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DIESEL FUEL AND THE METHOD OF PREPARING THE SAME

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This invention relates to improvements in high speed Diesel engine fuels and the method of obtaining the same.

In the operation of Diesel engines, in which the liquid fuel is injected directly into the cylinder, the interval between the time the fuel is injected and the time the fuel becomes ignited is called the "delay period" or "ignition lag." Better engine performance is obtained when the delay period or ignition lag is of short duration, since the "roughness" of running or the Diesel knock is directly proportional to the duration of the delay period. One of the desired properties of a Diesel fuel is therefore good ignition characteristics.

It is the primary object of this invention to provide a fuel, having improved ignition characteristics, for high speed Diesel engines.

It is another object of the present invention to provide a method of obtaining an improved Diesel engine fuel, having improved ignition characteristics. Other objects and advantages of our invention will become apparent from the following description thereof.

We have discovered that fuels, having improved ignition characteristics, for high speed Diesel engines, as evidenced by an increase in the cetane number, may be obtained by blending two Diesel fuel distillates from different crudes, one of which is a high sulfur crude, and treating the blend with sodium plumbite solution in the presence of a large excess of elemental sulfur.

We are aware that Diesel fuels have heretofore been treated with doctor solution in the presence of small amounts of sulfur. We are also aware that in the normal sweetening process the mercaptans are converted to mercaptides, and that the oil soluble higher molecular weight mercaptides are oxidized by sulfur to the disulfides. We are also aware that disulfides have been added to Diesel fuels. One of the distinguishing features of our invention is that we treat a blend of particular stocks with sodium plumbite solution in the presence of a large amount of sulfur, in excess of that required to sweeten the stock, but which will not result in the presence of corrosive sulfur in the oil. We believe that by treating our fuel in this manner we obtain certain compounds heretofore not produced in the normal sweetening process, which compounds impart to the finished product improved ignition characteristics.

In the known methods of sweetening petroleum distillates the following reactions are believed to take place:

(1) $2R—S—H+PbO \rightarrow Pb(SR)_2+H_2O$

(2) $Pb(SR)_2+S \rightarrow PbS+R_2S_2$

From an inspection of the above equations it will be seen that one atom of sulfur is necessary for each two mols of mercaptans sweetened. When the distillates are treated in the presence of an amount of sulfur in excess of that required to sweeten the distillate we believe the following reactions occur:

(3) $2RSH+PbO+xS \rightarrow R_2S_{x+1}+PbS+H_2O$

We have discovered that with certain kinds of stocks when the excess amount of sulfur used is approximately 7 times that theoretically required to sweeten the product, i. e., when x in the above equation is equal to at least 7, the finished product has much improved ignition characteristics.

In accordance with our invention a high sulfur fuel oil fraction, for example a fuel oil fraction from Winkler crude, or a blend of about 60% to 95% of a Mid-Continent fraction having a distillation range of about 400° F. to 750° F. and about 5% to 40% of a high sulfur fraction having a distillation range of about 350° F. to 750° F., from a high sulfur crude oil of the Winkler type, which blend has a distillation range of about 390° F. to 750° F. is treated with sodium plumbite in the presence of a large excess of sulfur, preferably 3 to 6 times the amount normally added to sweeten such oils. The oils are settled and washed in the usual manner.

The following specific example is illustrative of our invention: 85% Mid-Continent gas oil and 15% of a gas oil from Winkler crude having the following respective characteristics were blended together.

	Mid-Continent gas oil	Winkler gas oil
Gravity °A. P. I.	37.4	23.1
Viscosity at 100° F. seconds	38.6	42.6
Distillation:		
I. B. P. °F.	420	424
10% °F.	495	466
50% °F.	538	562
90% °F.	588	683
E. P. °F.	663	746

The characteristics of the blend are shown below:

Gravity °A. P. I.		35.1
Viscosity at 100°	Seconds	39.0
Distillation:		
I. B. P.	°F.	420
10%	°F.	495
50%	°F.	540
90%	°F.	608
E. P.	°F.	676

The sour oil by analysis (copper number) contained eight milligrams of mercaptan sulfur in each 100 cc. of the oil. To sweeten this oil would theoretically require four milligrams of sulfur for each 100 cc. of oil sweetened. However, 28 milligrams of sulfur or seven times the theoretical amount was added in treating the product. This indicates that there is not formed in the reaction dialkyl disulfides but dialkyl octasulfides. Although there may be other polysulfides formed, the average value of $x+1$ in the formula R_2S_{x+1} of Equation 3 must be equal to eight since all of the sulfur added was consumed.

The blend before treating had a cetene number of about 53 and after treating in the foregoing manner had a cetene number of about 57 showing a substantial increase in the cetene number indicating a product having much improved ignition characteristics.

A Diesel fuel oil having improved ignition characteristics may also be obtained by treating a distillate fuel stock with sodium plumbite and an amount of sulfur in large excess of the quantity theoretically required to sweeten the stock, distilling the so-treated distillate fuel stock to obtain a desired sweetened condensate, reducing the bottoms, and adding the reduced bottoms in small amounts to a Diesel fuel oil to raise the cetane number thereof. We prefer to employ a distillate fuel stock from a high sulfur crude, such as a distillate of the Winkler stove distillate type. Using stocks of this type we have found it preferable to treat the same with sodium plumbite and an excess amount of sulfur over that required to sweeten the stock. We have found that from six to eight times the theoretical amount of sulfur required to sweeten the stock may be used without having corrosive sulfur present in the finished product. This indicates that instead of disulfides, other polysulfides, probably dialkyl octasulfides, are formed.

In order to avoid the formation of disulfides by air oxidation and to enhance the formation of higher poly sulfides, for example, octa sulfides, it may be desirable, prior to subjecting the distillate to treatment with sodium plumbite and excess sulfur, to remove substantially all of the air from the distillate stock and to conduct the subsequent treatment in a closed system in the absence of air. The air may be removed from the distillate stock by blowing the same with an inert non-oxygenated gas or by distilling over a few percent of the low boiling fractions.

The distillate fuel stock treated with sodium plumbite in the presence of about seven times the theoretical amount of sulfur is distilled, preferably steam distilled, to give a desired condensate, and the residue or bottoms further reduced by vacuum distillation or by fire and steam distillation to give a reduced bottom amounting from about 1% to about 6% of the original distillate fuel stock. The reduced bottoms are then added in amounts of about 0.5% to 5% to Diesel fuel oils to raise the cetane number thereof.

A method of obtaining a Diesel fuel oil of improved ignition characteristics is exemplified by the following: A high sulfur distillate, such as for example, a Winkler stove distillate or a stove distillate from a crude oil of the Winkler type, having the inspection shown in Table I is treated with sodium plumbite and excess sulfur, and steam distilled to a 30% overhead of Winkler aviation gasoline having a distillation range of about 115° F. to 260° F.

TABLE I

Winkler stove distillate

Distillation:	Degrees F.
Initial B. P.	120
10%	192
50%	256
90%	317
Max	390

A portion of the 70% bottoms was then further reduced by vacuum distillation to produce a residue hereinafter referred to as residue I amounting to about 1.85% on the original stove distillate. Another portion was reduced by fire and steam distillation to give a residue hereinafter referred to as residue II amounting to about 4.9% on the original stove distillate.

Adding various amounts of residues I and II to a 52 cetane number Diesel fuel the following results were obtained:

Fuel	Cetane number
Control	52
Control+2% residue I	64
Control+4% residue I	71
Control+1% residue II	54
Control+2% residue II	56
Control+3% residue II	58

The above results show the effect of adding small amounts of reduced bottoms from a treated distillate fuel oil from a crude oil of the Winkler type.

While we have described our invention by certain specific examples we do not intend to limit the scope of our invention thereby, except insofar as the same is defined by the appended claims.

We claim:

1. The method of preparing a high speed Diesel engine fuel having improved ignition characteristics and substantially free of corrosive sulfur which comprises treating a fuel oil distillate from a high sulfur crude oil with sodium plumbite solution and a large excess of sulfur, said sulfur used amounting to from about 3 to 6 times the theoretical amount required to normally sweeten such a distillate.

2. The method of preparing a high speed Diesel engine fuel having improved ignition characteristics and substantially free of corrosive sulfur which comprises blending a gas oil having a low sulfur content characteristic of Mid-Continent gas oil with a gas oil having a high sulfur content and treating the blend with sodium plumbite solution in the presence of a large excess of sulfur.

3. In the treatment of a high speed Diesel engine fuel oil comprising a blend of a gas oil having a low sulfur content characteristic of Mid-Continent gas oil and a high sulfur gas oil, the method of increasing the cetene number of said blend which comprises treating the same with sodium plumbite solution in the presence of at least 6 times the amount of sulfur theoretically required to sweeten said blend, said treated blend being substantially free of corrosive sulfur.

4. The method of preparing a substantially corrosive sulfur-free high cetene number Diesel fuel comprising mixing 60% to 95% of a Mid-Continent gas oil with 40% to 5% of a high sulfur gas oil obtained from a high sulfur crude and treating said mixture with sodium plumbite

solution in the presence of about 7 times the amount of sulfur normally required to sweeten said mixture.

5. The method of obtaining a high speed Diesel engine fuel having improved ignition characteristics and substantially free of corrosive sulfur comprising mixing 60% to 95% of Mid-Continent distillate boiling within the range of about 350° F. to 750° F. with 40% to 5% of a high sulfur distillate boiling within the range from about 350° F. to 750° F. and treating said mixture with sodium plumbite solution in the presence of sulfur, said sulfur being added in amounts at least 600% over the theoretical amount required to normally treat such a mixture.

6. The method described in claim 4 in which the high sulfur distillate is a distillate obtained from a high sulfur crude of the Winkler type.

7. A high cetene number high speed Diesel engine fuel obtained by the method of claim 2.

8. A high speed Diesel engine fuel having improved ignition characteristics obtained by the method of claim 5.

9. The method of preparing a high speed Diesel engine fuel having improved ignition characteristics and substantially free of corrosive sulfur comprising treating a distillate fuel stock obtained from a high sulfur crude with sodium plumbite in the presence of sulfur, distilling the sweetened distillate fuel stock to obtain a condensate and a bottom stock, further reducing said bottom stock to give a reduced bottom amounting to about 1% to about 10% of the original distillate fuel stock and adding a small amount of said reduced bottoms to a Diesel fuel oil whereby the ignition characteristics of the latter are materially improved.

10. The method of obtaining Diesel engine fuel oils having desirable ignition characteristics and substantially free of corrosive sulfur comprising treating a stove distillate with sodium plumbite in the presence of sulfur, distilling off about 30% of the said sweetened stove distillate to produce an overhead having aviation gasoline characteristics and a 70% bottom, further reducing said bottom to give a reduced bottom amounting to about 1% to about 6% of the original stove distillate and adding 0.5% to 5% of said reduced bottoms to Diesel fuel oils.

11. The method of obtaining Diesel engine fuel oils having improved ignition characteristics and substantially free of corrosive sulfur comprising treating a stove distillate obtained from a crude oil of the Winkler type with sodium plumbite in the presence of sulfur amounting to about 7 times the theoretical amount of sulfur required to normally sweeten such a distillate, distilling the treated stove distillate to produce an overhead amounting to about 30% of the original stock and a bottom stock amounting to about 70% of the original stock, further reducing said bottom stock by suitable means to produce a reduced bottoms amounting to about 1% to about 6% of the original stove distillate and adding 0.5% to 5% of said reduced bottoms to distillate fuel oils having undesirable ignition characteristics.

12. The method described in claim 11 in which the stove distillate is deoxygenated before treatment with sodium plumbite and sulfur, said sulfur used amounting to about seven times the theoretical amount required to normally sweeten such a distillate.

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