

COLD FLOW IMPROVEMENT OF DISTILLATE FUELS USING ALPHA-OLEFIN COMPOSITIONS

TECHNICAL FIELD

[0001] The present invention relates to improving the cold flow of distillate fuels, and more particularly relates in one non-limiting embodiment to improving the cold filter plugging point of middle distillate fuels by chemical treatment.

TECHNICAL BACKGROUND

[0002] Upon encountering low temperatures, distillate fuels, and in particular middle distillate fuels, tend to develop fluidity problems. In one non-limiting definition, middle distillate fuels include jet fuel, kerosene, heating oil and diesel fuel. More particularly, the fluidity problems involve paraffins in the fuel agglomerate at low temperatures to form a waxy semi-solid or gel-like material that plugs pipes and filters, inhibiting transmission of the fuel to, for example, an engine.

[0003] Conventionally, this problem is treated by adding to the fuel a chemical composition called a low temperature fluidity modifier. The low temperature fluidity modifier can co-crystallize with or adsorb the paraffins in the fuel oil to precipitate the paraffin before agglomeration occurs or alternatively to modify paraffin crystal growth so that the resulting irregularity in size and shape of the crystals inhibits agglomeration or efficient packing of the crystals, thereby reducing the tendency toward plug formation. By contrast, pour point depressants are directed simply to viscosity reduction of fluids at low temperatures. Pour point reduction still involves some crystal modification but may not need to be as efficient or keep the crystals as small. Thus, while studies have shown a relation between low temperature fluidity of a fuel and the pour point or cloud point of the fuel, the mechanism of low temperature fluidity modifier operation and the problem to which low temperature fluidity modifiers are directed differ significantly from those of pour point depressants. Therefore, despite the

apparent relationship between low temperature fluidity and pour point, they typically require different treatments. Further, it may not be correctly assumed that a low temperature fluidity modifier will depress the pour point, or that a pour point depressant will improve low temperature fluidity.

[0004] Because low temperature modifiers operate by affecting the crystal growth of the paraffins in the fuel being treated, the selection and composition of a low temperature fluidity modifier for a particular fuel is based on the nature of the paraffins in that fuel. For example, low temperature modifiers typically are coordinated with the paraffins in the fuel so that the solubility characteristics of the modifier added to the fuel match the solubility characteristics of the paraffins in the fuel. Thus, if a fuel contains C₂₀₋₂₄ paraffins that crystallize at 10°F (-12°C), the modifier is typically designed to crystallize at about 10°F (-12°C) as well, thereby to interfere with the crystallization of the paraffins. Accordingly, it is well known to those of ordinary skill in the art of low temperature fluidity modification to select and to adjust the array of aliphatic chain lengths to balance overall solubility based on the paraffin content of the fuel to cause the additive to precipitate out of the fuel at the desired temperature. In fact, it is common to produce esterified olefin/maleic anhydride copolymers for use in low temperature fluidity modifier additive compositions by esterifying certain olefin/maleic anhydride copolymers with an array of aliphatic alcohols having chain lengths in the range of from about four to about forty carbon atoms, and to select the distribution of aliphatic chain lengths in that range in coordination with the paraffins in the fuel as discussed above.

[0005] U.S. Pat. No. 5,857,287 discloses adding to a fuel oil a composition of from about 1 to about 40 parts by weight ethylene/vinyl acetate copolymer having a vinyl acetate content of from about 10% by weight to about 50% by weight and a weight average molecular weight of from about 2,000 to about 10,000, and 1 part by weight esterified copolymer of at least one generally linear alpha-olefin of from about 18 to about 50 carbon atoms and maleic anhydride in an alpha-olefin to maleic anhydride molar ratio of from about 4:1 to about 1:2, the copolymer having a weight average molecular weight of from

about 2,000 to about 20,000, the esterified copolymer having been esterified with a plurality of aliphatic alcohols having from about four to about forty carbon atoms, imparts to the fuel oil surprisingly improved low temperature fluidity, provided that the alcohols include an eight carbon alcohol making up from about 50 to about 85 molar percent of the alcohols.

[0006] Despite the existence of a variety of low temperature fluidity modifiers, none provides completely satisfactory performance in all fuels. In fact, because of the disparities in the characteristics of fuel oils, particular low temperature fluidity modifiers meet with varying success from fuel to fuel. Thus, there is a continual search for ever more effective low temperature fluidity modifiers, particularly for use in a variety of fuels.

SUMMARY

[0007] There is provided, in one non-limiting form, a method for improving cold flow of a distillate fuel that involves adding to the distillate fuel an effective amount of an additive to improve a cold flow property. The additive may include, but is not necessarily limited to (a) polymerized alpha-olefins *per se*, (b) alpha-olefins copolymerized or reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates, methacrylic acid, alkyl methacrylates, and combinations thereof to give a reaction product, (c) alpha-olefins copolymerized or reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates, methacrylic acid, alkyl methacrylates, and combinations thereof to give a reaction product, where the reaction product is in turn blended with alkylphenol-formaldehyde resins, and/or (d) alpha-olefins copolymerized or reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates, methacrylic acid, alkyl methacrylates, and combinations thereof to give a reaction product, where the reaction product is in turn blended with alkylphenol-formaldehyde resins, which compositions are further blended with ethylene-vinyl acetate copolymers (EVA). The alpha-olefin may be understood as a first component.

[0008] There is also provided in an alternative non-restrictive embodiment, a distillate fuel composition that includes a distillate fuel and an additive, where the additive may be selected from (a), (b), (c) and/or (d) noted above, in an amount effective to improve the cold flow of the distillate fuel, particularly the cold filter plugging point (CFPP) of a middle distillate fuel.

[0009] In one non-limiting embodiment the components (a), (b), (c) and/or (d) are not esterified. In another non-limiting embodiment, the components (a), (b), (c) and/or (d) do not include esterified copolymers of alpha-olefins and maleic anhydride.

DETAILED DESCRIPTION

[0010] It has been discovered that compositions which include polymerized alpha-olefins used alone or alpha-olefins copolymerized with, grafted with, otherwise reacted with or even simply blended with additional components will give a synergistic improvement in a cold flow property of a distillate fuel as compared the expected sum of the additive effect of the components when used separately. In particular, unexpected improvement is seen when the improved cold flow property is compared with an otherwise identical distillate fuel composition absent the alpha-olefin component.

[0011] One cold flow property that may be improved by the additives and methods described herein is the cold filter plugging point (CFPP) which may be defined as the lowest temperature, expressed in °C or °F, at which a given volume of a diesel type of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. This test gives an estimate for the lowest temperature that a fuel will give trouble free flow in certain fuel systems. This is important since in cold temperate countries and environments a high CFPP fuel will clog up fuel filters and/or fuel lines in vehicle engines more easily.

[0012] The alpha-olefin suitable for use in the various compositions herein include those having carbon numbers ranging from 6 independently to 30, and even higher, in a non-limiting embodiment. In an alternative, non-

restrictive embodiment, the alpha-olefins may have a carbon number ranging from 10 independently to 28; alternatively from 12 independently to 16. When "independently" is used in conjunction with a range herein, any lower threshold may be combined with any upper threshold to give a suitable alternative range.

[0013] With respect to homopolymers of alpha-olefins, these may have a weight average molecular weight of from about 1000 independently to about 20,000; alternatively from about 2000 independently to about 10,000.

[0014] Another suitable composition herein includes functionalized alpha-olefins (a first component) copolymerized with or otherwise reacted with (for instance grafted with) a second component including, but not necessarily limited to, maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates, methacrylic acid, alkyl methacrylates, and combinations thereof. As used herein, the "alkyl" in alkyl acrylates and alkyl methacrylates is defined as a straight or branched alkyl group having carbon numbers ranging from 1 to 8, alternatively from 1 to 4.

[0015] It will be appreciated that it is not always possible to know when the alpha-olefin is reacted with a second component whether the reaction is copolymerization, a grafting reaction or another type of reaction, hence, the interaction is described herein as "copolymerized or reacted with" to cover all possibilities by definition. The result is termed a reaction product. However the reactions are reproducible and the cold flow property improvement is reproducible for a variety of the polymers, copolymers and other reaction products.

[0016] Alpha-olefins copolymerized/grafted with maleic anhydride may have a weight ratio ranging from 1% maleic anhydride to 50% maleic anhydride of the alpha-olefin, alternatively from 5 wt% to 25 wt% of alpha-olefin. Expressed as mole ratio, the mole ratio of maleic anhydride to alpha-olefin may range from 0.03/1 independently to 3/1; alternatively from 0.15/1 independently to 2/1.

[0017] Alpha-olefins copolymerized/grafted with acrylic acid may have a weight ratio ranging from 1% acrylic acid to 20% acrylic acid to the alpha-olefin, alternatively from 3 wt% to 10 wt% of alpha-olefin. Expressed as mole ratio, the

mole ratio of acrylic acid to alpha-olefin may range from 0.04/1 independently to 0.9/1; alternatively from 0.1/1 independently to 0.4/1.

[0018] Alpha-olefins copolymerized/grafted with vinyl acetate may have a weight ratio ranging from 1% vinyl acetate to 40% vinyl acetate of the alpha-olefin, alternatively from 10 wt% to 25 wt% of alpha-olefin. Expressed as mole ratio, the mole ratio of vinyl acetate to alpha-olefin may range from 0.04/1 independently to 2/1; alternatively from 0.4/1 independently to 1/1.

[0019] With respect to copolymers, graft polymers or other reaction products with the alpha-olefins, these reaction products may have a weight average molecular weight of from about 1000 independently to about 20,000; alternatively from about 2000 independently to about 10,000. For the alkylphenol-formaldehyde resin components, they may range in weight average molecular weight from about 2000 independently to about 20,000; alternatively from about 5000 independently to about 12,000. For the EVA copolymer components, they may range in weight average molecular weight from about 1000 independently to about 10,000; alternatively from about 2000 independently to about 4000.

[0020] The alpha-olefins may be homopolymerized using methods well known in the art, and further, the alpha-olefins may be reacted with the second components using methods well known in the art. These polymerization and other reactions may be carried out at a temperature between about 60 and about 180°C, and a pressure between about 0 and about 200 psig. The reactions may be carried out in the absence or presence of a catalyst. If a catalyst is used, suitable catalysts include, but are not necessarily limited to, peroxide catalysts, such as di-t-butyl peroxide, benzoyl peroxide, lauroyl peroxide, and t-butyl hydroperoxide and the like.

[0021] As noted previously, the functionalized alpha-olefins (that is, those reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates, methacrylic acid, alkyl methacrylates, and combinations thereof) may be blended with alkylphenol-formaldehyde resins. In one non-limiting embodiment the weight ratio of the

functionalized alpha-olefins with alkylphenol-formaldehyde resins ranges from about 5/1 independently to about 100/1; alternatively from about 1/1 independently to about 20/1.

[0022] Further, the functionalized alpha-olefins noted above may be blended with alkylphenol-formaldehyde resins, and further blended with ethylene-vinyl acetate copolymers (EVA). In these blends or further reactions, the amount of EVA may range from about 99% independently to about 1 wt%; alternatively from about 98% independently to about 2 wt%, based on the amount of functionalized alpha-olefins and alkylphenol-formaldehyde resin.

[0023] With respect to determining the effective amount of the additive useful to obtain the best results in the distillate fuel, *e.g.* middle distillate fuel, one good suitable procedure is simply empirical testing, since as previously noted, the cold flow improver may need to be matched to the paraffins in the fuel. Nevertheless, to give some idea of suitable dosage ranges for these cold flow improvers, if the alpha-olefin portion that is blended or reacted with the second component or EVA ranges between about 1 independently to about 50 vol%, alternatively between about 5 independently to about 20 vol%, then the dosage range in middle distillate fuels of the final product blend or reaction product would be about 10 ppm-vol independently to about 10,000 ppm-vol; alternatively from about 50 ppm-vol independently to about 500 ppm-vol. In other words, the dosage of the alpha-olefin portion would range between about 1 ppm-vol independently to about 5,000 ppm-vol; alternatively from about 2.5 ppm-vol independently to about 100 ppm-vol.

[0024] The middle distillate fuels in which the methods and compositions described herein are expected to be effective include, but are not necessarily limited to, jet fuel, kerosene, heating oil and diesel fuel, whether or not they include fatty acid methyl esters (FAME). The now common practice of introducing FAME into middle distillate fuels may lead to additional wax crystal formation from saturated FAME. Additionally, some fuel companies are considering adding hydrogenated vegetable oils as biofuel components, which may introduce further paraffinic waxes into the middle distillate fuels. However, the

additives and methods described herein are expected to be effective in these fuels as well. The distillate fuels as described herein do not encompass polymerized alpha-olefins (PAO) as a major component thereof, that is, a synthetic fuel where PAO is a major (more than 50 volume percent) component thereof. In other words, PAO is not a synthetic base stock for the fuels herein.

[0025] It is expected that the additives described herein will be compatible with other conventional fuel additives.

[0026] The invention will now be described with reference to particular Examples which are not intended to limit the invention but rather simply to illuminate it further.

EXAMPLES 1-9

[0027] CFPP tests were run for three four different middle distillate fuels: Kern, Coffeyville, Cenex #3, and Hovensa. The components are as defined in Table I.

TABLE I

Cold Flow Improver Additives	
DF5063	EVA polymer, 50% active*
T3005	EVA polymer, 50% active
C1608	C30+ alpha-olefin-maleic anhydride polymer, 25% active
1787-123	C20-24 alpha-olefin-acrylic acid polymer, 50% active
1787-125	C20-24 alpha-olefin-acrylic acid polymer, 80% active
1787-189	C20-24/C24-28 alpha-olefin polymer, 25% active
1789-001	C20-24 alpha-olefin-vinyl acetate, (polymer) 25% active
1789-097	C20-24 + C24-28 alpha-olefin-vinyl acetate (19%), (polymer) 25% active
1789-155	C20-24 + C24-28 alpha-olefin-vinyl acetate (9.5%), (polymer) 25% active

*Active refers to actual polymer; the balance is aromatic solvent.

[0028] Table II presents the CFPP test results for four different fuels using a total of 200 ppm (includes solvent) dosage for each Example, except the blank. The comparative Examples are 2 and 4 where no alpha-olefin component is present. It may be seen that the other Examples, which had an alpha-olefin component, gave noticeable and unexpected improvements as compared to Examples 2 and 4. More specifically, compare Examples 3 and 6-9 with Example 2, and compare Example 5 with Example 4.

TABLE II
CFPP Test Results

Ex.	Additive	ppm dose	Kern	Coffeyville	Cenex#3	Hovensa
1	Blank	0	-4F (-20C)	9F (-13C)	9F (-13C)	18F (-8C)
2	DF5063	200	0F (-18C)	-15F (-26C)	5F (-15C)	16F (-9C)
3	DF5063/ C1608	180/20	-26F (-32C)	-17F (-27C)	—	—
4	T3005	200	-8F (-22C)	-18F (-28C)	—	—
5	T3005/ C1608	180/20	-29F (-34C)	-18F (-28C)	—	—
6	DF5063/ 1787-123	200/20	—	—	-8F (-22C)	—
7	DF5063/ 1787-125	200/20	—	—	-11F (-24C)	—
8	DF5063/ 1787-189	180/20	-26F (-32C)	-16F (-27C)	-17F (-27C)	—
9	DF5063/ 1789-001	180/20	-22F (-30C)	-16F (-27C)	-16F (-27C)	—
10	DF5063/ 1787-189	180/40	-29F (-34C)	—	-15F (-26C)	-6F (-21C)
11	DF5063/ 1789-097	180/20	-31F (-35C)	—	-15F (-26C)	-2F (-19C)
12	DF5063/ 1789-155	180/20	-26F (-32C)	—	-9F (-23C)	-4F (-20C)

[0029] It is to be understood that the invention is not limited to the exact details of reactants, proportions and dosages mentioned and described, as modifications and equivalents thereof will be apparent to one skilled in the art. The invention is therefore to be limited only by the scope of the appended claims. Further, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific combinations of alpha-olefin components and second components, full esters of alpha-olefin-maleic anhydride copolymers, half esters of alpha-olefin-maleic anhydride copolymers, different alkylphenol-formaldehyde resins, different proportions of the various reactants and the like falling within the described parameters herein, but not specifically identified or tried in a particular composition method or apparatus, are expected to be within the scope of this invention.

[0030] The terms "comprises" and "comprising" used in the claims herein should be interpreted to mean including, but not limited to, the recited elements.

[0031] The present invention may also suitably comprise, consist of or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. For instance, the method for improving cold flow of a distillate fuel may consist of or consist essentially of adding to the distillate fuel an effective amount of an additive to improve a cold flow property, where the additive is (a) polymerized alpha-olefins, (b) alpha-olefins copolymerized or reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates, methacrylic acid, alkyl methacrylates, and combinations thereof to give a reaction product, (c) alpha-olefins copolymerized or reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates and combinations thereof to give a reaction product, where the reaction product is in turn blended with alkylphenol-formaldehyde resins, and/or (d) alpha-olefins copolymerized or reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates and combinations thereof to give a reaction product, where the reaction

product is in turn blended with alkylphenol-formaldehyde resins, which compositions are further blended EVA copolymers.

[0032] Alternatively there may be provided a distillate fuel composition having improved cold flow that consists of or consists essentially of a distillate fuel and an effective amount to improve a cold flow property of the distillate fuel of an additive, where the additive is either (a), (b), (c) and/or (d) as described above.

CLAIMS

What is claimed is:

1. A method for improving cold flow of a distillate fuel comprising adding to the distillate fuel an effective amount of an additive to improve a cold flow property, where the additive is selected from the group consisting of:

polymerized alpha-olefins;

alpha-olefins copolymerized or reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates, methacrylic acid, alkyl methacrylates, and combinations thereof to give a reaction product;

alpha-olefins copolymerized or reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates, methacrylic acid, alkyl methacrylates, and combinations thereof to give a reaction product, where the reaction product is in turn blended with alkylphenol-formaldehyde resins; and

alpha-olefins copolymerized or reacted with a second component selected from the group consisting of maleic anhydride, acrylic acid, vinyl acetate, alkyl acrylates, methacrylic acid, alkyl methacrylates, and combinations thereof to give a reaction product, where the reaction product is in turn blended with alkylphenol-formaldehyde resins, which compositions are further blended with ethylene-vinyl acetate (EVA) copolymer.

2. The method of claim 1 where the alpha-olefin has from 6 to 30 carbon atoms.

3. The method of claim 1 when:
where the alpha-olefin is copolymerized with or reacted with maleic anhydride, the mole ratio of maleic anhydride to alpha olefin ranges from 0.03/1 to 3/1;
where the alpha-olefin is copolymerized with or reacted with acrylic acid, the mole ratio of acrylic acid to alpha-olefin ranges from 0.04/1 to 0.9/1; and
where the alpha-olefin is copolymerized with or reacted with vinyl acetate, the mole ratio of vinyl acetate to alpha-olefin ranges from 0.04/1 to 2/1.
4. The method of claim 1 where:
the weight average molecular weight of the reaction product ranges from 1000 to 20,000;
the weight average molecular weight of the alkylphenol-formaldehyde resins ranges from 2000 to 20,000; and
the weight average molecular weight of the EVA copolymer ranges from 1000 to 10,000.
5. The method of any one of claims 1, 2, 3 or 4 where the effective amount of the additive ranges from 10 ppm-vol to 10,000 ppm-vol.
6. The method of any one of claims 1, 2, 3 or 4 where the improved cold flow property is improved cold filter plugging point (CFPP), and where the CFPP is improved as compared to an otherwise identical distillate fuel absent the alpha-olefin component.
7. The method of any one of claims 1, 2, 3 or 4 where the additive is not esterified.

8. A distillate fuel composition having improved cold flow comprising:
a distillate fuel; and
an effective amount to improve a cold flow property the distillate fuel of
an additive, where the additive is selected from the group
consisting of:
polymerized alpha-olefins;
alpha-olefins copolymerized or reacted with a second
component selected from the group consisting of maleic
anhydride, acrylic acid, vinyl acetate, alkyl acrylates,
methacrylic acid, alkyl methacrylates, and combinations
thereof to give a reaction product;
alpha-olefins copolymerized or reacted with a second
component selected from the group consisting of maleic
anhydride, acrylic acid, vinyl acetate, alkyl acrylates,
methacrylic acid, alkyl methacrylates, and combinations
thereof to give a reaction product, where the reaction
product is in turn blended with alkylphenol-
formaldehyde resins; and
alpha-olefins copolymerized or reacted with a second
component selected from the group consisting of maleic
anhydride, acrylic acid, vinyl acetate, alkyl acrylates,
methacrylic acid, alkyl methacrylates, and combinations
thereof to give a reaction product, where the reaction
product is in turn blended with alkylphenol-
formaldehyde resins, which compositions are blended
with ethylene-vinyl acetate (EVA) copolymer.
9. The distillate fuel of claim 8 where the alpha-olefin has from 6 to 30
carbon atoms.

10. The distillate fuel of claim 8 when:
where the alpha-olefin is copolymerized with or reacted with maleic anhydride, the mole ratio of maleic anhydride to alpha olefin ranges from 0.03/1 to 3/1;
where the alpha-olefin is copolymerized with or reacted with acrylic acid, the mole ratio of acrylic acid to alpha-olefin ranges from 0.04/1 to 0.9/1; and
where the alpha-olefin is copolymerized with or reacted with vinyl acetate, the mole ratio of vinyl acetate to alpha-olefin ranges from 0.04/1 to 2/1.
11. The distillate fuel of claim 8 where:
the weight average molecular weight of the reaction product ranges from 1000 to 20,000;
the weight average molecular weight of the alkylphenol-formaldehyde resins ranges from 2000 to 20,000; and
the weight average molecular weight of the EVA copolymer ranges from 1000 to 10,000.
12. The distillate fuel of any one of claims 8, 9, 10 or 11 where the effective amount of the additive ranges from 10 ppm-vol to 10,000 ppm-vol.
13. The distillate fuel of any one of claims 8, 9, 10 or 11 where the improved cold flow property is improved cold filter plugging point (CFPP), and where the CFPP is improved as compared to an otherwise identical distillate fuel absent the alpha-olefin component.
14. The distillate fuel of any one of claims 8, 9, 10 or 11 where the additive is not esterified.