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STABLE FUEL OIL COMPOSITIONS

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This invention relates to stable fuel oil compositions. More particularly, the invention relates to stable fuel oil compositions which are composed of straight run and catalytically cracked oils.

When a heavy petroleum oil is subjected to catalytic cracking by any of the conventional processes such as the fixed bed, moving bed or fluid processes, wherein the heavy oil is contacted with a cracking catalyst such as a natural clay catalyst or a synthetic silica-alumina or silica-magnesia catalyst, the conversion products comprise not only gasoline hydrocarbons but also heavier distillate hydrocarbons, such as hydrocarbons boiling in the fuel oil range; that is, hydrocarbons boiling within the range of about 350° to about 750° F. Although the burning characteristics of such oils are fairly good, it is generally the practice when using these catalytically cracked oils as fuels to mix them with straight run distillate oils of similar boiling range in order to produce mixed oils having better burning characteristics than the catalytically cracked oils, and also in order to balance refinery production.

These mixed straight run and catalytically cracked distillate oils, however, have been found to have the disadvantage of being relatively unstable in storage. After a few months in storage at atmospheric temperature, they tend to form a precipitate or sludge which is unsightly and which reduces their usefulness as burning oils in certain types of installations. It has been found that the storage characteristics of a mixed oil are poorer than the characteristics of either oil alone. The reason for this is not clearly understood but it may be that the solubility of certain degradation products of the catalytically cracked oil is less in the mixed oil than in the catalytically cracked oil.

The present invention relates to fuel oil compositions comprising mixed catalytically cracked and straight run distillate fuel oils which compositions are of improved stability with respect to sludge deposition and therefore of good appearance and adapted for effective use in fuel oil furnaces and as diesel fuels even after being stored for extended periods. We have discovered that such an improved mixed fuel oil can be obtained by incorporating in the oil a small amount of a combination of a trialkylphosphite in which the alkyl groups are open or cyclic alkyl groups containing 4 to 12 carbon atoms and a salt of a metal of group II of the periodic table and a dialkyl dithiophosphoric acid in which the

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alkyl groups are also open or cyclic and contain 4 to 12 carbon atoms. The barium, calcium, magnesium and zinc salts of such dialkyl dithiophosphoric acids are especially important. A preferred combination comprises the barium salts of mixed dialkyl dithiophosphoric acids in which the alkyl groups are open chain and contain an average of 6 to 8 carbon atoms, in combination with tributylphosphite. As will appear from the specific examples, we have found that while a compound of either of these classes is relatively ineffective when incorporated in a mixed fuel oil, the combination is effective in inhibiting sludge formation. The two compounds may be employed in varying proportions with respect to one another, provided the compound present in the smaller amount is present in an amount corresponding to at least about 0.005 per cent by weight of the finished oil. In general it is preferred to employ the compounds in weight ratios varying from about 1:4 to 4:1.

It has not been determined in what way combinations of compounds of these classes function to improve the characteristics of the mixed fuel oil and therefore the invention is not limited to any theory of operation. It might appear that they function as solubilizing agents for the sludge, but this function is more or less negatived by the fact that whereas a mixed fuel oil in the absence of such a combination forms additional amounts of sludge so long as it is stored, at least over any feasible test storage period, the incorporation of a combination of this class in the oil inhibits the formation of sludge even after some sludge has been formed, and the already formed sludge does not disappear. By adding a small amount of combination of compounds as described to a mixed fuel oil containing an amount of sludge making the oil undesirable for use in many burner installations because of sludge deposits, the oil can be employed in such installations without leaving undesirable deposits. In this case it appears that although the sludge does not disappear, its characteristics are so changed as to prevent its deposition on a typical burner screen or on other parts of a burner.

The addition of the combination in very small amounts has been found to produce the best results. Thus, fully effective results are obtained when using between about 0.05 and about 0.15 per cent of the combination by weight of the mixed fuel oil even when the mixed oils have high sulfur content and pronounced sludging tendencies. However, adequate results are obtained

when using as little as 0.01 per cent of the combination. In this case, in many instances full inhibition of sludge formation is not obtained but the mixed oil is satisfactory for use because the combination changes the physical, and perhaps chemical, nature of the sludge so that it does not cause rapid clogging of screens and other parts of burners. While larger quantities than 0.15 per cent can be used, no advantage appears to result. The use of larger quantities necessarily increases the ash and carbon residue test values of the mixed oils, and sometimes also causes darkening.

The compounds may be incorporated in the mixed fuel oil in any suitable manner. For example, they may be added either separately or together to either or both of the catalytically cracked or straight run oils prior to mixing the two or they may be added to the mixed oil. When the compounds are incorporated in the mixed oil, it is unnecessary to do this immediately after mixing the oil as they are effective even after some sludge has formed. It will usually be preferable to add the compounds prior to any sludge formation as this will either eliminate sludge formation, or reduce the amount of sludge formed, depending upon the specific characteristics of the oils employed in making up the mixed oil. The compounds can be added as such but it is preferred to employ them in the form of concentrated solutions in an oil carrier. After addition, some circulation of the mixed oil is desirable to insure the early production of a uniform composition, but this is not absolutely necessary.

The problem with which the present invention is concerned exists only when a catalytically cracked oil and a straight run oil are combined in such proportions as to cause a substantial effect such as previously described. The invention is important when the ratio of the volume of the catalytically cracked oil to the straight run oil is within the range of 9:1 to 1:9. It is especially advantageous when applied to mixed oils containing these oils in a volume ratio within the range of 4:1 to 1:4.

In order to determine the effectiveness in mixed fuel oils of compounds of the classes disclosed above, two tests were carried out, a light stability test and a storage test. The light stability test was carried out by exposing a 100 cc. sample of the oil to be tested to a light source rich in ultra-violet rays, for periods of 4 hours alternated with periods of 20 hours during which the oil was stored in the dark. The test was completed after 40 hours exposure to the light. At the end of each dark storage period the samples were examined for the presence of precipitated sediment or sludge. The exposure to light was accomplished by putting samples of fuel oil in 4-ounce bottles which were unstoppered to allow access of air. These bottles were placed within a circular metal enclosure at a distance of 22 inches from the light source which was a Westinghouse 400 watt type DH–1 mercury vapor lamp mounted vertically in the center of the housing. It was found that a temperature rise of 20° F. occurs during the exposure period. The interval of darkness was necessary to allow any dispersed sludge to settle and to permit oxygen to replace any used up in the light-induced reaction. The effect of the exposure to light was judged by swirling the bottle and estimating the quantity of precipitate which had settled. This was recorded as Trace, Light, Medium or Heavy.

The storage test was carried out by pouring 1500 cubic centimeters of the fuel to be tested into a two-quart Mason jar and immersing an 8 inch by 1½ inch by $\frac{1}{32}$ inch SAE 1020 cold rolled steel strip in the oil. The steel surface to oil ratio approximates that existing in a 55 gallon steel drum. The jar was then closed with a vented lid and was stored in total darkness. Periodically sampling and testing were carried out as rapidly as possible in subdued light. The extent of deterioration of the fuel was determined by the amount of precipitate observed and designated as Trace, Light, Medium or Heavy. Any staining or corrosion of the steel strip was noted.

In the following tables there are given the results of light stability and storages tests made on mixed fuel oils of the character indicated in the absence of an additive and containing a compound or compounds of the classes disclosed above. The compounds employed in these tests were the barium salt of a mixture of dialkyl dithiophosphoric acids, in which the alkyl groups were open chain and contained an average of about 7 carbon atoms, which is designated in the following tables as Compound I, and tributylphosphite. Compound I was employed in the form of a 50 per cent solution in a hydrocarbon oil, but the percentages of this compound used in the tests are based on the weight of the compound itself.

The ratios of the oils employed are volume ratios and the percentages of the added compounds are percentages of the weight of the mixed oil. The term "No. 2" indicates an oil boiling within the range of about 350° to 750° F. and having a minimum API gravity of 26.

The following Table I presents the data obtained in light stability tests.

Table I

Mixed Oil	Light Stability Test: No. of Hours Exposure to Ultra-Violet Light Required to Sludge Oil to—				Amount of Sludge at End of Test
	Trace	Light	Medium	Heavy	
1. 50/50 Blend Eastern Venezuela Straight Run No. 2 Fuel Oil and Fluid Catalytically Cracked No. 2 Disillate, No Additive.	0	12	28	40	Heavy.
2. Blend No. 1 plus 0.05% Compound I.	4	20	40	-------	Medium.
3. Blend No. 1 plus 0.025% Compound I.	4	12	28	-------	Do.
4. Blend No. 1 plus 0.1% Tributylphosphite.	4	8	20	24	Heavy.
5. Blend No. 1 plus 0.05% Tributylphosphite.	4	8	20	28	Do.
6. Blend No. 1 plus 0.025% Compound No. 1 and 0.05% Tributylphosphite.	4	24	------	-------	Light.

It will be seen from Table I that Compound I, the barium salt of the mixed dialkyl dithiophosphoric acids, when added to a mixed fuel oil causes only moderate improvement in the stability of the oil to the light test, and that tributylphosphite lessens the stability of the mixed oil toward light. Using these two compounds together, however, produces a finished oil having markedly improved light stability characteristics.

In the following Table II there are tabulated the results obtained in storage tests on mixed oils alone and stabilized fuel oil compositions of the invention.

Table II

Mixed Oil	Storage Test—Precipitate Formed and Condition of Metal Strip		
	1 Month	3 Months	6 Months
1. 50/50 Blend Eastern Venezuela Straight Run No. 2 Fuel Oil and Fluid Catalytically Cracked No. 2 Distillate, No Additive.	Trace OK	Medium, Sl. Stain	Heavy, Stained.
2. Blend No. 1 plus 0.025% Compound I and 0.05% Tributylphosphite.	do	Light, OK	Light, OK.
3. 80/20 Blend Eastern Venezuela Straight Run No. 2 Fuel Oil and Fluid Catalytically Cracked No. 2 Distillate, No Additive.	Light, OK	Medium, OK	Medium+*, Stained.
4. Blend No. 3 plus 0.025% Compound I and 0.05% Tributylphosphite.	do	Light, OK	Light*, OK.
5. 50/50 Blend West Texas Straight Run No. 2 Fuel Oil and Thermofor Catalytically Cracked No. 2 Distillate, No Additive.	Medium, OK	Medium, OK	Heavy, Rust.
6. Blend No. 5 plus 0.05% Compound I and 0.1% Tributylphosphite.	Trace+, OK	Trace+, OK	Light+, OK.
7. Blend No. 5 plus 0.025% Compound I and 0.05% Tributylphosphite.	Trace, OK	Trace, OK	Light, OK.
8. 80/20 Blend West Texas Straight Run No. 2 Fuel Oil and Thermofor Catalytically Cracked No. 2 Distillate, No Additive.	Medium, Stained	Heavy, Stained	Heavy, Stained.
9. Blend No. 8 plus 0.05% Compound I and 0.1% Tributylphosphite.	Trace, OK	Trace+, OK	Light, Sl. Rust.
10. Blend No. 8 plus 0.025% Compound I and 0.05% Tributylphosphite.	do	Trace+, Sl. Rust	Do.

*Five months only.

From Table II it will be seen that various mixtures of straight run and catalytically cracked distillate fuel oils are materially improved with respect to stability in storage by the addition of mixtures of Compound I and tributylphosphite.

Although the compounds employed in the tests, the results of which are given in the tables, are preferred for use in the fuel oil compositions of the invention, it will be understood that other members of the classes of compounds disclosed above may be used to prepare fuel oil compositions of substantially the same improved properties. Examples of other suitable dialkyl dithiophosphoric acid compounds are the barium, calcium, magnesium and zinc salts of such acids wherein the alkyl groups are hexyl, cyclohexyl, octyl, decyl, dodecyl or mixtures of these groups and isomers such as 2-ethylhexyl, 2,4,4-trimethylpentyl, 2,4,4,6,6-pentamethylheptyl.

In place of tributylphosphite there may be used triamylphosphite, trioctylphosphite, monobutyldioctylphosphite, etc. The tributylphosphite may be the normal butyl, isobutyl, or tertiary butyl compound.

The tests employed in obtaining the data set out above are especially severe tests of the compounded oils and the results are given in terms of the quantity of sludge deposited without regard to the nature of the sludge. In practice, however, the quantity of sludge formed is frequently not as important as the physical characteristics of the sludge. The addition of a very small amount of a combination of a compound of the classes described to a mixed fuel oil affects the characteristics of the sludge, making it lighter and apparently more easily dispersed so that sludge deposition in use is avoided or at least materially lessened. To accomplish variation in the nature of the sludge as well as some control over the actual formation of sludge as little as 0.005 per cent by weight of the mixed oils of each component of the combination, or a total of 0.01 per cent of the combination can be used. Thus, we generally prefer to employ each component in an amount equal to about 0.005 to about 0.05 per cent by weight of the mixed oils. In any case, no more than about 0.25 per cent of the combination should be used since with larger amounts undesirable color changes frequently occur.

If desired, the stable fuel oil compositions may contain in addition to the compounds previously discussed oxidation inhibitors, corrosion inhibitors, antifoam agents, flash point control agents, ignition quality improvers, or combustion improvers and other additives adapted to improve the oils in one or more respects.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit or scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A fuel oil composition comprising a major proportion of a mixture of straight run and catalytically cracked distillate fuel oils tending to deposit sludge and containing a small amount of a combination of a salt of a metal of group II and a dialkyl dithioposphoric acid in which the the alkyl groups contain 4 to 12 carbon atoms, and of a trialkylphosphite in which the alkyl groups contain 4 to 12 carbon atoms, said small amount being sufficient to inhibit sludge deposition from said mixture of oils and comprising at least 0.005% by weight of said mixture of oils of each of said salt of said dialkyl dithiophosphoric acid and of said trialkylphosphite and not more than 0.25% of said combination by weight of said mixture of oils.

2. A fuel oil composition comprising a major proportion of a mixture of straight run and catalytically cracked distillate fuel oils tending to deposit sludge and containing a small amount of a combination of the barium salt of mixed dialkyl dithiophosphoric acids in which the alkyl groups are open chain and contain an average of about 7 carbon atoms, and of a trialkylphosphite in which the alkyl groups contain 4 to 12

carbon atoms, said small amount being sufficient to inhibit sludge deposition from said mixture of oils and comprising at least 0.005% by weight of said mixture of oils of each of said salt of said dialkyl dithiophosphoric acid and of said trialkylphosphite and not more than 0.25% of said combination by weight of said mixture of oils.

3. A fuel oil composition comprising a major proportion of a mixture of straight run and catalytically cracked distillate fuel oils tending to deposit sludge and containing a small amount of a combination of a salt of a metal selected from the group consisting of barium, calcium, magnesium and zinc, and a dialkyl dithiophosphoric acid in which the alkyl groups contain 4 to 12 carbon atoms, and if tributylphosphite, said small amount being sufficient to inhibit sludge deposition from said mixture of oils and comprising at least 0.005% by weight of said mixture of oils of each of said salt of said dialkyl dithiophosphoric acid and of said tributylphosphite and not more than 0.25% of said combination by weight of said mixture of oils.

4. A fuel oil composition comprising a major proportion of a mixture of straight run and catalytically cracked distillate fuel oils tending to deposit sludge and containing a small amount of a combination of the barium salt of mixed dialkyl dithiophosphoric acids in which the alkyl groups are open chain and contain an average of about 7 carbon atoms, and of tributylphosphite, said small amount being sufficient to inhibit sludge deposition from said mixture of oils and comprising at least 0.005% by weight of said mixture of oils of each of said salt of said dialkyl dithiophosphoric acid and of said tributylphosphite and not more than 0.25% of said combination by weight of said mixture of oils.

5. A fuel oil composition comprising a major proportion of a mixture of straight run and catalytically cracked distillate fuel oils tending to deposite sludge and containing a small amount of a combination of a salt of a metal selected from the group consisting of barium, calcium, magnesium and zinc, and a dialkyl dithiophosphoric acid in which the alkyl groups contain 4 to 12 carbon atoms, and of a trialkylphosphite in which the alkyl groups contain 4 to 12 carbon atoms, said small amount being sufficient to inhibit sludge deposition from said mixture of oils, and comprising from about 0.005 to about 0.05 per cent by weight of said mixture of oils of each of said salt of said dialkyl dithiophosphoric acid and of said trialkylphosphite.

6. A fuel oil composition as defined in claim 5 in which said salt of said dialkyl dithiophosphoric acid is the barium salt of mixed dialkyl dithiophosphoric acids in which the alkyl groups are open chain and contain an average of about 7 carbon atoms, and said trialkylphosphite is tributylphosphite.

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