuclear aromatic hydrocarbons sufficient to prevent sediment formation during storage, said petroleum tar being one which when blended with said distillate petroleum oil alone in amounts of about 20% tar and about 80% distillate oil would normally tend to form sediment during storage.

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