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AMMONIUM CARBOXYLATE POUR POINT DEPRESSANTS FOR FUEL OIL COMPOSITION

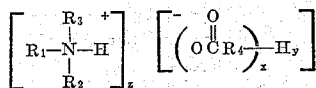
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This invention relates to distillate fuel oil compositions and pour point depressors for use in such distillate fuel oil compositions.

In storage and use of heavy oils, such as lubricating oils, problems associated with pour point have long been in existence and have been recognized in the art. The pour point of an oil is defined as the lowest temperature at which the oil will pour or flow when chilled without disturbance under specified conditions. Recently, it has been discovered that pour point problems also exist in the storage and use of distillate fuel oils, particularly at low temperatures. Pour point problems arise through the formation of solid or semi-solid waxy particles within an oil composition. For example, in the storage of furnace oils or diesel oils during the winter months, temperatures may decrease to a point well below 0° F., e.g. as low as -15 to -25° F. The decreased temperatures often cause crystallization and solidification of wax in the distillate fuel oil. This problem has been in part remedied by lowering the end point of oils used for blending furnace and diesel oils. It has also been suggested that the distillate fuel oils may be dewaxed such as by urea dewaxing. However, readjustment of end points causes loss of valuable product as blending material to distillate fuel oil stocks. Further, dewaxing operations are expensive.

Another approach in solving the problem has been to attempt to find a pour point depressor which will decrease the pour point of a distillate fuel oil. However, it has been found that the pour point depressors normally used for lubricating oils and other heavy oils are generally ineffective in lowering the pour point of a distillate fuel oil.

This invention provides new pour point depressors which are useful in fuel oil compositions. The fuel oil compositions of this invention comprises a distillate fuel oil and a small amount of the pour point depressor. The pour point depressor of this invention is a salt of a secondary or tertiary monoamine and has the structural formula:



wherein R₁ and R₂ are alkyl groups containing from about 10 to about 22 carbon atoms, and R₃ is hydrogen or an alkyl group containing from one to about 22 carbon atoms, x and z are each integers of from 1-4 and y is an integer of from 0 to 1. In the preferred compositions, R₃ is hydrogen or an alkyl group having from 10 to 22 carbon atoms and z is not greater than x. The R groups, i.e. R₁, R₂, R₃ and R₄, may be saturated or unsaturated, i.e., may have from 0 to 4 or more double bonds but preferably contain no more than two double bonds. R₄ is derived from a saturated or unsaturated

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nonaromatic carboxylic acid. R₄ is hydrogen or a hydrocarbon group containing from one to about 22 carbon atoms. The above formula includes the salts of the secondary or tertiary monoamine and carboxylic acids which include the monocarboxylic acids, polycarboxylic acids, e.g., the dibasic and tribasic acids as well as polymers of unsaturated carboxylic acids.

The above-defined salts are useable in distillate fuel oils in minor amounts sufficient to lower the pour point of the distillate fuel oil. I have also discovered that the salts are useable as a synergist for hydrocarbon polymer pour point depressants in distillate fuel oil compositions; and, conversely, the hydrocarbon polymer pour point depressant may be considered a synergist for the above-defined salts. Thus, in one embodiment of this invention, a synergistic mixture of the salt and hydrocarbon polymer is provided. In such synergistic mixture, the amount of each ingredient depends on the amount of synergism desired or needed. The two components may be included, for example, in a distillate fuel oil in ratios of from 1:10 to 10:1 or more or less of either based on the other. As a general example, 200 parts or more of one ingredient may be employed based on the other if desired. Preferably, the salt and hydrocarbon polymer are included in ratios of from 1:10 to 10:1 parts by weight and especially preferred synergistic mixture contains the salt and polymer in about equal proportions.

The amine salts and the synergistic mixture may each be used in the distillate fuel oil in amounts sufficient to lower the pour point of the distillate fuel oil, e.g., from about 0.001 to about 5 weight percent or more or less as desired and preferably from about 0.005 to about 0.5 weight percent. The amine salts and synergistic mixture may each also be prepared in concentrate form in a suitable solvent such as a hydrocarbon or alcohol solvent, e.g. benzene, toluene, xylene, isopropanol, methanol and the like. Suitable concentrates may contain from 10 to 65 weight percent or more of the salt or synergistic mixture and the remaining 35 to 90 weight percent consisting essentially of hydrocarbon solvent. Where the salt and/or hydrocarbon polymer has a low solubility in the distillate fuel oil, solvents such as aromatic hydrocarbons and alcohols may be used in the distillate fuel oil in sufficient amounts to solubilize the addition agent.

The amine salts can be prepared by reacting the corresponding secondary or tertiary amine with the corresponding carboxylic acid under normal reaction conditions for salt formation between amines and carboxylic acids. Such reaction conditions, e.g., time, temperature and the like are well known in the art. For example, salt formation may be effected by mixing the reactants at room temperature. The reaction rate may be increased if desired by slight warming.

The amine salts are the salts of the secondary and tertiary alkyl amines with a carboxylic acid or polymer of the carboxylic acid. The amine portion of the salt contains at least 2 alkyl groups having from 10 to 22 carbon atoms, the remaining nitrogen substituent being hydrogen or an alkyl group of from 1 to 22 carbon atoms. The carboxylic acid contains from 1 to 22 carbon atoms and the polymers of a carboxylic acid may, of course, contain more than 22 carbon atoms. Where acids are herein referred to as polymers or carboxylic acids having from 1 to 22 carbon atoms, it is intended that the carbox-

ylic acid itself contains from 1 to 22 carbon atoms in its monomeric form. More specific examples of amine salts are the saturated or unsaturated secondary or tertiary alkyl amine salts of saturated or unsaturated C_1 - C_{22} acids or polymers thereof, such as dihydrogenated tallow amine formate, trihalogenated tallow amine octanoate, didecyl amine acetate, tridecyl amine oxalate, di(tridecyl amine) oxalate, methyl didodecyl amine oleate, tridocosyl polyamine linoleate, trilauryl amine hexeneoate, trimyristyl amine methacrylate, dicoco amine butyrate, dimyristyl amine palmitate, tristearyl amine pentanoate, hexyl didecyl amine oleate, methyl dihydrogenated tallow amine acrylate, dioleoyl amine crotonate, dioleoyl amine stearate, methyl diicosyl amine dilinoleate, methyl dihydrogenated tallow amine linolenate, trisoybean amine laurate, dilinolenyl amine myristate, di(octyl didecyl amine) sebacate, mono(trilauryl amine) adipate, di(methyl dihydrogenated tallow amine) adipate, di(dicoco amine) maleate, mono(methyl dimyristyl amine) fumarate, di(dihydrogenated tallow amine) malonate, tri(methyldioleoyl amine) trilinoleate, dilauryl amine hexadecate-raenoate, di(tristearyl amine) trilinoleate, tri(tripalmityl amine) stearate, di(methyl dicoco amine) glutarate, mono(trisoybean amine) glutarate, trihydrogenated tallow amine dodecadienoate, trilauryl amine cycloheptanecarboxylate, dioleoyl amine cyclo-octane-carboxylate, methyl diicosyl amine cyclobutane carboxylate, methyl didecyl amine cyclo octatetraene-carboxylate, dilauryl amine tetrahydrobenzoate, octyl dimyristyl cyclo pentenecarboxylate, didecyl amine cyclopropane-carboxylate, trihalogenated tallow amine abietate and other salts especially including the secondary or tertiary alkyl amine salts of linoleic acid and polylinoleic acids, e.g., those including mixtures of monomer, dimer, trimer and higher polymers of linoleic acid such as are available commercially as a by-product from the production of sebacic acid. A particular example of an excellent mixture of polylinoleic acid is Emery Empol 1022 which contains mostly dilinoleic acid but also contains the monomer trimer and higher polymers.

The amine salts, stated above, are prepared by the reaction of the corresponding amine and carboxylic acid. In forming the salts, commercial amines are very useful and are recommended because of their availability and often relatively low cost. Such commercial amines include the secondary and tertiary amines such as are known as dihydrogenated tallow amine, methyl dihydrogenated tallow amine, trihydrogenated tallow amine, and trilauryl amine. In the nomenclature used herein with reference to amines and carboxylic acid salts of amines, terms such as "coco," "soybean," "tallow" and the like indicate the source of acid from which the group indicated thereby has been derived. Each such group is usually a mixture of carbon chains differing slightly in length and/or configuration. However, these groups are well known to those skilled in the fuel oil art.

In the embodiment of this invention wherein a synergistic combination is provided, the synergistic combination is a mixture of the amine salt defined above with a low molecular weight low density hydrocarbon polymer of ethylene. The polymer may be either a homopolymer of ethylene or a copolymer of ethylene with another hydrocarbon monomer, e.g., butylene, isobutylene, propylene, amylene, hexylenes, etc. and mixtures thereof hereinafter the term "polymer" will be used in referring to either or both of the homopolymer and the copolymer.

The polymers are oil-soluble polymers and may have a molecular weight in the range of from about 100 to about 10,000. However, the molecular weights of the polymers are often extremely difficult to determine due to their low molecular weight in the presence of residual solvents, and the presence of low molecular weight polymer of widely varying chain lengths. Thus, the range of molecular weights and reported molecular weights used herein are merely to be taken as estimated guides

for those skilled in the art. As a better definition of the polymers, the polymers are those hydrocarbon polymers that have an intrinsic viscosity of about 0.05 to about 0.25 and preferably from about 0.08 to about 0.15 dl./g. as determined by the ASTM Test D-1601-59-T in decalin solvent at 135° C.

The polyethylene homo-polymer may be any substantially linear oil-soluble polyethylene polymer or fraction thereof. Although the homopolymer is substantially linear, it has some branching such as to decrease its crystallinity and permit oil solubility. The polyethylene is preferably a product or by-product from the peroxide catalyzed polymerization of ethylene. Polymerization reactions using peroxide catalysts are well known in the art and any of these may, for example, be used to produce the desired pour point depressor of this invention. The low molecular weight polyethylene by-products are usually oily liquid hydrocarbon mixtures, hydrocarbon greases or hydrocarbon waxes obtained in small quantities in the mass polymerization of ethylene at elevated temperatures and pressure using a free radical polymerization catalyst, and such by-products from polymerization catalyzed by the presence of peroxides (or oxygen which forms peroxides) are particularly suitable. The product may advantageously be a low density product, for example the homopolymer by-product described by J. W. Ragsdale, U.S. 2,863,850, patented December 9, 1958. Other such products are well known in the art.

The copolymer is a copolymer of ethylene with an olefin monomer. The olefinic monomer preferably contains from 3-6 carbon atoms, but higher molecular weight monomers, e.g., having up to 10 or more carbon atoms, may also be used. It is intended that any monomer which is copolymerizable with ethylene may be used. The copolymer may be "linear," i.e., it may be referred to as a linear copolymer but may still contain alkyl groups along the chain at each position where the olefinic monomer is polymerized into the chain. The more highly branched polymers may also be used although the linear polymers are preferred. The polymers, i.e., homopolymers and copolymers, referred to herein as "linear" may be actually only substantially linear but are non-crosslinked.

The copolymer may advantageously be a copolymer prepared by copolymerization of the olefinic monomer and ethylene in the presence of a sodium activated molybdena or alumina catalyst. Also useable, for example, are the substantially linear copolymers containing branched chains such as can be derived by copolymerization in the presence of a peroxide catalyst at high temperatures and high pressures. A particularly preferred copolymer is a copolymer of ethylene and propylene containing less than 25%, i.e., between 0 and 25%, and preferably from about 1 to about 10%, propylene, i.e., propylene units based on total composition of the copolymer. The remainder of the preferred copolymer consists of units derived from ethylene.

Useable polymers in accordance herewith may also be obtained by extraction of higher molecular weight polymers. Extraction may be accomplished using a solvent and/or antisolvent. The extracted polymer is useable if it falls within the definition of the polymers of this invention as to characteristics and particularly as to intrinsic viscosity. Such extracted fraction usually has a higher branch index and a lower intrinsic viscosity than the starting material, as well as a higher total solubility in distillate fuels and a lower crystallinity. Examples of suitable solvents are the low molecular weight hydrocarbons such as hexane, butane, pentane, heptane, etc., and examples of anti-solvents useable therewith are the low molecular weight alcohols such as methanol, ethyl alcohol, isopropyl alcohol, n-butanol, etc. Naphtha is a particularly advantageous solvent because it does not require the use of an anti-solvent. However, because polymers having the desired characteristics are available commercially and because polymers can be "tailor-made" to have the desired

characteristics, it is particularly preferred to use such polymers which do not need prior extraction to fall within the scope of the present pour point depressants; extraction adds and expensive step to preparation of the polymers.

Such polymers as described above are well known in the art and are readily available commercially. Many of the useable polymers are obtained as by-products from commercial polymerization processes as undesirable low molecular weight materials and, because of their availability and economic attractiveness, such by-product polymers are advantageous for use herein.

An especially preferred polymer for use in accordance with the present invention is the polyethylene polymer disclosed in our copending application Serial No. 105,910, filed April 27, 1961, as a continuation-in-part of S.N. 51,529, filed August 24, 1960, now abandoned. The polymer described therein is an oil-soluble low molecular weight substantially linear (i.e., non-crosslinked) low density hydrocarbon homopolymer of ethylene having an intrinsic viscosity of from about 0.08 to about 0.15 and preferably from about 0.10 to 0.12 dl./g. in decalin solvent at 135° C. determined in accordance with the ASTM D-1601-59-T. The particular homopolymer of ethylene therein described has a branch index of at least 6 and preferably 6 to 10. The branch index as used herein is the common branch index which is determined as the number of methyl groups per 100 carbon atoms of polymer. In the especially preferred homopolymers of ethylene, the branching is well known to consist almost exclusively of ethyl and butyl side chains. Because methyl groups can only terminate branches, the total number of carbon atoms in the side chains per 100 carbon atoms of homopolymer is at least 12 and preferably in the range of 15 to 35.

The polymers useable in accordance with this invention are preferably totally soluble in distillate fuels oils in concentrations of at least 10% by weight at room temperature (25° C.). Particularly preferred are the polymers having such solubility as well as intrinsic viscosity values with the above ranges, without prior extraction or other fractionation.

The crystallinity of the polymer may advantageously be below about 15% and preferably below about 10% as estimated from the differential thermal analysis by the method of B. Ke, Journal of Polymer Science, vol. 42, page 15 (1960).

The distillate oil or distillate fuel oil is a hydrocarbon oil, such as for example, a diesel fuel, a jet fuel, a heavy industrial residual fuel (e.g., Bunker C), a furnace oil, a heater oil fraction, kerosene, a gas oil, or any other like light oil. Of course, any mixtures of distillate oils are also intended. The distillate fuel oil may be virgin or cracked petroleum distillate fuel oil. The distillate fuel oil may advantageously boil in the range of from about 200 to about 750° F., and preferably in the range of 350 to 650° F. The distillate fuel oil may contain or consist of cracked components, such as for example, those derived from cycle oils or cycle oil cuts boiling heavier than gasoline, usually in the range of from about 450 to about 750° F. and may be derived by catalytic or thermal cracking. High-sulfur-containing and low-sulfur-containing oils such as diesel oils and the like may also be used. The distillate oil, may, of course, contain other components such as addition agents used to perform particular functions, for example, rust inhibitors, corrosion inhibitors, anti-oxidants, sludge stabilizing compositions, etc.

The preferred distillate fuel oils have an initial boiling point in the range of from about 350 to about 475° F. The distillate fuel oil may advantageously have an A.P.I. gravity of about at least 30 and a flash point (Tag closed cup) not lower than about 110° F. and preferably above about 115° F.

The following are examples of the preparation of amine salts suitable for use as distillate oil addition agents in accordance with this invention.

Example No.	Composition
1-----	Tri(hydrogenated tallow) amine formate.
2-----	Di(tri(hydrogenated tallow) amine) oxalate.
3-----	Di(di(hydrogenated tallow) amine) dilinoleate.
4-----	Tri(di(hydrogenated tallow) amine) trilinoleate.
5-----	Di(hydrogenated tallow) amine linoleate.
6-----	Di(hydrogenated tallow) amine oleate.
7-----	Di(hydrogenated tallow) amine stearate.
8-----	Di(di(hydrogenated tallow) amine) adipate.
9-----	Mono(di(hydrogenated tallow) amine) dilinoleate.
10-----	Di(di(hydrogenated tallow) amine) trilinoleate.
11-----	Mono(di(hydrogenated tallow) amine) trilinoleate. ¹
12-----	Tri(hydrogenated tallow) amine polylinoleate. ¹
13-----	Disoybean amine polylinoleate. ¹
14-----	Dicoco amine polylinoleate. ¹
15-----	Salt of di(hydrogenated tallow) amine and mixed higher fatty acids.
16-----	Salt of di(hydrogenated tallow) amine and tall oil.

See footnote 1, col. 7.

As used herein, wt./vol. percent indicates concentration in grams per 100 ml.

The following preparations were also made for purposes of comparison:

Preparation	Composition
25-----	Polyethylene grease. ²
I-----	A low density low molecular weight ethylene-propylene copolymer produced in about 10% yield as a by-product from the polymerization of ethylene and propylene in the presence of a sodium activated molybdena on alumina catalyst having the characteristics: Units derived from propylene: 1-10% by wt. Intrinsic Viscosity (decalin solvent at 135° C.): 0.13 dl./g. Differential Thermal Analysis Crystallinity: 9.0%. Density: 0.935. was extracted with hexane to obtain a hexane-soluble extract and a hexane-insoluble residue; the latter was discarded. A portion of the hexane-soluble extract was extracted with naphtha and the naphtha extract was recovered as Preparation II. Another portion of the hexane-soluble extract was blended in a weight ratio of 1:1.13 with the low density copolymer as a melt and cooled to room temperature. The resulting blend was Preparation III.
II & III-----	
30-----	
35-----	
IV-----	A cyclohexane-soluble fraction of the low molecular weight copolymer described in II & III.

See footnote 2, col. 7.

Concentrates of addition agents of this invention were prepared as follows:

Concentrate	Composition
1-----	10 grams of Example 3 containing a slight excess of di(hydrogenated tallow) amine were dissolved in 35 cc. light catalytic cycle oil at 80° C. The resulting solution was cooled with dilution to room temperature to 14.3 wt./vol. percent. The diluted concentrate was then filtered.
2-----	10 grams of Example 3 were processed as above except no excess of the amine was present and dilution was to 20 wt./vol. percent.
3-----	Example 4 in light catalytic cycle oil in an amount of 14.3 wt./vol. percent formulated as in Concentrate 1.
4-----	Di(hydrogenated tallow) amine polylinoleate ¹ in light catalytic cycle oil in an amount of 14.3 wt./vol. percent formulated as in Concentrate 1.
5-----	The salt of dilinoleic acid and crude mixed higher fatty amines in light catalytic cycle oil in an amount of 14.3 wt./vol. percent formulated as in Concentrate 1.
6-----	The crude mixed higher fatty amine salt of Hardesty D-50 ¹ acids in light catalytic cycle oil in an amount of 14.3 wt./vol. percent formulated as in Concentrate 1.
7-----	Light catalytic cycle oil containing 20 wt./vol. percent of Example 9, formulated as in Concentrate 1.
8-----	Light catalytic cycle oil containing 20 wt./vol. percent of Example 10, formulated as in Concentrate 1.
9-----	Light catalytic cycle oil containing 20 wt./vol. percent of Example 11, formulated as in Concentrate 1.
10-----	Dimethyl (hydrogenated tallow) amine polylinoleate ¹ dissolved in light catalytic cycle oil to 5.16 wt./vol. percent.
11-----	Light catalytic cycle oil containing Concentrate 4 and an amount of Preparation II equal to the amount by weight of amine salt contained therein.
12-----	Light catalytic cycle oil containing Concentrate 4 and an amount of Preparation III equal to the amount by weight of amine salt contained therein.
13-----	Light catalytic cycle oil containing Concentrate 4 and an amount of Preparation IV equal to the amount by weight of amine salt contained therein.
14-----	Concentrate 1 mixed with an amount of Preparation I equal to the amount of amine salt contained therein.
15-----	Concentrate 2 mixed with an amount of Preparation I equal to the amount of amine salt contained therein.

Concen- trate	Composition
16.....	Concentrate 3 mixed with an amount of Preparation I equal to the amount of amine salt contained therein.
17.....	Concentrate 4 mixed with an amount of Preparation I equal to the amount of amine salt contained therein.
18.....	Concentrate 5 mixed with an amount of Preparation I equal to the amount of amine salt contained therein.
19.....	Concentrate 6 mixed with an amount of Preparation I equal to the amount of amine salt contained therein.
20.....	Concentrate 7 mixed with an amount of Preparation I equal to the amount of amine salt contained therein.
21.....	Concentrate 8 mixed with an amount of Preparation I equal to the amount of amine salt contained therein.
22.....	Concentrate 9 mixed with an amount of Preparation I equal to the amount of amine salt contained therein.

¹ Made by neutralization of a mixture of linoleic and polylinoleic acids analyzed as follows:

Acid identity:	
Monomer	10%
Dimer	35%
Trimer	40%
Tetramer and higher	15%
Acid equivalent weight	About 355
Acid No.	150-164
Free fatty acid	75-82%

² Polyethylene grease was prepared as follows: 1,000 grams of crude U.S.I. by-product polyethylene was added to 8 liters of light naphtha. The mixture was heated with stirring to 195° F. at which point the solution was complete. About 100 grams of filtering clay was added and the mixture was allowed to cool with stirring to room temperature overnight. The cooled mixture was then filtered to remove insolubles. The filtrate was distilled to a pot temperature of 200° F. and then stripped of residual naphtha by applying a 200 mm. vacuum. 650 grams of polyethylene grease were obtained as a product. The product had the following general characteristics:

Intrinsic viscosity (decalin solvent at 135° C.)	0.11
Branch index	Greater than 6
Differential thermal analysis crystallinity	9.3

To illustrate this invention, addition agents of this invention were added to various distillate fuel oils and the effects of the addition agents on the pour point of the fuel oil were measured. The following distillate fuel oils were used:

- Fuel A—A light catalytic cycle oil.
 Fuel B—Virgin gas oil.
 Fuel C—A furnace oil blend having a pour point of about 0° F.
 Fuel D—Desulfurized gas oil.
 Fuel E—Light catalytic cycle oil (ASTM distillation: initial 420° F., and end point 621° F.)
 Fuel F—A blend of 276 parts light catalytic cycle oil (ASTM distillation: initial 465° F., and end point 636° F.) and 480 parts middle catalytic cycle oil.
 Fuel G—A blend of 535 parts of light catalytic cycle oil and 215 parts of middle catalytic cycle oil.
 Fuel H—A blend of equal parts light catalytic cycle oil (ASTM distillation: initial 404° F., end point 577° F.) and virgin diesel fuel oil.
 Fuel J—A blend of 568 parts desulfurized gas oil and 189 parts kerosene diesel oil.
 Fuel K—A blend of 530 parts light catalytic cycle oil (ASTM distillation: initial 420° F., end point 621° F.) and 227 parts diesel oil.
 Fuel L—A blend of 250 parts virgin gas oil, 280 parts heater oil, 167 parts middle catalytic cycle oil, and 60 parts light catalytic cycle oil.
 Fuel M—A blend of 187 parts light catalytic cycle oil, 75 parts middle catalytic cycle oil, 338 parts virgin furnace oil, and 150 parts heater oil.
 Fuel N—A furnace oil blend containing 41% light catalytic cycle oil, 46% virgin gas oil, and 13% heavier fuels.
 Fuel O—Light catalytic cycle oil (ASTM distillation: initial 404° F., end point 577° F.)

The parts or percents referred to in the above compositions of Fuels A through O are parts or percents by volume.

Pour point determinations

Using distillate fuel oils identified above as base oils and using examples and concentrates identified above as

addition agents, various fuel oil compositions were prepared containing amounts of total pour point depressor indicated in the tables below. The total pour point depressor includes total amine salt and/or polymer. The "solid points" of the fuel oil compositions were determined as reported in the tables. The "solid points" are convertible to ASTM pour points by adding 5° F. to each value.

Fuel Oil	Additive, Identity	Solid Points, ° F., at Total Pour Point Depressor Wt. Percent Concentration						
		0.00	0.01	0.02	0.03	0.04	0.05	0.1
15	A..... Example 1.....	-2	0	-4	-4	-5	-2	-25
	A..... Example 2.....	-2	0	-3	-2	-24	-40	-55
	B..... do.....	+7	+2	+1	0	0	-2	-20
	A..... Example 3.....	-2	-2	-29	-36	-33	-50	-54
	B..... do.....	+7	-1	-23	-25	-35	-38	-48
	A..... Example 4.....	-2	-3	-23	-30	-35	-37	-49
	B..... do.....	+7	-10	-20	-30	-42	-41	-42
20	B..... Example 5.....	+7	-10	-13	-52	-57	-60	-70
	A..... Example 6.....	-2	-13	-21	-41	-46	-43	-45
	A..... Example 7.....	-2	-2	-4	-5	-12	-13	-14
	A..... Example 8.....	-2	+2	-4	-5	-12	-13	-18
	A..... Example 11.....	-2	-3	-15	-20	-24	-13	-52
	A..... Example 15.....	-2	-10	-10	-10	-11	-62	-70
	A..... Example 16.....	-2	-6	-40	-51	-55	-59	-70
25	A..... Concentrate 1.....	-2	-11	-40	-41	-46	-52	-50
	A..... Concentrate 2.....	-2	-5	-30	-30	-34	-38	-45
	A..... Concentrate 3.....	-2	-10	-18	-16	-25	-38	-42
		0.000	0.005	0.010	0.015	0.020	0.025	0.030
30	A..... Example 12.....	-2	-2	-6	-5	-2	-10	-10
	A..... Example 13.....	-2	+2	-2	-7	-12	-20	-18
	A..... Example 14.....	-2	-1	-3	-6	-5	-25	-22
	A..... Concentrate 1.....	-2	-1	-19	-25	-34	-39	-42
	B..... do.....	+7	+2	-7	-18	-20	-29	-31
	A..... Concentrate 2.....	-2	0	-10	-26	-34	-36	-40
	B..... do.....	-2	0	-12	-21	-24	-29	-33
	A..... Concentrate 3.....	-2	-3	-24	-34	-36	-38	-40
35	B..... do.....	-2	-1	-10	-13	-24	-23	-29
	A..... Concentrate 4.....	-2	-4	-19	-33	-44	-55	-53
	C..... do.....	-5	-4	-7	-7	-8	-14	-10
	D..... do.....	-10	-14	-42	-40	-47	-54	-48
	E..... do.....	-12	-11	-12	-41	-40	-40	-52
	F..... do.....	+13	+8	+8	+8	+2	-2	-2
	G..... do.....	-26	-23	-29	-33	-32	-32	-32
	H..... do.....	-16	-24	-25	-29	-30	-28	-28
40	J..... do.....	-19	-20	-43	-53	-53	-56	-57
	K..... do.....	-29	-29	-29	-29	-29	-29	-29
	L..... do.....	0	-2	-12	-17	-20	-24	-29
	M..... do.....	+2	-13	-17	-18	-23	-40	-43
	N..... do.....	-1	-11	-19	-22	-27	-27	-29
	O..... do.....	-24	-24	-25	-29	-30	-28	-28
	A..... Concentrate 5.....	-2	-7	-7	-8	-10	-6	-6
	B..... do.....	+7	0	0	2	0	-2	-2
45	A..... Concentrate 6.....	-2	-12	-17	-14	-8	-10	-8
	B..... do.....	+7	-1	-3	-3	-4	-2	-2
	A..... Concentrate 7.....	-2	+1	-3	-28	-32	-50	-43
	A..... Concentrate 8.....	-2	-2	-24	-21	-22	-22	-26
	B..... do.....	+7	0	0	0	0	-25	-28
	A..... Concentrate 9.....	-2	-8	-13	-20	-23	-31	-20
	B..... do.....	+7	0	-7	-12	-17	-18	-19
50	A..... Concentrate 10.....	-2	-2	-3	-7	-8	-9	-10
	A..... Concentrate 11.....	-2	-17	-32	-42	-49	-50	-54
	A..... Concentrate 12.....	-2	-11	-34	-41	-44	-46	-52
	D..... do.....	-10	-20	-40	-44	-50	-54	-60
	E..... do.....	-12	-19	-26	-41	-44	-52	-62
	F..... do.....	+13	+8	+4	0	-34	-36	-38
	G..... do.....	-26	-28	-30	-28	-40	-50	-52
	H..... do.....	-16	-18	-19	-23	-32	-50	-54
55	J..... do.....	-14	-26	-48	-60	-60	-68	-68
	K..... do.....	-24	-23	-50	-52	-52	-64	-60
	L..... do.....	0	-6	-8	-14	-18	-26	-36
	M..... do.....	+2	-1	-14	-20	-22	-26	-34
	O..... do.....	-24	-25	-32	-50	-60	-64	-64
	P..... do.....	-2	-11	-23	-30	-40	-44	-45
60	B..... do.....	-10	-22	-31	-36	-43	-51	-55
	E..... do.....	-12	-15	-29	-37	-48	-50	-48
	F..... do.....	+13	+4	+4	+2	-20	-21	-30
	H..... do.....	-16	-18	-18	-16	-19	-33	-43
	J..... do.....	-19	-27	-39	-46	-55	-57	-64
	K..... do.....	-29	-20	-35	-47	-50	-52	-57
	L..... do.....	0	-3	-9	-16	-22	-25	-28
65	N..... do.....	-1	-9	-12	-16	-24	-25	-25
	O..... do.....	-24	-26	-28	-34	-52	-52	-56
	P..... do.....	-2	-14	-32	-39	-44	-51	-56
	A..... Concentrate 14.....	-2	-11	-33	-39	-45	-50	-55
	A..... Concentrate 15.....	-2	-14	-34	-39	-45	-47	-53
	A..... Concentrate 16.....	-2	-13	-30	-34	-41	-47	-50
	C..... do.....	-5	-9	-8	-16	-26	-25	-28
70	D..... do.....	-10	-23	-38	-50	-56	-62	-70
	B..... do.....	-12	-14	-41	-50	-52	-62	-63
	F..... do.....	+13	+7	0	-2	-22	-20	-46
	G..... do.....	-26	-50	-58	-43	-70	-70	-70
	H..... do.....	-16	-18	-31	-43	-47	-48	-48
	J..... do.....	-19	-32	-44	-50	-58	-62	-72
	K..... do.....	-29	-28	-42	-47	-52	-70	-70
75	L..... do.....	0	-4	-10	-18	-27	-35	-40

Fuel Oil	Additive, Identity	Solid Points, ° F., at Total Pour Point Depressor Wt. Percent Concentration						
		0.000	0.005	0.010	0.015	0.020	0.025	0.030
N	do	-1	-10	-12	-18	-24	-28	-30
O	do	-24	-32	-56	-54	-46	-64	-62
P	do	-2	-10	-12	-14	-11	-18	-20
A	Concentrate 18	+7	-1	-1	-2	-6	-9	-8
B	do	-2	-12	-13	-16	-16	-23	-25
A	Concentrate 19	+7	0	-3	-4	-5	-6	-11
B	do	-2	-12	-26	-36	-47	-53	-56
A	Concentrate 20	-2	-14	-35	-38	-52	-49	-56
B	do	+7	-2	-10	-13	-22	-25	-29
A	Concentrate 21	-2	-13	-26	-36	-38	-40	-46
B	do	+7	-4	-4	-8	-12	-17	-22
		0.000	0.035	0.040	0.045	0.050	0.055	0.060
C	Concentrate 4	-5	-20	-38	-26	-40	-47	-48
C	Concentrate 17	-5	-35	-42	-54	-62	-59	-70

Preparations I through IV, identified above, were also checked as to solid point depressor activities for purposes of comparison. The results were as follows:

Preparation No.	I	I	II	III	IV	IV
Base Oil.....	A	C	A	A	A	B
Concentration of Preparation in Base Oil:						
0.000.....	-2	-5	-2	-2	-2	+7
0.005.....	-14	-8				
0.01.....	-17	-11	-10	-9	-11	0
0.015.....	-24	-10				
0.02.....	-26	-13	-22	-13	-14	0
0.025.....	-31	-16				
0.03.....	-33	-16	-25	-16	-9	0
0.04.....			-30	-18	-12	-1
0.05.....			-32	-20	-10	-4
0.1.....			-46	-27	-14	-4

The conjoint action of the polymer and amine salt is readily ascertainable with reference to the above data. Concentrates 14 through 22 correspond to Concentrates 1 through 9 respectively except that only half as much amine salt is included in Concentrates 14-22 and an amount by weight of low density low molecular weight polyethylene equal to the weight of amine salt is included. The data show marked improvement in solid points. This is particularly surprising in that the polyethylene (Preparation I) used, although it did show some pour point depressant activity, was alone markedly inferior to the combination and often even inferior to the amine salt which it replaces in the combination of Concentrates 14-22. The conjoint action is also demonstrated by comparing the combination polymers and amine salts of Concentrates 11, 12 and 13 with the performance of the amine salt alone in Concentrate 4 and the performance of the polymer alone in Preparations II, III and IV, respectively.

Stability test, aging conditions

Further, it has been determined that distillate fuel oil compositions provided by this invention are stable under conditions of storage, i.e., do not lose their pour point depressing ability. As a demonstration of this advantage of the present compositions, fuel oil compositions were prepared from Concentrate 1 and Fuel Oil A containing differing concentrations of the amine salt.

The fuel oil compositions were stored for twelve weeks under increased temperature conditions (110° F.) to simulate storage of fuel oils under long periods of time.

Throughout the test, the pour points of the distillate oils were determined each week with results as follow:

Salt Identity	Wt. per cent	Original Solid Point	Solid Points, ° F., after storage at 110° F.					
			1 wk.	2 wk.	3 wk.	4 wk.	5 wk.	12 wk.
Conc. 1.....	0.10	-42	-49	-48	-51	-52	-48	-53
Conc. 1.....	0.05	-38	-33	-34	-33	-37	-38	-25
Conc. 1.....	0.04	-31	-32	-22	-33	-29	-22	-14
Conc. 1.....	0.03	-27	-20	-15	-24	-20	-13	-6
Conc. 1.....	0.02	-20	-8	-14	-15	-5	-8	-2
Conc. 1.....	0.01	-2	+1	+2	+1	+2	+2	+2

The results of the aging test show effective pour point depression even after weeks of storage under higher-than-normal storage temperature conditions. Thus, the present addition agents would not deteriorate over extended periods of storage under normal fuel oil storage conditions.

Pumpability

In addition to providing pour point depressor activities, the addition agents of this invention may also be used to improve the pumpability of the fuel oil, i.e., decrease the deposition of wax-like crystals on filter screens and within pumps, lines and valves. The improved pumpability is believed to be a result of improved mobility of the wax crystals through modification of the wax crystals. The addition agents of this invention apparently function to so modify the wax crystals. For purposes of testing for pumpability, a concentrate containing 2.344% of the di (hydrogenated tallow) amine salt of mixture of linoleic and poly-linoleic acids hereinbefore described in detail was prepared by heating a mixture of 37.1 grams of said acids and 55.5 grams di (hydrogenated tallow) amine to 90° C. and dissolving the heated mixture in 1 gallon of Fuel Oil C. Two liters of the resulting concentrate were added to 47 gallons of furnace oil. The solid point of the resulting fuel oil composition was -24° F. (average of 6 determinations). The fuel oil composition was then tested for pumpability through a 2" pipe both with and without a filter screen, at various temperatures. The results were as follows:

Fuel Oil Temperature, ° F.	Pumpability, Gallons Per Minute	
	With Filter Screen	Without Filter Screen
+18.....	50.9	52.5
+1.....	50.9	51.6
-5.....	49.3	53.2
-11.....	51.6	53.2
-18.....	52.5	53.2
-23.....	53.2	52.5
-32.....	53.2	53.2

¹ Some foaming.

The above results demonstrate pumpability of the fuel oil composition through a 2" pipe (with or without a filter screen) at temperatures even below the solid point.

Although concentrates containing 10 to 65 weight percent of the agents of this invention are preferred, the concentrates may contain as little as from 2 to 5 percent or less of the amine salt or amine salt plus polymer. Such concentrates may conveniently be prepared by dissolving the pour point depressor in a suitable organic solvent therefor in such amounts.

The organic solvent preferably boils within the range of from about 100° F. to about 700° F. The preferred organic solvents are hydrocarbon solvents, for example, petroleum fractions such as naphtha, heater oil, mineral spirits and the like, because of their clean burning properties. The solvents selected should, of course, be selected with regard to possible beneficial or adverse effects it may have on the ultimate fuel oil composition. Thus, the

solvent should preferably burn without leaving a residue and should be non-corrosive with regard to metal, and especially ferrous metals.

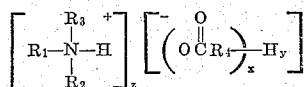
Other desirable properties are obvious from the intended use of the solvent.

All percentages given herein are percentages by weight unless otherwise indicated.

It is evident from the foregoing that I have provided distillate fuel oil compositions containing secondary or tertiary amine salts as pour point depressors effective in very small amounts and I have further provided improved pour point depressors including such salts and a polymer as herein defined.

I claim:

1. A fuel oil composition comprising a major amount of a distillate fuel oil and an amount in the range of 0.001 to 5 weight percent of a quaternary ammonium salt having the structural formula:



wherein R_1 and R_2 are alkyl groups having from about 10 to about 22 carbon atoms, R_3 and R_4 are each selected from the class consisting of hydrogen and a C_1 to C_{22} alkyl group, x and z are each integers of from 1 to 4 inclusive and y is an integer of from 0 to 1 inclusive and where x is 1, y is 0.

2. The fuel oil composition of claim 1 wherein said distillate fuel oil contains a cracked component derived by cracking a cycle oil boiling heavier than gasoline.

3. The fuel oil composition of claim 1 which contains in addition to said ammonium salt, from 0.01 to 5 weight percent of an oil-soluble low-density low molecular weight hydrocarbon polymer of ethylene selected from the class consisting of polyethylene and copolymers of ethylene with C_3 to C_5 mono-olefinic hydrocarbon which polymers have an intrinsic viscosity of from 0.05 to 0.25 dl./g.

4. The fuel oil composition of claim 3 wherein said polymer is polyethylene.

5. The fuel oil composition of claim 3 wherein said polymer is a copolymer of ethylene and propylene.

6. The fuel oil composition of claim 1 wherein R_3 is an alkyl group having from 10 to 22 carbon atoms.

7. The fuel oil composition of claim 1 wherein said salt is di (hydrogenated tallow) amine polylinoleate.

8. The fuel oil composition of claim 1 wherein said carboxylic acid is formic acid.

9. A synergist mixture consisting essentially of an oil-soluble low-density low molecular weight hydrocarbon polymer of ethylene and the amine salt of claim 1 in a weight ratio of said polymer to said amine in the range of

1:10 to 10:1, wherein said polymer is a substantially linear polymer having an intrinsic viscosity in the range of from about 0.05 to about 0.25 dl./g. selected from the class consisting of polyethylene and copolymers of ethylene with a mono-olefinic monomer having from 3 to 6 carbon atoms inclusive.

10. The synergistic mixture of claim 9 wherein said hydrocarbon polymer is an ethylene-propylene copolymer having an intrinsic viscosity in the range of from about 0.10 to about 0.15 dl./g. and having an overall crystallinity below about 10%.

11. The synergistic mixture of claim 9 wherein said polymer is substantially linear polyethylene having an intrinsic viscosity in the range of from about 0.08 to about 0.15 dl./g. and having a branch index of at least 6.

12. A fuel oil composition concentrate containing from about 10% to about 65% of the ammonium salt of claim 1 and the remaining 35% to about 90% consisting essentially of a hydrocarbon solvent, boiling at a temperature in the range of from about 100° F. to about 700° F., said concentrate being capable of dilution with a distillate fuel oil to an amine salt concentration in the range of from about 0.001 to about 0.5 weight percent.

13. A fuel oil composition concentrate containing from about 10% to about 65% of the mixture of ammonium salt and polymer of claim 3 and from about 35% to about 90% consisting essentially of a hydrocarbon solvent, boiling at a temperature in the range of from about 100° F. to about 700° F., said concentrate being capable of dilution with a distillate fuel oil to a concentration of said mixture in the range of from about 0.001 to about 0.5 weight percent.

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