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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 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 natural clay catalysts 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. In addition thermally cracked distillates are sometimes mixed with straight run distillate oils of similar boiling range to produce fuel oils.

The problem of instability, as a practical matter, is troublesome primarily in the case of fuel oils consisting of mixed cracked and straight run oils. In the case of straight run distillates sludging or precipitation is not normally troublesome. However, in certain instances some straight run fuel oils will deposit sludge and may give trouble in service because of either inadequate or improper refining, or due to a natural instability attributable to some constituent not ordinarily present. This is exemplified by distillates containing large amounts of sulfur, either as original components of the crude or present in the form of elemental sulfur and sulfur compounds added incidentally during the doctor treating of such distillates. In such cases, in addition to free sulfur and sulfur compounds, quantities of litharge may also remain in the oil. In addition, naphthenic acids may not be completely removed in the caustic washing process, and these may contribute to instability and the formation of precipitates in the subsequent storage and handling of such straight run fuels. It is believed that the problem encountered with straight run fuels is essentially one of oxidation and the formation of insoluble oxygenated compounds which result from contact with atmospheric and dissolved oxygen in the distillate. This problem is a different one from that encountered in the storage and use of mixed cracked and straight run oils.

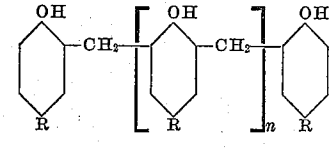
In the case of cracked distillates the chemical nature of the components is considerably different from that of straight run materials, cracked distillates being, as a rule, highly aromatic and containing appreciable amounts of olefins and aromatic-olefin mixed-type compounds. Such compounds by virtue of their unsaturated character are particularly susceptible to polymerization reactions leading to the formation of relatively high molecular weight resinous or polymeric materials which may or may not contain appreciable amounts of oxygen.

The tendency of fuel oils to cause the clogging of screens, conduits, and other parts of burners, therefore, varies with different fuel oils. However, it has been found that the tendency of a mixed cracked and straight run fuel oil to form objectionable sediment is greater than that of either oil alone. This is probably due to the fact that the decomposition products are less soluble in the mixed oil and therefore tend to precipitate out. Since the straight run component, being essentially paraffinic in nature, is a very poor solvent for the highly polymerized aromatic-olefin type compounds which are formed from the cracked component, it probably has the effect of reducing the solvent power of the cracked distillate itself for such polymeric material. As a result, precipitation of those materials will occur. It is believed that the sludge formed in such cases is of a different character from the sludge formed as a result of oxidation of straight run fuel oils.

The present invention relates to fuel oil compositions comprising mixed cracked and straight run distillate fuel oils, which compositions are of improved stability with respect to sludging 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.

It has been discovered that such an improved mixed fuel oil composition can be obtained by incorporating in the mixed fuel oils a small amount of an oil-soluble divalent metal salt of a condensation product of a substituted phenol having an available ortho position and an aldehyde, wherein the metal is selected from group II of the periodic table. The substituent attached to the phenol is selected from the group consisting of alkyl, aryl, cycloalkyl, aralkyl and alkaryl groups.

The phenol formaldehyde condensate which we prefer has the following probable general formula:



wherein R represents a substituent selected from the group described above, and *n* represents an integer from 0 to 8. When the substituent is an alkyl group a straight or branched chain radical of from 4 to 18 carbon atoms is generally employed. However, we prefer alkyl radicals having straight or branched chains of from 6 to 12 carbon atoms. In addition mixtures of phenols containing one or more ortho- and/or para-substituted phenols may be employed, such as mixtures containing a variety of alkyl and cycloalkyl substituted phenols. Thus the alkyl

groups or other substituents on each ring in the molecule may be different. The condensation will occur so long as there is an available ortho position on the phenol ring. Phenolic compounds used as starting materials are meta-, or ortho-, and/or para-substituted alkyl, aryl, cycloalkyl, alkaryl, or aralkyl phenols. Included are such radicals as butyl, amyl, hexyl, octyl, nonyl, decyl, lauryl, stearyl, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, benzyl, phenethyl, phenyl, tolyl, and xylyl.

It is not clear as to what way the divalent metal salts of the class described 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 compound forms additional amounts of sludge so long as it is stored, at least over any feasible test storage period, the incorporation of a compound of this class in the oil inhibits the formation of additional sludge even after some sludge has been formed, although the already formed sludge does not disappear. We have discovered, however, that by adding a small amount of a compound of this class to a mixed fuel oil containing an amount of sludge making the oil undesirable for use in a household burner because of sludge deposits, the oil can be employed in such a burner without leaving the 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.

These compounds can be prepared by any suitable method, and their method of preparation forms no part of the present invention. Usually such compounds are prepared by reacting a substituted phenol, such as octyl phenol, with formaldehyde in the presence of an acid catalyst such as hydrogen chloride. The molecular ratio of the alkyl phenol to the aldehyde may be given as $n:n-1$ where n is a number from 2 to 10. However, in lieu of formaldehyde other aldehydes can be employed, for example, acetaldehyde, propionaldehyde or butyraldehyde. In fact any formaldehyde-yielding compound is suitable such as paraformaldehyde. The condensate so obtained is then converted to the divalent metal salt by any of the well-known methods. For example, the condensate may be reacted directly with the metallic hydroxide, or by a double decomposition reaction. A number of these phenol-formaldehyde condensation products are commercially available. One preferred compound contains about five molecules of the substituted phenol per molecule of the condensate.

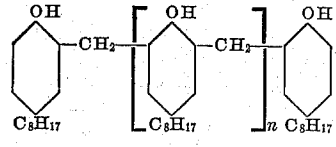
In preparing the fuel oil compositions of this invention metals whose salts are useful are divalent metals selected from group II of the periodic table, for example, magnesium, calcium, zinc and barium. The other metals of group II are also included, such as cadmium or strontium. However, since they are easy to obtain, we prefer to use the calcium and barium salts.

The addition of the compound in very small amounts has been found to produce excellent results. Thus, our composition comprises a major amount of the mixed straight run and cracked distillate fuel oils and a minor amount sufficient to inhibit sludge deposition of a salt of a phenol-formaldehyde condensate. Fully effective results are obtained when using between about 0.01 and about 0.1 per cent of the additive by weight of the mixed fuel oil for addition even to mixed oils having high sulfur content and pronounced sludging tendencies. Moreover, satisfactory results are obtained when using as little as 0.005 per cent. In this instance, in many cases full inhibition of sludge formation is not otbained but the mixed oil is satisfactory for use because the additive 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 0.1 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 may also cause darkening.

The divalent metal salt of a condensation product of the substituted phenol and formaldehyde may be incorporated in the mixed fuel oil in any suitable manner. For example, it may be added to either or both of the cracked or straight run oils prior to mixing the two or it may be added to the mixed oil. When the compound is incorporated in the mixed oil, it is unnecessary to do this immediately after mixing the oil as the compound is effective even after some sludge has formed. It will usually be preferable to add the compound prior to any sludge formation as this will either eliminate sludge formation, or reduce the amount of sludge which will be formed, depending upon the specific characteristics of the oils employed in making up the mixed oil and upon the amount of the compound added. The compound can be added as such but it is preferred to employ it in the form of a concentrated soltuion 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.

It is emphasized that the problem with which the present invention is concerned exists primarily when a cracked oil and a straight run oil are combined in such proportion as to cause a substantial effect such as previously described. The invention is important when the ratio of the volume of the 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 the following tables there are given the results of light stability tests made on the mixed fuel oils of the character indicated, in the absence of an additive, and containing compounds of the class disclosed above. The composition employed in these tests was the calcium salt of a phenolformaldehyde condensation product having substantially the following formula, wherein n is 3 on the average:



This composition is referred to in the following tables as composition A. The percentages of the composition used in the tests are weight percentages of the composition in the oils.

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 approximately 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. A

"No. 2" oil is defined in "ASTM Standards on Petroleum Products and Lubricants" D 396–48 T. The term "No. 2" indicates a ditsillate oil for general purpose domestic heating for use in burners not requiring a No. 1 fuel oil, and having the following properties: Flash point ° F.—100 or legal (min.), pour point ° F.—20 (max.), water and sediment percent by vol.—0.1 (max.), carbon residue per cent by weight—0.35 on 10% residuum, distillation temperature ° F. 90% point—675 (max.), viscosity Saybolt Universal seconds at 100° F.—40 (max.), gravity °API—26 (min.) and maximum sulfur content—1 per cent.

TABLE I

Light stability test

Oil	No. of Hours Exposure to Ultra-Violet Light Required to Sludge Oil to—			Amount of Sludge at End of Test
	Trace	Light	Medium	
50/50 Blend Eastern Venezuela Straight Run and Fluid Catalytically Cracked No. 2 Distillate (Blend No. 1).	4	8	32	Medium.
Blend No. 1 Plus 0.025% Composition A.	4	36	----	Light.
Blend No. 1 Plus 0.05% Composition A.	4	----	----	Trace+.
Blend No. 1 Plus 0.1% Composition A.	4	----	----	Trace+.

TABLE II

Light stability test

Oil	Hours of exposure required to sludge sample to "light"	Amt. of Sludge at end of 40 hrs. exp.
50/50 Blend Eastern Venezuela Straight Run No. 2 Fuel Oil and Fluid Catalytically Cracked No. 2 Distillate (Blend No. 2)	12	medium.
Blend No. 2 Plus 0.025% of Composition A	----	light−.
Blend No. 2 Plus 0.05% Composition A	----	trace+.
Blend No. 2 Plus 0.1% of Composition A	----	trace+.
60/40 Kuwait Straight Run and Catalytically Cracked Distillate (60% Kuwait and 40% Cracked—Blend No. 3)	12	medium+.
Blend No. 3 Plus 0.05% Composition A	52	light−.
50/50 Blend Eastern Venezuela Straight Run and Fluid Catalytically Cracked Distillate (Blend No. 4)	20	medium.
Blend No. 4 Plus 0.0125% Composition A	52	trace+.
Blend No. 4 Plus 0.05% Composition A	72	trace+.

A storage test was also carried out to determine the stability of the fuel oil compositions disclosed herein. This 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 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 straining or corrosion of the steel strip was noted.

In the following tables there are tabulated the results obtained in storage tests on the oils alone and stabilized fuel oil compositions of the invention. The salt employed in the tests was composition A.

TABLE III

Laboratory storage tests on No. 2 fuel oil

Make-up of Fuels, Percent by Vol.:				
Eastern Venezuela Straight Run.	50	50	50	50.
Fluid Catalytically Cracked Distillate.	50	50	50	50.
Concentration of Additive:				
Percent by weight on oil of Composition A.	----	0.025	0.05	0.1.
Storage Time:				
1 month—				
Sludge	none	trace	none	none.
Appearance of Steel	OK	OK	OK	OK.
2 months—				
Sludge	----	----	none	
Appearance of Steel	----	----	OK	
3 months—				
Sludge	medium	light	none	none.
Appearance of Steel	stained	OK	OK	OK.
4 months—				
Sludge	----	light	none	none.
Appearance of Steel	----	OK	OK	OK.
6 months—				
Sludge	heavy	light+	very slight trace.	none.
Appearance of Steel	stained	stained	OK	OK.
11 months—				
Sludge	----	----	trace	none.
Appearance of Steel	----	----	OK	OK.

TABLE IV

Laboratory storage tests on No. 2 fuel oil

Make-up of Fuels, Percent by Vol.:			
Eastern Venezuela Straight Run	50	50	50.
Fluid Catalytically Cracked Distillate.	50	50	50.
Concentration of Additive:			
Percent by weight on oil of Composition A.	----	0.0125	0.05.
Storage Time:			
1 month—			
Sludge	trace	none	none.
Appearance of Steel	OK	OK	OK.
2 months—			
Sludge	light+	slight trace.	slight trace.
Appearance of Steel	slight stain	OK	OK.
3 months—			
Sludge	----	trace	slight trace
Appearance of Steel	----	OK	OK.
4 months—			
Sludge	medium+	----	
Appearance of Steel	stained	----	

From the results given in the foregoing tables it will be seen that the mixed oils possess poor stability properties. These results also show that mixtures of straight run and catalytically cracked oils are materially improved with respect to stability to sludge formation by the addition of the metal salts of the phenol-formaldehyde condensation product disclosed. The blends employed in Tables III and IV were made up from different batches of straight run and catalytically cracked oils. The stability of the mixed oil to sludge formation is improved with the addition of as little as 0.0125 per cent of the composition; however, major improvement is obtained by the addition of 0.025 per cent. Substantially the same, and in some cases somewhat improved results are obtained when adding about 0.05 per cent. Also stability to sludge formation is obtained when larger amounts are employed but no advantage is gained with the use of larger amounts and necessarily the ash and carbon residue test values of the finished oil are increased, which is undesirable. Therefore, when positive control of sludge formation is desired, it is preferred to employ at least 0.0125 per cent of the metal salt of a phenol condensate and it is not necessary to employ more than 0.05 per cent. In any case the total amount of the salt need not exceed 0.1 per cent of the mixed oils.

The tests employed in obtaining the data set out in the tables 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 the compounds of the class described to a mixed fuel oil affects the characteristics of the sludge, making it lighter and apparently more easily dispersed so that sludge deposition 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 the substituted phenol-formaldehyde divalent metal salt can be used. Consequently, as previously pointed out we generally prefer to employ the salt in an amount equal to about 0.005 to about 0.05 per cent by weight of the mixed oils.

Although the phenol condensate salt employed in the tests, the results of which are given in the tables, is preferred for use in the fuel oil compositions of the invention, it will be understood that other members of the class of compounds disclosed above may be used to prepare fuel oil compositions of substantially the same improved properties. Examples of other suitable salts of resinous phenol-formaldehyde condensation products are the zinc, magnesium and barium salts of the products formed when other phenols such as butyl, amyl, cyclohexyl or lauryl phenol are reacted with formaldehyde or other aldehydes.

If desired, the stable fuel oil compositions may contain, in addition to the compounds previously discussed, oxidation inhibitors, flash point control agents, corrosion inhibitors, anti-foam agents, ignition quality improvers,

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 amount of a mixture of straight run and cracked distillate fuel oils tending to deposit sludge and a minor amount of from 0.01 to 0.1 per cent by weight of the mixed fuel oil of the calcium salt of the condensation product of formaldehyde and an octyl phenol, said condensation product containing about five mols of octyl phenol per molecule of condensate.

2. A fuel oil composition comprising a major amount of a mixture of straight run and cracked fuel oil distillates tending to deposit sludge, and a minor amount, sufficient to inhibit sludge deposition from said mixture of fuel oil distillates, of the calcium salt of the condensation product of formaldehyde and an octyl phenol, said condensation product containing about 5 molecules of octyl phenol per molecule of condensate.

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