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FUEL OIL COMPOSITION

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This invention relates to compositions comprising a mixture of combustible hydrocarbon oils with addition agents. It is more particularly concerned with No. 2 fuel oils containing additives adapted to inhibit the appearance of sediment during prolonged storage periods.

As is well known to those skilled in the art, most fuel oils, although free from sediment initially, have a tendency to form sludge or sediment during prolonged storage periods. Thus, when such fuel oils are stored in tanks or drums, awaiting distribution or use, insoluble matter, generically referred to as "sediment," is formed. This sediment is extremely detrimental to the efficient operation of burners and engines utilizing these fuel oils. Such well-known difficulties as screen-clogging and nozzle-clogging are encountered. Although the exact cause of such sedimentation in fuel oils is not clearly established, it has been postulated that it is due to oxidation of the fuel oil.

Therefore, in order to produce satisfactory fuel oils, it is necessary to solve two problems. The first problem, of course, is to prevent the formation of the sediment. The second one is to prevent the agglomeration of the insoluble matter which is formed into relatively large masses and to maintain it so that it will pass through the burner system without clogging. Proposed solutions for these problems have involved the use of two or more additives; one to prevent sedimentation and the other to prevent screen and nozzle clogging. Amino compounds, phenols, and the like have been proposed as additives of the former type. Examples of the additives for the latter purpose are metal salts of fatty acids, metal sulfonates, and partial esters of polyhydric alcohols.

It has now been found that certain specific metal salts will inhibit sedimentation in fuel oils and also maintain in suspension any sediment or sludge which is formed. It has now been discovered that the lower alkaline-earth metal salts of the acids derived from the sulfate paper pulp process, when added to fuel oils in minor amounts, effectively inhibit the formation of sediment therein.

Accordingly, it is a broad object of the present invention to provide improved fuel oils. Another object is to provide distillate fuel oils which have a reduced tendency to form sediment or sludge during prolonged storage periods. A further object is to provide a method for inhibiting sedimentation in distillate fuel oils and for preventing screen and nozzle clogging. A specific object is to provide a distillate fuel oil containing minor

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amounts of specific metal salts of the acids derived from the sulfate paper pulp process, namely the lower molecular weight alkaline-earth metal salts.

The present invention provides a distillate fuel oil containing a minor amount, sufficient to inhibit sludging and sedimentation during storage, of a neutral metal salt of tall oil, wherein the metal component is an alkaline-earth metal having a molecular weight of less than 87.

The fuel oils which are improved in accordance with the present invention are hydrocarbon fractions having an initial boiling point of at least about 300° F. and an end point not higher than about 750° F., and boiling substantially continuously throughout their distillation range. Such fuel oils are generally known as distillate fuel oils. It must be strictly understood, however, that this term is not restricted to straight-run distillate fractions. As is well known to those skilled in the art, the distillate fuel oils can be straight-run distillate fuel oils, catalytically or thermally cracked distillate fuel oils, or mixtures of straight run distillates, 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, 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 hydrocarbon fractions, however, is the distillation range. As mentioned hereinbefore, this range will lie between about 300° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower range falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially continuously throughout its distillation range.

Especially preferred among the fuel oils contemplated herein are Nos. 1, 2, and 3 fuel oils used in domestic heating and as diesel fuel oils. The domestic heating oils generally conform to the specifications set forth in ASTM specifications D396–48T. Specifications for diesel fuels are defined in ASTM specifications D975–48T. Such fuel oils have a tendency to form sediment or sludge during storage.

The salts utilizable in accordance with the present invention are the neutral metal salts of tall oil, wherein the metal component thereof is an alkaline-earth metal (Group IIA of the periodic chart) having a molecular weight less than 87, i. e., beryllium, magnesium, and cal-

cium. The calcium and/or magnesium salts are especially preferred. These acids are commonly known as "tall oil acids," or even merely as "tall oil." Accordingly, throughout the present specification and in the claims, the term, "tall oil," is used to denote these acids. The salts are identified as "tallates," e. g., magnesium tallate or calcium tallate.

Tall oils are mixtures of fatty acids, rosin acids, and unsaponifiable matter derived from the sulfate process for pulping wood. During the process of pulping wood by the sulfate method (as distinguished from the sulfite method), the pulping liquor soon becomes contaminated with a soap. This soap can be removed by acidifying the liquors and skimming the water-insoluble organic material from the surface of the liquor. The skimmings are known to the art as crude tall oil, sometimes spelled "talloel" or "talloil." The crude tall oil can be refined to various degrees, as by solvent-refining or by distillation. Crude tall oil and refined, or semi-refined, tall oil are available commercially from a number of sources. Tall oil is derived chiefly from domestic sources and from European sources, particularly from the Scandinavian countries. However, for the purposes of this invention, the preferred tall oils are the domestic tall oils, particularly those derived from the pulping of Southern Pine.

As is well known to those skilled in the art, from the standpoint of chemical constitution, tall oil contains a mixture of saturated and unsaturated fatty acids, rosin acids, and unsaponifiable matter. The fatty acids include stearic acid, oleic acid, linoleic acid, linolenic acid, and the like. Although other fatty acids are undoubtedly present, the fatty acid content is usually calculated in terms of oleic acid which is the predominant fatty acid component. The rosin acids are those acids which have the empirical formula, $C_{20}H_{30}O_2$. As is well known, they occur in many isomeric forms. However, abietic acid is the rosin acid most commonly found in tall oils. The relative acid content of tall oils will vary over a relatively wide range. This is due, in part, to the particular source of the tall oil, i. e., the kind of wood from which it is derived. In addition, by suitable blending and/or refining operations, the manufacturers of tall oil can supply it in a wide range of acidic proportions. Regardless of the relative amounts of acids contained therein, any commercial tall oil is utilizable for the purposes of this invention. Typical chemical and physical properties of tall oils are set forth in Table I. It must be strictly understood, however, that such properties in and of themselves do not completely define tall oil. As is demonstrated hereinafter, salts of mixtures of fatty acids and rosin acids, which mixtures met the specifications of Table I, were entirely unsatisfactory for the purposes of the present invention. Accordingly, it is inaccurate to define tall oil by any means other than as a mixture of fatty acids, rosin acids, and unsaponifiable matter derived from the sulfate process of wood pulping. As those skilled in the art will readily appreciate, such a definition is embraced within the simple term, "tall oil."

TABLE I

Specific gravity @ 25° C.	0.9–1.1
Viscosity, S. S. U. @ 210° F.	40–220
Color, Lovibond:	
Yellow	25–60
Red	1–35
Moisture, per cent	0.1–3.0
Ash, per cent	0.03–1.0
Acid number	100–200
Saponification number	100–200
Fatty acids, per cent	30–70
Rosin acids, per cent	30–70
Unsaponifiables, per cent	1–12
Iodine value, Wijs	140–210

TABLE 1 Continued

The alkaline-earth metal tallates can be made by any of the well-known methods for salt formation. Accordingly, the salt can be made by a double decomposition reaction between an alkali-metal tallate, e. g., sodium tallate, and a water-soluble salt of beryllium; calcium or magnesium, such as calcium hydroxide, calcium chloride, calcium nitrate, magnesium chloride, magnesium sulfate, beryllium chloride, beryllium nitrate, and the like. A similar double decomposition reaction can be achieved by starting with an amine or an ammonium salt of tall oil. Since crude tall oil is obtainable in the form of the sodium salt, i. e., unacidified, this crude salt can be used as the starting material to form the desired alkaline-earth metal salt. As has been mentioned hereinbefore, a mixture of calcium and magnesium tallates can be used. This mixed salt can be prepared by reacting a mixture of water-soluble calcium and magnesium salts, e. g., calcium chloride and magnesium chloride, with the alkali-metal tallate. On the other hand, the mixture can be achieved by merely adding equivalent amounts of calcium tallate and magnesium tallate to the fuel oil, thus achieving the mixture, in situ. It is to be strictly understood, however, that other means of salt formation can be used, such as, for example, heating tall oil with a basic oxide like calcium oxide, with the elimination of water. This invention is not restricted to any particular method whereby the salt is formed.

In order to inhibit effectively the formation of sediment or sludge in fuel oils, the alkaline-earth metal tallate is added thereto in concentrations varying between about 25 pounds per thousand barrels of oil and about 200 pounds per thousand barrels of oil. Preferably, the concentration varies between about 50 and about 200 pounds per thousand barrels. In terms of weight per cent, based on the weight of the fuel oil, the concentrations vary, preferably, between about 0.01 per cent and about 0.1 per cent. These concentrations are also effective to maintain in suspension any sludge or sediment which may be formed; thereby preventing screen and nozzle clogging.

The fuel oils of this invention can contain other additives for the purpose of achieving other results. Thus, for example, there can be present foam inhibitors, dyes or other coloring matter, color inhibitors, anti-rust agents, and ignition and burning quality improvers. Examples of such additives are silicones, azo dyes, dinitropropane, amyl nitrate, metal sulfonates, and the like.

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

The four different commercial tall oils used to

prepare the salts of the specific working examples are identified herein as tall oil W, tall oil X, tall oil Y, and tall oil Z. The pertinent characteristics of these tall oils are set forth in Table II.

TABLE II

	Tall oil W	Tall oil X	Tall oil Y	Tall oil Z
Specific gravity	0.98	0.99	0.95–0.97	0.976
Viscosity, S. S. U. at 210° F.	116	165–205	50–70	119
Color, Lovibond:				
Yellow	25–30	50	55	70
Red	10–15	25	30	20
Acid number	172	156–164	180–185	166
Saponification value	174	160–170	181–186	174
Rosin acids, percent	42.2	43–47	33–36	45.4
Fatty acids, percent	49.5	46–50	57–62	47.8
Sterols, etc., percent	6–7	6–7	5–7	6.6
Iodine number, Wijs	159	150–165	175–185	143

All of these tall oils were derived from domestic, wood pulping by the sulfate process. Tall oil W is a crude tall oil. Tall oil X is a refined tall oil. Tall oil Y is another refined tall oil which has been refined by a double distillation process. Tall oil Z is still another refined tall oil which has been refined by solvent extraction.

In all cases, the salts were prepared by reacting the tall oil acids with an aqueous solution of sodium hydroxide to form the sodium salt thereof. This salt was then reacted, by a double decomposition method, with an aqueous solution of a sulfate or halide of the desired metal, e. g., with calcium chloride or magnesium sulfate.

The tests used to determine the sedimentation characteristics of the fuel oils are the 212° F. storage test and the 110° F. storage test. In the 212° F. storage test, a 500-milliliter sample of the fuel oil under test is placed in a convected oven maintained at 212° F., for a period of 24 hours. Then, the sample is removed from the oven and cooled for one hour. The cooled sample is filtered through a tared asbestos filter (Gooch crucible) to remove the insoluble matter. The weight of such matter, in milligrams, is reported as the amount of sediment. The 110° F. storage test is conducted in a similar manner, with the exceptions that a temperature of 110° F. was used and that the test was run for 6-week and for 12-week periods.

Three different fuel oils have been used for the purpose of demonstrating the present invention. Fuel oil A is a blend of 70 per cent distillate stock derived from continuous catalytic cracking and 30 per cent air-caustic sweetened straight run distillate stock. Fuel oil B is a blend of 57 per cent distillate stock derived from continuous catalytic cracking, 28 per cent distillate stock derived from fixed-bed catalytic cracking, and 15 per cent straight run distillate stock. Fuel oil C is a blend of 60 per cent distillate stock derived from continuous catalytic cracking, 30 per cent distillate stock derived from fixed-bed catalytic cracking, and 10 per cent straight run distillate stock. All of these fuels are domestic No. 2 fuel oils having the properties set forth in Table III.

TABLE III

	Fuel oil A	Fuel oil B	Fuel oil C
Gravity, A. P. I.	30.1	33.4	33.4
A. S. T. M. dist., ° F.:			
I. B. P.	355	334	315
E. B. P.	645	650	610
Sulfur, percent	0.87	0.73	0.41
Carbon residue, percent	0.15	0.10	0.16
Pour point, ° F.	+5	+5	0
Viscosity, centistokes at 100° F.	2.4	2.3	2.3

MAGNESIUM SALTS

Example 1

The magnesium salt of tall oil W was blended at various concentrations in portions of fuel oil A. The resultant blends were tested in the 212° F. and the 110° F. storage tests. Also, blends in fuel oil B were tested in the 212° F. and the 110° F. storage tests. Pertinent data for these tests are set forth in Table IV.

Example 2

Blends of various amounts of the magnesium salt of tall oil Y in fuel oils A and B were subjected to the 110° F. storage test. Test data are set forth in Table IV.

Example 3

Blends of fuel oil A containing 60 and 150 pounds, respectively, per thousand barrels of the magnesium salt of tall oil X were tested in the 212° F. and the 110° F. storage tests. Fuel oil B, containing the same salt at a concentration of 60 pounds per thousand barrels, was tested in the 110° F. storage test. Pertinent test data are set forth in Table IV.

Example 4

Blends of the magnesium salt of tall oil Z at different concentrations in fuel oils A, B, and C were tested in the 110° F. storage test. The results therefor are set forth in Table IV.

TABLE IV

Salt	Conc., lbs./1000 bbls.	Weight of sediment, in milligrams							
		Fuel oil A			Fuel oil B			Fuel oil C	
		212° F.	110°F.		212° F.	110°F.		110°F.	
			6 wks.	12 wks.		6 wks.	12 wks.	6 wks.	12 wks.
Blank		35	110	181	72	45	91	37	109
1. Mg salt of tall oil W	50		28	44					
	60	7	36	93	4	29	31		
	100		23	48					
	150	3							
	200		16	29					
2. Mg salt of tall oil Y	25					31	65		
	50					11	19		
	100		28	42		6	14		
	150		24	44					
3. Mg salt of tall oil X	60	7	43	130		24	45		
	150	5	28	47					
4. Mg salt of tall oil Z	50		44	114		15	47	10	21
	100		35	66		3	18	6	13
	200		28	39					

Example 5

For purposes of comparison, blends of magnesium abietate and of magnesium oleate in fuel oils A and B were tested in the 212° F. and the 110° F. storage tests. The abietate approximates the salt of the rosin acid component of tall oil, and the oleate approximates the salt of the fatty acid component thereof. Additionally, blends containing a 50–50 weight per cent mixture of magnesium abietate and magnesium oleate were similarly tested. These latter blends approximate the accepted composition of the tall oil soap. Pertinent test data therefor are set forth in Table V.

TABLE V

Salt	Conc., lbs./1000 bbls.	Weight of sediment, in milligrams					
		Fuel oil A			Fuel oil B		
		212° F.	110° F.		212° F.	110° F.	
			6 wks.	12 wks.		6 wks.	12 wks.
Blank fuel oil		35	110	174	72	56	147
Mg abietate	60	26	78	160	33	80	105
	150	31	98	173			
Mg oleate	60	32	88	173	80	114	137
	150	34	114	210			
50–50 Mg oleate + Mg abietate	60	30	76	176	59	87	112
	150	27	98	169			

It will be apparent from the foregoing that the magnesium salts of rosin acid and of fatty acids are ineffective for the purposes of the present invention. It will also be noted that a "synthetic" tallate produced by blending the magnesium salts of the component rosin and fatty acids is likewise ineffective. The magnesium tallates, on the other hand, effectively inhibit the formation of sediment.

CALCIUM SALTS

Example 6

Blends of fuel oils A and B containing various amounts of the calcium salt of tall oil Y were tested in the 212° F. and the 110° F. storage tests. Pertinent test data therefor are set forth in Table VI.

TABLE VI

Salt	Conc., lbs./1000 bbls.	Weight of sediment, in milligrams					
		Fuel oil A			Fuel oil B		
		212° F.	110° F.		212° F.	110° F.	
			6 wks.	12 wks.		6 wks.	12 wks.
Blank fuel oil		35	110	174	72	45	91
Ca salt of tall oil Y	25	19	54			52	53
	50	8	32			27	52
	60	7	25	83	3	15	21
	100	1	20			8	6
	150	1	13	21			

Example 7

A mixed salt comprising about 50 per cent by weight of the calcium salt of tall oil Y and about 50 per cent by weight of the magnesium salt of tall oil Y was blended in fuel oil A, at concentrations of 60 and 150 pounds per thousand barrels. These blends were subjected to the 212° F. and the 110° F. storage tests. A blend of the same mixed salt in fuel oil B, at a concentration of 60 pounds per thousand barrels was subjected to the same storage tests. The test results therefor are set forth in Table VII.

TABLE VII

Salt	Conc., lbs./1000 bbls.	Weight of sediment, in milligrams					
		Fuel oil A			Fuel oil B		
		212° F.	110° F.		212° F.	110° F.	
			6 wks.	12 wks.		6 wks.	12 wks.
Blank fuel oil		35	110	174	72	56	147
Mixed Ca+Mg salt of tall oil Y	60	10	30	113	3	12	18
	150	1	16	26			

Example 8

For purposes of comparison, blends of calcium abietate and of calcium oleate in fuel oils A and B were tested in the 212° F. and the 110° F. storage tests. The abietate approximates the salt of the rosin acid component of tall oil, and the oleate approximates the salt of the fatty acid component thereof. In addition, blends containing a 50–50 weight per cent mixture of calcium abietate and magnesium oleate were similarly tested. These latter blends approximate the accepted composition of the tall oil soap. Pertinent test data therefor are set forth in Table VIII.

TABLE VIII

Salt	Conc., lbs./1000 bbls.	Weight of sediment, in milligrams					
		Fuel oil A			Fuel oil B		
		212° F.	110° F.		212° F.	110° F.	
			6 wks.	12 wks.		6 wks.	12 wks.
Blank fuel oil		35	110	173	72	56	147
Ca abietate	60				43	66	97
	150	40	154	220			
Ca oleate	60				267	98	113
	150	22	132	203			
50–50 Ca oleate +Mg abietate	60				57	78	91
	150	35	144	235			

It will be apparent from the foregoing data that the calcium salts of rosin acid and of fatty acids are ineffective for the purposes of the present invention. It will also be noted that a "synthetic" tallate produced by blending the calcium salts of the component rosin and fatty acids is likewise ineffective. The calcium tallates and the mixed calcium and magnesium tallates, on the other hand, effectively inhibit the formation of sediment.

TALLATES COMPARED

Example 9

The calcium, magnesium, barium and strontium salts, respectively, of tall oil Y were blended in fuel oil B at various concentrations. The resultant blends were tested in the 110° F. storage test. The pertinent results therefor are set forth in Table IX.

TABLE IX

Salt	Conc., lbs./1000 bbls.	Weight of sediment, milligrams	
		Fuel oil B	
		110° F.	
		6 weeks	12 weeks
Blank fuel oil		45	91
Ca salt of tall oil Y	25	52	53
	50	27	52
	100	8	6
Mg salt of tall oil Y	25	31	65
	50	11	19
	100	6	14
Blank fuel oil		56	>67
Ba salt of tall oil Y	10	48	>33
	25	82	
	50	118	
Blank fuel oil		42	89
Sr. salt of tall oil Y	25	65	69
	50	65	67
	100	61	93

It will be apparent from the foregoing data that, even within the relatively small group of the alkaline-earth metals, only those members lighter than strontium are useful as salt forming metals in the present invention. The barium and the strontium salts of tall oil, i. e., the heavier salts, are wholly ineffective. In fact, these salts tend to increase the amount of sludge and sediment formation, rather than to inhibit it, as the lighter metal salts do.

SLUDGE DISPERSION

Example 10

Two test procedures were used to determine the screen clogging tendencies of fuel oils. In Test I, the fuel oil was circulated through a simulated domestic oil burner fuel delivery system comprising a 100-mesh external strainer, a fuel pump containing a 100-mesh basket-type screen, a one gallon per hour nozzle with a 100-mesh screen, and a fuel oil reservoir. The test oil was continuously cycled from the reservoir, through the system, and back to the reservoir. A sludge consisting, by weight, of 55 per cent water, 36 per cent fuel oil, 8 per cent organic matter, and one per cent rust and dirt was added to the reservoir in daily portions of 50 cubic centimeters each, for the first five days of a ten-day test run. At the end of the test period, the weight of sludge deposited on the pump screen was determined.

Test II is identical to Test I, except that the test period was only of two days' duration and the sludge was added, during the first day, in five 10-cubic centimeter portions directly in the fuel line a few inches before the pump suction. This test very closely simulates actual field conditions.

Blends of fuel oil A containing 50 pounds per thousand barrels of the calcium and of the magnesium salts, respectively, of tall oil Z were subjected to these two tests. The comparative results are set forth in Table X.

TABLE X

Test	Blank, g.	Mg salt of tall oil Z, g.	Ca salt of tall oil Z, g.
I	1.70	0.824	0.565
II	1.28	0.683	0.589

The foregoing specific working examples have demonstrated the specific effectiveness of tallate salts of the alkaline-earth metals heavier than strontium, for the inhibition of sedimentation and for the dispersion of sludge in distillate fuel oils. It will be apparent therefrom that the other alkaline-earth metal tallates and other calcium and magnesium salts are ineffective.

Although the present invention has been described in conjunction 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. 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 sludging and sedimentation during storage, of a neutral metal salt of tall oil obtained from the sulfate process of wood pulping, wherein the metal component is an alkaline-earth metal having a molecular weight less than 87.

2. A distillate fuel oil containing between about 25 pounds per thousand barrels and about 200 pounds per thousand barrels of a neutral magnesium salt of a tall oil obtained from the sulfate process of wood pulping.

3. A distillate fuel oil containing between about 25 pounds per thousand barrels and about 200 pounds per thousand barrels of a neutral calcium salt of a tall oil obtained from the sulfate process of wood pulping.

4. A distillate fuel oil containing between about 25 pounds per thousand barrels and about 200 pounds per thousand barrels of a neutral, mixed calcium and magnesium salt of a tail oil obtained from the sulfate process of wood pulping.

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