United States Patent Office

3,036,901

Patented May 29, 1962

3,036,901

RESIDUAL FUELS CONTAINING INSOLUBLE ADDITIVES

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No Drawing. Filed Nov. 24, 1958, Ser. No. 775,706
14 Claims. (Cl. 44—51)

The present invention relates to hydrocarbon oils improved by means of additive agents and more particularly relates to petroleum residual fuel oils having finely-divided, oil-insoluble, metallic additives stably dispersed therein by calcium acetate hydrates.

Metallic additives are widely employed in petroleum residual fuel oils for reducing the formation of stack solids during combustion, for abating high temperature corrosion caused by vanadium and other contaminants found in crude oils, and for curtailing low temperature corrosion attributable to the presence of sulfur in the oil. The materials most frequently used as metallic additives in such oils include iron oxide, magnesium oxide, magnesium hydroxide, magnesium sulfate, dolomite, kaolin, alumina, calcium oxide and the like. Since these additives are insoluble in hydrocarbons, they tend rapidly to settle out of residual fuels and must therefore be added to the oil just before it is injected into the furnace or boiler in which it is to be burned. The equipment necessary for incorporating metallic additives into residual fuels in this manner is expensive and is generall adaptable only to large, complex installations.

In order to overcome the difficulties encountered when oil-insoluble metallic additives are used in residual fuels, it has been suggested that soluble metallic compounds be substituted for the insoluble materials set forth above. Soaps of high molecular weight organic acids, metallic sulfonates and metallic naphthenates for example, and other oil-soluble additives are reasonably effective in fuel oils requiring low additive concentrations but are not satisfactory for use in fuels with which the additive requirements are high. Such soluble compounds have relatively low metal contents and must be used in very high concentrations in order to provide high concentrations of the additive metal. At such high concentrations, the combustion properties of the fuels are often adversely affected. Moreover, oil-soluble metallic compounds are in most cases much too expensive to be used as additives for residual fuels.

The present invention permits the use of metallic additives in residual fuel oils without the difficulties which have characterized the use of additives in such fuels in the past. In accordance with the invention, it has now been found that highly stable suspensions of finely-divided, oil-insoluble, metallic additives in residual fuels can be prepared by first reacting a calcium base with acetic acid to form a calcium acetate hydrate in situ in the fuel and thereafter employing the hydrate thus formed to suspend the oil-insoluble additive in the fuel. Tests have shown that fuels containing insoluble metallic additives suspended in this manner may be stored without appreciable settling out of the additives and that materials so suspended are fully as effective as additives incorporated into residual fuels by conventional methods. The invention thus permits the use of metallic additives at substantially lower cost than had been possible heretofore.

The calcium acetate hydrates which are used to suspend insoluble additives in residual fuel oils in accordance with the invention are formed in situ in the oil by the reaction of a calcium base with acetic acid. Suitable calcium bases include calcium hydroxide, calcium oxide, calcium carbonate and the like. Calcium hydroxide is particularly effective and is preferred. If calcium oxide or

carbonate is employed as the calcium base, a small amount of water may be added in order to furnish the water of hydration. In forming the hydrate, a smooth slurry of the calcium base in a portion of the residual fuel or a similar heavy hydrocarbon oil is first prepared. The calcium base contained in the slurry is then neutralized to form the hydrate by adding acetic acid. To prevent overheating due to the exothermic reaction, the acid should be added slowly and the mixture should be agitated. Depending upon the temperature reached by the reaction mixture, the hydrate formed may be calcium acetate monohydrate, $Ca(CH_3COO)_2.H_2O$, calcium acetate dihydrate, $Ca(CH_3COO).2H_2O$, or a mixture of these two. At temperatures below about 180 to 200° F., the dihydrate is formed. Above these temperatures the dihydrate tends to lose 1 mol of the water of hydration and is converted into the monohydrate. The monohydrate in turn is stable well over 300° F. and hence does not break down during storage of the fuels in which it is contained. It is generally preferred to restrict the reaction temperature to temperatures below about 180° F. in order that the dihydrate may be formed. Although the monohydrate and the dihydrate both have excellent stabilizing properties, it has been found that the dihydrate is slightly more effective.

Following preparation of the calcium acetate hydrate as described above, the finely-divided, oil-insoluble, metallic additive to be incorporated into the fuel is added. The quantity of metallic additive used may vary over a wide range but it is usually preferred to use from about 1 to about 40 parts by weight of the additive per part of the hydrate. The metallic compound is added only after the heat of reaction evolved in forming the hydrate has subsided. Heating during addition of the metallic compounds is not required. The oil containing the hydrate and the finely-divided metallic compound are blended to form a smooth paste or slurry. Additional oil may then be added to increase fluidity. The product thus formed is then homogenized by passing it through a Gaulin homogenizer, a Charlotte mill, a Morehouse mill, or the like. By thus homogenizing the concentrate containing the hydrate and the insoluble additive, a more uniform product is obtained.

The additive concentrate is then added to the residual fuel in an amount sufficient to give the desired concentration of the metallic additive. The additive concentration will vary depending upon the particular oil-insoluble additive employed and the purpose for which it is to be used. For overcoming the corrosive effects of vanadium and similar contaminants found in crude oils, it is generally preferred to add a calcium, magnesium, aluminum, nickel or similar metal compound to the oil in an amount such that the weight ratio of the added metal to the vanadium in the fuel ranges from about 1 to 1 to about 4 to 1. Residuals fuels generally contain from about 10 to about 1000 parts per million of vanadium. The concentration of the added metal will generally range between about 0.001 percent and about 0.2 percent by weight. Similar quanties of iron oxide, alumina, kaolin, dolomite and other metallic additives may be added to overcome the effects of sulfur corrosion and to reduce stack solids during combustion. The total concentration of finely-divided insoluble solids may thus range between about 0.001 percent and about 0.5 percent by weight. The insoluble additives employed may have an average particle size ranging from about 0.05 to about 25 microns. It is preferred that the additive be ground to an average particle size of from about 0.05 to about 10 microns.

The residual fuels in which oil-insoluble metallic additives are incorporated as described above are derived from petroleum crude oil and comprise the residual prod-

ucts obtained from refining operations such as the distillation of crude oils, the flashing or distillation of thermally cracked products and redistilling operations. Such fuels consist primarily of residual material but may contain distillate fractions added to reduce viscosity or improve other properties. In the United States, residual fuels are generally classified into three grades. These grades are defined in United States Department of Commerce Commercial Standard CS–12–48. The lightest residual fuel is called a No. 4 fuel oil and is generally employed in burner installations not equipped with preheating facilities. This fuel contains relatively large amounts of distillate materials. The next grade is No. 5 oil which contains some distillate materials and is intended for use in installations having limited preheating equipment. No. 6 oil is the heaviest grade of residual fuel and normally consists wholly of residues. The principal differences between the various grades lie in their viscosities and boiling ranges. Typical properties of Nos. 4, 5 and 6 fuel oils are shown in the following table:

TABLE I

Typical Residual Fuel Properties

Commercial Standard CS–12–48 Classification	No. 4	No. 5	No. 6
Color	Black	Black	Black
Gravity, °API	21	17	12
Sp. Gr.	0.93	0.95	0.99
Carbon Residue, Wt. percent	3.0	5.0	12.0
Viscosity, Centistokes/100° F	14	50	980
Pour Point, ° F	20	30	65

The residual fuel oils containing insoluble additives suspended in accordance with the invention may also contain oil-soluble additives such as rust inhibitors, pour point depressants and the like.

The invention is further illustrated by the following examples:

Example 1.—A heavy No. 6 residual fuel oil derived from a Venezuelan crude was inhibited against vanadium corrosion by the incorporation therein of 1600 parts per million of magnesium added as magnesium oxide. The magnesium oxide was incorporated into the fuel by first preparing a calcium acetate hydrate in situ in a small portion of the fuel oil. The fuel oil and hydrated lime were charged to a kettle equipped with an efficient means of agitation and a smooth slurry of lime in the oil was prepared by intimate mixing. Glacial acetic acid was then slowly added to the slurry to neutralize the lime and form a gel-like calcium acetate hydrate. Stirring was continued during addition of the acetic acid until the heat evolved by the neutralization reaction had subsided. The hydrate produced consisted primarily of calcium acetate dihydrate. Magnesium oxide derived by the calcination of magnesite was then blended into the calcium acetate hydrate-residual fuel product. After intimate mixing had produced a smooth paste, the product was passed through a Morehouse mill set with a 0.003 inch clearance. The formulation and properties of the additive concentrate thus prepared are as follows.

FORMULATION OF ADDITIVE CONCENTRATE

Ingredients:	Percent weight
Acetic acid, glacial	4.0
Hydrated lime	2.6
Magnesium oxide (magnesite-calcined)	45.0
Residual fuel oil	48.4

Properties:

Appearance—Excellent smooth product
Mol. ratio (Mg/Ca), 32.2/1
Wt. ratio (Mg/Ca), 20/1

The concentrate was blended into the bulk of the fuel to give a final magnesium content of 1600 parts per million by weight.

Example 2.—A residual fuel oil containing magnesium oxide suspended by a calcium acetate hydrate which was prepared as described in the preceding example was tested to determine stability of the additive in the fuel by settling tests. The oil was introduced into a 7 ft. high settling column and maintained at a constant 125° F. temperature for a period of two weeks. During this time samples of the oil were withdrawn from the column and analyzed to determine the amount of additive which had settled out. A parallel test was run on a sample of the same fuel oil to which 1600 parts per million of magnesium oxide had been added by mechanical mixing of the additive and the fuel. The average particle size of the magnesium oxide was the same in both cases, about 10 microns. The results of these tests are shown in the following table, from which it can be seen that the use of the calcium acetate hydrate to suspend the finely-divided metallic additive resulted in a fuel manifestly superior to that obtained when the additive was simply incorporated by mechanical mixing.

Loss of Additive by Settling, Percent of Original Concentration [1]

Settling Time, Days	Additive Suspended by Calcium Acetate Hydrate as Described Above	Additive Suspended by Mechanical Mixing of Additive and Fuel
0	0	0
2	0	35
7	0	41
14	0	42

[1] Original concentration 1600 p.p.m. Mg added as MgO to residual fuel.

Example 3.—An additive concentrate containing finely-divided ferric oxide was prepared by employing acetic acid, hydrated lime, ferric oxide and residual fuel oil in the following proportions.

FORMULATION OF ADDITIVE CONCENTRATE

Ingredients:	Percent weight
Acetic acid	5.0
Hydrated lime	3.3
Fe_2O_3	45.5
Residual fuel oil	46.2

The fuel oil and hydrated lime were charged to a vessel equipped with efficient means of stirring. The lime and oil were intimately mixed and the acetic acid was then added with continuous stirring. After the heat of reaction had subsided and gel formation had been obtained, the powdered ferric oxide was dispersed in the oil-hydrate product to form a smooth paste. A quantity of oil equal to the amount originally employed was added to increase the fluidity of the concentrate. A Morehouse mill set at 0.002 inch clearance was employed to homogenize the product and obtain a concentrate in which the ferric oxide was uniformly distributed. The concentrate was blended into a heavy Bunker C residual fuel oil to give an iron content, expressed as elemental iron, of 0.014 wt. percent.

The fuel oil containing ferric oxide which was prepared as described in the preceding paragraph was placed in a centrifuge and rapidly centrifuged for two hours at 1800 revolutions per minute in order to determine the effectiveness of the calcium acetate hydrate for dispersing the ferric oxide. Two hours of centrifugation are approximately equal to two months of settling, as calculated from Stokes' law. At the end of the two hour period the additive concentration in the fuel was again determined and it was found that the oil contained 0.0125 wt. percent of elemental iron. During centrifugation equivalent to two months' settling only about 10% of the additive was lost, indicating that the hydrate was quite effective for dispersing the ferric oxide.

Example 4.—Residual fuels containing 300 parts per million of elemental iron were prepared by the method described in the preceding example and by mixing and shearing an oil and finely-divided ferric oxide in conven-

tional mechanical equipment. In both cases the ferric oxide employed had an average particle size of about 1 micron. The two fuels thus prepared were then separately burned in a furnace and the effect of the iron on stack solids, as compared against the fuel containing no additive, was determined. It was found that the fuel containing ferric oxide suspended by a calcium acetate hydrate and that in which the additive was incorporated by mixing and shearing were equally effective, indicating that the method of the invention does not interfere with the action of metallic additives in residual fuels. The results obtained were as follows:

Method of Suspending Fe_2O_3	Fe, p.p.m.	Percent Reduction in Stack Solids
Calcium acetate hydrate formed in situ and homogenizing	300	12
Mixing and Shearing	300	12

It will be understood that calcium acetate hydrate may be formed in situ in hydrocarbon oils and employed to suspend a wide variety of finely-divided metallic additives in such oils. Although the foregoing examples demonstrate the suspension of magnesium oxide and ferric oxide by means of such hydrates, magnesium oxide, dolomite, kaolin, alumina and other additives may be similarly employed. In many cases it will be desirable to use a mixture of finely-divided metallic additives in order to simultaneously reduce stack solids, high temperature corrosion, low temperature corrosion and the like.

What is claimed is:

1. A method of stably suspending a finely-divided, oil-insoluble additive in a petroleum residual fuel oil which comprises blending a calcium base in a heavy hydrocarbon oil to form a smooth slurry; neutralizing said base in said oil with acetic acid to form a calcium acetate hydrate; adding from about 1 to about 40 parts by weight, based upon said hydrate, of a finely-divided, oil-insoluble solid metal compound to said oil; homogenizing said oil containing said hydrate and said metal compound; and thereafter adding said homogenized oil mixture to said residual fuel oil in an amount to give a metal compound concentration ranging between about 0.001% to about 0.5% by weight.

2. The method as defined by claim 1 wherein said finely divided oil-insoluble solid metal compound is ferric oxide.

3. The method as defined by claim 1 wherein said calcium base is hydrated lime.

4. The method as defined by claim 1 wherein said finely divided oil-insoluble solid metal compound is an iron compound.

5. The method as defined by claim 1 wherein said finely divided oil-insoluble solid metal compound is an alkaline earth compound.

6. The method as defined by claim 1 wherein said finely divided oil-insoluble solid metal compound has an average particle size of between 0.05 and 25 microns.

7. The method as defined by claim 1 wherein said residual fuel is a vanadium-containing Bunker C fuel oil.

8. The method as defined by claim 1 wherein said calcium acetate hydrate is a dihydrate.

9. A method of stably suspending a finely divided oil-insoluble alkaline earth metal compound in a petroleum residual fuel oil, which comprises blending hydrated lime in a heavy hydrocarbon oil to form a smooth slurry, neutralizing said hydrated lime in said hydrocarbon oil with acetic acid at a temperature below about 180° F. to form a calcium acetate hydrate, adding from about 1 to 40 parts by weight based upon said hydrate of a finely divided oil-insoluble solid alkaline earth metal compound having an average particle size of between 0.5 and 25 microns to said oil, homogenizing said oil containing said hydrate and said alkaline earth metal compound, and thereafter adding said homogenized oil mixture to said residual fuel in an amount to give an alkaline earth metal compound concentration ranging between about 0.002 and 0.5% by weight.

10. The method as defined by claim 9 wherein said alkaline earth compound is a magnesium compound.

11. The method as defined by claim 9, wherein said alkaline earth compound is magnesium oxide.

12. The method as defined by claim 9, wherein said alkaline earth compound is magnesium hydroxide.

13. A petroleum residual fuel oil composition as prepared by the method of claim 1.

14. A petroleum residual fuel oil composition as prepared by the method of claim 10.

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