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## STABILIZED DISTILLATE FUEL OIL

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This invention relates to the improvement of non-lubricating petroleum fractions. It is more particularly concerned with distillate fuel oils containing additives adapted to inhibit the appearance of sediment during prolonged storage periods, to prevent screen-clogging, and to prevent rusting of ferrous metal surfaces.

It is well known that fuel oils are prone to form sludge or sediment during periods of prolonged storage. This sediment, of course, has an adverse effect on burner operation, because it has a tendency to clog screens and nozzles. In addition to sediment formed during storage, most fuel oils contain other impurities, such as rust, dirt, and entrained water. The sediment and impurities tend to settle out on equipment parts, such as nozzles, screens, filters, etc., thereby clogging them and causing the equipment to fail.

A further factor, incident to the storage and handling of fuel oils, is the "breathing" of storage vessels. This results in the accumulation of considerable amounts of water in the tanks, which presents a problem of rusting in the tanks. Then, when the oil is removed for transportation, sufficient water may be carried along to cause rusting of ferrous metal surfaces in pipelines, tankers, and the like.

Generally, it has been the practice to overcome the aforedescribed difficulties with a separate additive for each purpose, i.e., with a sediment inhibitor, an anti-screen clogging agent, and an antirust agent. The use of several additives, however, gives rise to problems of additive compatibility, thus restricting the choice of additive combinations. In addition, of course, the use of a plurality of additives unduly increases the cost of the fuel. It has been proposed to overcome two difficulties, e.g., sedimentation and screen clogging, with one additive. Insofar as is known, however, no single addition agent has been found effective against sedimentation, screen and nozzle clogging, and rusting of ferrous metal surfaces.

It has now been found that all three problems, i.e., sedimentation, screen clogging, and rusting, can be solved by the use of a single fuel oil addition agent. It has been discovered that a distillate fuel oil containing minor amounts of certain metal salts of nitrated hydrocarbons is effectively inhibited, simultaneously, against all three aforementioned difficulties.

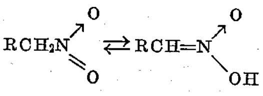
Accordingly, it is a broad object of this invention to provide a fuel oil having properties improved with a minimum number of addition agents. Another object is to provide a fuel oil having a single additive adapted to inhibit sedimentation, to prevent screen clogging, and to prevent rusting of ferrous metal surfaces with which it comes in contact. A specific object is to provide a fuel oil that contains certain metal salts of nitrated hydrocarbons that achieve these results. Other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description.

The present invention provides a distillate fuel oil containing a minor amount, sufficient to inhibit sedimentation and screen clogging and to prevent rusting of ferrous metal surfaces in contact therewith, of a metal salt of a nitrated paraffinic hydrocarbon, said nitrated hydrocarbon being produced by reacting a paraffinic hydrocarbon having between about 12 carbon atoms and about 34 carbon atoms with nitric acid, at a temperature of between about 175° C. and about 195° C., and said metal being from groups IIA and IIB of the periodic chart of the elements.

The addition agents of this invention are metal salts of nitrated paraffinic hydrocarbons. The paraffinic hydrocarbons utilizable herein are paraffinic hydrocarbons having between about 12 carbon atoms and about 34 carbon atoms per molecule. These paraffins can be relatively pure hydrocarbons or they can be mixtures of paraffinic hydrocarbons, such as a paraffin wax and predominantly paraffinic petroleum fractions. The paraffinic hydrocarbons can be straight-chain or branched-chain. Non-limiting examples of these hydrocarbons are dodecane; 2,4,5,7-tetramethyloctane; tridecane; tetradecane; 4,5-dipropyloctane; hexadecane; 3-ethyltetradecane; octadecane; eicosane; 2,6,11,15-tetramethylhexadecane; heneicosane; docosane; 2-methyltricosane; isohexacosane; triacontane; and tetratriacontane. As has been mentioned hereinbefore paraffin waxes are utilizable. These waxes melt between about 40° C. and about 72° C. and include paraffin wax, ozokerite, ceresin wax, slack wax, and scale wax.

As the first step in making the addition agents contemplated herein, the paraffinic hydrocarbon is nitrated. This is effected by reacting the hydrocarbon with nitric acid; with the hydrocarbon in the liquid phase and the nitric acid in the vapor phase, i.e., at temperatures between about 175° C. and about 195° C. The nitric acid can be of a concentration varying between about 70 percent and about 90 percent. During the nitration reaction, it is desirable to sweep the reaction vessel with an inert gas, such as nitrogen, in order to remove water from the nitric acid and the reaction.

As is well known to those familiar with the art, the nitro-paraffins can exist in two desmotropic forms. This relationship can be expressed by the following general equilibrium equation:



$$\mathrm{RCH_2N}\begin{matrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{matrix} \rightleftarrows \mathrm{RCH{=}N}\begin{matrix}\nearrow \mathrm{O}\\ \diagdown \mathrm{OH}\end{matrix}$$

It is the latter, or aci-form, material that forms salts.

The salts of the aforedescribed nitro-paraffins that are utilizable in the fuel oil compositions of this invention are the salts of the metals of groups IIA and IIB of the periodic chart of the elements. Salts of magnesium, barium, calcium, and zinc are especially preferred. These compounds are prepared by the reaction between the aci-form nitro-paraffin (which reacts as a carboxyl group) and a solution of the group II metal. In practice, it is preferred to react the metals in lower alcohol solutions of inorganic salts or alcoholates, such as, by way of non-limiting example, barium methylate or ethylate, magnesium methylate or ethylate, zinc chloride in methanol or ethanol, calcium chloride in methanol or ethanol, and the like.

The metal salts of nitro-paraffins are obtained by gradually heating a mixture of nitro-paraffin and an alcoholic solution of metal alkoxide in oil or kerosene as solvent to 175° C. to drive off the alcohol. The temperature is maintained at 175° C. from 1 to 3 hours to complete the formation of the metal salts.

The fuel oils that are improved in accordance with this invention are hydrocarbon fractions having an initial boiling point of at least about 100° F. and an end boiling point no higher than about 750° F., and boiling substantially continuously throughout their distillation range. Such fuel oils are generally known as distillate fuel oils. It is to be understood, however, that this term is not restricted to straight-run distillate fractions. The distillate fuel oils can be straight-run distillate fuel oils, catalytically or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight-run distillate fuel oils, naphthas and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well known commercial methods, such as, acid or caustic treatment, hydrogenation, solvent refining, clay treatment, etc.

The distillate fuel oils are characterized by their relatively low viscosities, pour points, and the like. The principal property which characterizes the contemplated hydrocarbons, however, is the distillation range. As mentioned hereinbefore, this range will lie between about 100° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower boiling range falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially continuously throughout its distillation range.

Particularly contemplated among the fuel oils are Nos. 1, 2, and 3 fuel oils used in heating and as Diesel fuel oils, and the jet combustion fuels. The domestic fuel oils generally conform to the specifications set forth in ASTM Specifications D396–48T. Specifications for diesel fuels are defined in ASTM Specifications D975–48T. Typical jet fuels are defined in Military Specification MIL–F–5624B.

The amount of nitro-paraffin salt additive that is added to the distillate fuel oil in accordance with this invention will depend, of course, upon the intended purpose and the particular salt selected, as they are not all equivalent in their activity. Some may have to be used in greater concentrations than others to be effective. In most cases, in which it is desired to obtain all three beneficial results, namely, to inhibit sedimentation, to reduce screen clogging, and to prevent rusting of ferrous metal surfaces, additive concentrations vary between 10 pounds per thousand barrels of oil and about 200 pounds per thousand barrels of oil will be employed. It may not always be desired, however, to accomplish all three aforementioned results. In such cases, where it is desired to effect only one or two results, lower concentrations can be used. Thus, if it is desired only to prevent rust under dynamic conditions, as in a pipeline, it has been found that concentrations as low as about 25 p.p.m., i.e., about 5 pounds of additive per thousand barrels of oil, are effective. In general, therefore, the amount of nitro-paraffin salt that can be added to the distillate fuel oil, in order to achieve a beneficial result, will vary generally between about 5 pounds per thousand barrels of oil and about 200 pounds per thousand barrels of oil. Preferably, it will vary between about 10 and about 200 pounds per thousand barrels of oil.

If it is desired, the fuel oil compositions can contain other additives for the purpose of achieving other results. Thus, for example, there can be present foam inhibitors and ignition and burning quality improvers. Examples of such additives are silicones, dinitropropane, amyl nitrate, metal sulfonates, and the like.

The following specific examples are for the purpose of illustrating the fuel oil compositions of this invention, and of exemplifying the specific nature thereof. It is to be strictly understood, however, that this invention is not to be limited by the particular additives and fuel oils, or to the operations and manipulations described therein. Other nitroparaffin salts and fuel oils, as discussed hereinbefore, can be used, as those skilled in the art will readily appreciate.

## EXAMPLE 1

A reaction vessel containing 296 grams of liquid paraffin wax was provided with a submerged (in the wax) coil having an external inlet and a submerged porous plate outlet. The paraffin wax was heated to 175° C. and 90 grams nitric acid (specific gravity=1.421) were introduced dropwise into the coil. The temperature was maintained at 175–185° C. throughout the addition period (4 hours). At the operating temperature the nitric acid vaporized and bubbled through the paraffin wax through the porous plate. A stream of nitrogen was used in the coil to prevent nitric acid vapor from backing up into the coil and to remove water from the nitric acid and the reaction. The nitro-paraffin wax, thus obtained, had a nitrogen content of 1.89 percent, by weight.

## EXAMPLE 2

A mixture of 161 grams of nitrated wax (Example 1), 29.8 grams of barium in the form of barium methylate solution in methanol, and 322 grams of paraffinic oil (100 SSU at 100° F.) as a diluent was agitated and heated gradually to 175° C. The temperature was then maintained at about 175° C. for 3 hours to drive off the methanol. The reaction product which contained 63 percent oil was then filtered through filtering clay (diatomaceous earth). The fluid filtrate product was an oil solution of barium salt of nitro-paraffin wax, containing 5.9 weight percent barium and 0.59 weight percent nitrogen.

## EXAMPLE 3

A mixture of 50 grams of nitrated wax (Example 1), 4 grams of magnesium in the form of magnesium methylate solution in methanol, and 100 grams of kerosene (boiling range=343 to 519° F.) as a diluent was gradually heated to 175° C., with stirring. The temperature was maintained at about 175° C. for 3 hours to drive off the methanol. Then, the product which contained approximately 65 percent kerosene was filtered through filtering clay. The final product was a fluid kerosene solution of the magnesium salt of nitro-paraffin wax, containing 2.44 weight percent magnesium and 0.45 weight percent nitrogen.

## EXAMPLE 4

A mixture of 23 grams of zinc chloride dissolved in 100 cc. of methanol and 7.1 grams of sodium in the form of sodium methylate solution in methanol was refluxed at 65° C. for 3 hours to form zinc methylate. The reaction mixture which contained the zinc methylate and sodium chloride became turbid. To the reaction mixture was added at room temperature 50 grams of nitrated wax (Example 1) and 200 grams of kerosene (boiling range equal 343 to 519° F.) as a diluent. The mixture was gradually heated to 175° C. with agitation to drive off the methanol. The temperature was maintained at about 175° C. for 3 hours to complete the formation of zinc nitro-paraffin wax. The reaction mixture which contained approximately 76 percent kerosene was filtered through filtering clay, producing as the filtrate, a fluid kerosene solution of the zinc nitro-wax salt, containing 2.68 weight percent zinc and 0.27 weight percent nitrogen.

## EXAMPLE 5

A mixture of 19 grams of calcium chloride dissolved in 150 cc. of methanol and 7.1 grams of sodium in the form of sodium methylate solution in methanol was refluxed at 65° C. for 3 hours to form calcium methylate. The reaction mixture which contained the calcium methylate and sodium chloride became turbid. To the reaction mixture was added at room temperature 50 grams of nitrated wax (Example 1) and 100 grams of kerosene (boiling range equal 343 to 519° F.) as a diluent. The mixture was gradually heated to 175° C. to drive off the methanol and maintained at about that temperature for 3 hours to complete the formation of the calcium nitroparaffin wax salt. The mixture which contained approximately 63 percent kerosene was filtered through filtering clay. The produce (filtrate) was a kerosene solution of a calcium salt of nitro-paraffin wax, containing 0.87 weight percent calcium and 0.49 weight percent nitrogen.

## EXAMPLE 6

In the apparatus described in Example 1, 27 grams of nitric acid (specific gravity equal 1.421) were added dropwise through the submerged coil to react with 50 grams of n-dodecane. The temperature was maintained at 180–185° C. during addition. The final product, nitrated dodecane, contained 2.12 weight percent nitrogen.

## EXAMPLE 7

A mixture of 25 grams of nitrated n-dodecane (Example 6), 5.2 grams of barium in the form of barium methylate solution in methanol, and 75 grams of kerosene diluent was gradually heated to 175° C. to drive off the methanol. The reaction was maintained at about 175° C. for 3 hours to complete the formation of the barium salt of nitro-dodecane. The reaction mixture became gelatinous. A mixture of 80 grams of xylene and 70 grams of isopropanol was added. The reaction mixture became fluid. The reaction mixture which contained approximately 90 percent solvent was then filtered through filtering clay. The final product was a solution of the barium salt of nitro-dodecane, containing 2 weight percent barium and 0.2 weight percent nitrogen.

## EXAMPLE 8

A mixture of 25 grams of nitrated dodecane (Example 6), 2.76 grams of magnesium in the form of magnesium methylate solution in methanol, and 75 grams of kerosene diluent was gradually heated to 175° C. to drive off the methanol and that temperature was maintained for 3 hours. Then, the mixture was filtered through filtering clay. The product filtrate was diluted with 50 grams of xylene. The final product was a solution of the magnesium salt of nitro-dodecane, containing 1.38 weight percent magnesium and 0.32 weight percent nitrogen.

### *Sedimentation*

The test used to determine the sedimentation characteristics of the fuel oils is the 110° F. storage test. In this test, a 500-milliliter sample of the fuel oil under test is placed in a convected oven maintained at 110° F. for a period of 6 weeks. Then, the sample is removed from the oven and cooled. The cooled sample is filtered through a tared asbestos filter (Gooch crucible) to remove insoluble matter. The weight of such matter in milligrams is reported as the amount of sediment. A sample of the blank, uninhibited oil is run along with a fuel oil blend under test. The effectiveness of a fuel oil containing an inhibitor is determined by comparing the weight of sediment formed in the inhibited oil with that formed in the uninhibited oil.

## EXAMPLE 9

The additives described in Examples 2 through 5 were blended in a test fuel oil and the blends were subjected to the 110° F. storage test. The test results comparing the blended fuels and uninhibited fuels are set forth in Table I. The test fuel oil is a blend of 60 percent distillate stock obtained from continuous catalytic cracking and 40 percent straight-run distillate stock. It has a boiling range of between about 320° F. and about 640° F. and is a typical No. 2 fuel oil.

TABLE I.—110° F. STORAGE TEST—6 WEEKS

| Inhibitor, Example | Inhibitor conc'n, lb./1,000 bbls. | Sediment, mg./liter |
|---|---|---|
| 2 | 0 | 81 |
| | 100 | 43 |
| 3 | 0 | 59 |
| | 50 | 8 |
| 4 | 0 | 59 |
| | 100 | 12 |
| 5 | 0 | 59 |
| | 100 | 39 |

### *Screen Clogging*

The anti-screen clogging characteristics of a fuel oil were determined as follows: The test is conducted using a Sundstrand V3 or S1 home fuel oil burner pump with a self-contained 100-mesh Monel metal screen. About 0.05 percent, by weight, of naturally-formed fuel oil sediment, composed of fuel oil, water, dirt, rust, and organic sludge is mixed with 10 liters of the fuel oil. This mixture is circulated by the pump through the screen for 6 hours. Then, the sludge deposit on the screen is washed off with normal pentane and filtered through a tared Gooch crucible. After drying, the material in Gooch crucible is washed with a 50–50 (volume) acetone-methanol mixture. The total organic sediment is obtained by evaporating the pentane and the acetone-methanol filtrates. Drying and weighing the Gooch crucible yields the amount of inorganic sediment. The sum of the organic and inorganic deposits on the screen can be reported in milligrams recovered or converted into percent screen clogging.

## EXAMPLE 10

Using the test fuel oil described in Example 9, blends of the additives of Examples 2 through 8 in this fuel were prepared. Each blend was subjected to the screen clogging test, as aforedescribed. Test results are set forth in Table II.

TABLE II.—SCREEN CLOGGING

| Additive of Example | Conc'n, lbs./1,000 bbls. | Screen clogging, percent |
|---|---|---|
| Blank | 0 | 100 |
| 2 | 50 | 2 |
| 3 | 100 | 3 |
| 4 | 100 | 49 |
| 5 | 100 | 27 |
| 7 | 100 | 12 |
| 8 | 50 | 2 |

### *Rusting*

The method used for testing anti-rust properties of the fuel oils was the ASTM Rust Test D–665 operated for 48 hours at 80° F. using distilled water. This is a dynamic test that indicates the ability to prevent rusting of ferrous metal surfaces in pipelines, tubes, etc.

## EXAMPLE 11

Blends of the additives described in Examples 2 through 8 in the fuel oil of Example 9 were subjected to the ASTM Rust Test D–665. Pertinent data are set forth in Table III.

TABLE III.—ASTM RUST TEST

| Additive of Example | Conc'n, p.p.m. | Test result |
|---|---|---|
| Blank | 0 | Fail. |
| 2 | 25 | Pass. |
| 3 | 50 | Do. |
| 4 | 50 | Do. |
| 5 | 50 | Do. |
| 7 | 50 | Do. |
| 8 | 50 | Do. |

It will be apparent, from the data set forth in Tables I through III, that the nitro-paraffin salts of this invention are highly effective to reduce sedimentation and screen clogging and to inhibit rusting of ferrous metal surfaces under dynamic conditions. As is to be expected results will vary among specific materials used. In order to accomplish any given improvement, many of the additives can be used in relatively small amounts, as for dynamic rust prevention. If, on the other hand, it is desired to accomplish all the aforementioned beneficial results, this can be accomplished at the practical additive concentration of 50–100 pounds per thousand barrels of fuel oil.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. A distillate fuel oil containing a minor amount, sufficient to inhibit sedimentation and screen clogging and to prevent rusting of ferrous metal surfaces in contact therewith, of a metal salt of a nitrated paraffinic hydrocarbon, said nitrated hydrocarbon being produced by reacting a paraffinic hydrocarbon having between about 12 carbon atoms and about 34 carbon atoms with nitric acid, at a temperature varying between about 175° C. and about 195° C., and said metal being from groups IIA and IIB of the periodic chart of the elements.

2. A distillate fuel oil containing between about 5 pounds and about 200 pounds, per thousand barrels of fuel, of a metal salt of a nitrated paraffinic hydrocarbon, said nitrated hydrocarbon being produced by reacting a paraffinic hydrocarbon having between about 12 carbon atoms and about 34 carbon atoms with nitric acid, at a temperature varying between about 175° C. and about 195° C., and said metal being from groups IIA and IIB of the periodic chart of the elements.

3. A distillate fuel oil containing between about 10 pounds and about 200 pounds, per thousand barrels of fuel, of a metal salt of nitrated paraffin wax, said nitrated paraffin wax being produced by reacting paraffin wax with nitric acid, at a temperature varying between about 175° C. and about 195° C., and said metal being from groups IIA and IIB of the periodic chart of the elements.

4. A distillate fuel oil containing between about 10 pounds and about 200 pounds, per thousand barrels of fuel, of the barium salt of nitrated paraffin wax, said nitrated paraffin wax being produced by reacting paraffin wax with nitric acid, at a temperature varying between about 175° C. and about 195° C.

5. A distillate fuel oil containing between about 10 pounds and about 200 pounds, per thousand barrels of fuel, of the magnesium salt of nitrated paraffin wax, said nitrated paraffin wax being produced by reacting paraffin wax with nitric acid, at a temperature varying between about 175° C. and about 195° C.

6. A distillate fuel oil containing between about 10 pounds and about 200 pounds, per thousand barrels of fuel, of the zinc salt of nitrated paraffin wax, said nitrated paraffin wax being produced by reacting paraffin wax with nitric acid, at a temperature varying between about 175° C. and about 195° C.

7. A distillate fuel oil containing between about 5 pounds and about 200 pounds, per thousand barrels of fuel, of a metal salt of nitrated dodecane, said nitrated dodecane being produced by reacting dodecane with nitric acid, at a temperature varying between about 175° C. and about 195° C., and said metal being from groups IIA and IIB of the periodic chart of the elements.

8. A distillate fuel oil containing between about 10 pounds and about 200 pounds, per thousand barrels of fuel, of the barium salt of nitrated dodecane, said nitrated dodecane being produced by reacting dodecane with nitric acid, at a temperature varying between about 175° C. and about 195° C.

9. A distillate fuel oil containing between about 10 pounds and about 200 pounds, per thousand barrels of fuel, of the magnesium salt of nitrated dodecane, said nitrated dodecane being produced by reacting dodecane with nitric acid, at a temperature varying between about 175° C. and about 195° C.

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