

[54] **INCREASING LOW TEMPERATURE
FLOWABILITY OF MIDDLE
DISTILLATE FUEL**

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[22] Filed: **Mar. 17, 1969**

[21] Appl. No.: **807,952**

[52] U.S. Cl. **44/62, 44/70, 44/80,**
44/63

[51] Int. Cl. **C1011/18**

[58] Field of Search **44/62, 70, 80, 63; 252/56,**
252/59; 208/15, 17, 28, 33

[56] **References Cited**

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[57] **ABSTRACT**

The low temperature flowability of a middle distillate petroleum fuel oil, boiling within the range of about 250° to about 700° F. at atmospheric pressure is improved by adding to the fuel oil from about 0.001 to about 1.0 wt. % of a flow improving additive such as a copolymer of ethylene with another ethylenically unsaturated monomer such as an unsaturated ester or an alpha olefin, along with from about 0.01 to about 0.099 wt. % of an essentially saturated hydrocarbon fraction which is substantially free of normal paraffinic hydrocarbons and which has a number average molecular weight in the range of about 600 to about 3000.

4 Claims, No Drawings

INCREASING LOW TEMPERATURE FLOWABILITY OF MIDDLE DISTILLATE FUEL

FIELD OF THE INVENTION

This invention concerns an improvement in the low temperature flowability of a waxy-cloudy middle distillate petroleum fuel through flow lines and filters. The petroleum refinery products which are included in the category known as middle distillate fuels, are aviation turbo-jet fuels, fuel oils and diesel fuels. They are more fully described in such specifications as MIL-F-25558B (USAF) for turbo jet fuels, ASTM D-396-67 for fuel oils and ASTM D-975-67 for diesel fuel oils. The quality of these products is defined by a number of specification tests. Of interest to this invention are those specifications which are related to the low temperature performance of the above products. They are the ASTM freezing point, and the ASTM cloud and pour points. These tests define the temperature at which either the separation of wax from the oil is first observed, or the temperature at which sufficient amounts of wax separate from the oil to cause its gelation. The wax which separates when middle distillate fuels are being cooled consists almost exclusively of hydrocarbon type compounds known as *n*-paraffins. The lowest temperature at which the oil will still flow is generally known as the pour point. When the fuel temperature goes below the pour point and the fuel is no longer freely flowable, difficulty arises in transporting the fuel through flow lines and pumps, as, for example, when attempting to transfer the fuel from one storage vessel to another by gravity or under pump pressure or when attempting to feed the fuel to a burner. Additionally, the wax crystals that have come out of solution tend to plug fuel lines, screens and filters. This problem has been well recognized in the past and various additives have been suggested to improve the flow of wax-cloudy oils. Such flow-improving additives are expected to perform two functions, one of which is to destroy the cohesive forces between the wax crystals and thereby inhibit gelation of the fuel oils. The second, but equally important function of these additives is to arrest the growth of precipitating wax crystals and thereby enable the wax-cloudy oils to pass through the screens and filters that are commonly used in fuel oil delivery systems. Usually the cloud point of the fuel oil is affected very little or not at all by these flow-improving additives.

The upper limit for the temperature at which wax crystals separate from middle distillate petroleum fuels ranges usually from -50° F. for turbine-jet fuels to 30° F. for summer grade No. 2 fuel oils. The refiner manufactures these products by blending suitable refinery streams in appropriate ratios. These streams are heavy naphtha, which is wax-free at temperatures as low as -70° F. and has an end boiling point of about 460° F. (ASTM D-86), kerosene which usually has an ASTM freezing point lower than -40° F. and an end boiling point of about 530° to 560° F. (ASTM D-86), and gas oil which has an ASTM cloud point of about 30° to 70° F. and an end boiling point of about 650° to 720° F. (ASTM D-86). These are so-called straight run products, i.e., the products of distillation of petroleum crude oils. Also used as blending components in the preparation of middle distillate fuels are products boiling in about the same ranges as those discussed above, but obtained by thermal or catalytic cracking of heavier petroleum fractions which boil in the range of about 600° to about 1100° F.

It is highly unlikely that wax would separate even under the most severe winter conditions possible in the civilized areas of the earth, from the middle distillate blending components other than gas oils, either of straight run or cracked type. Thus, for all practical purposes, gas oils are the only wax-bearing middle distillate streams. The low temperature quality of the fuel blends has customarily been improved in the past either by reducing the amount of a typical gas oil (FBP up to 670° F.) in the blend or by the undercutting of such gas oils to final boiling points of 625° F. or even lower. Regardless of which one of the two methods is employed, the overall volume of the middle distillate pool is reduced, resulting ultimately in

a shortage of the product, higher production costs to the refiner, and higher prices to the consumer. Neither of these methods could satisfactorily meet the demand for middle distillate fuel oils suitable for extremely low temperatures, which has become particularly high in the second half of this century because of the development of jet aircraft engines as well as the high level of industrial and military activity in the arctic regions. In recent years pour depressant or flow improving additives have become of great assistance in fulfilling this objective. Although they did not prevent wax separation at lower temperatures, they modified the structure of the crystals to such degree that wax-cloudy fuels could be used to perform satisfactorily.

DESCRIPTION OF THE PRIOR ART

It is known in the prior art to employ a pour point depressant or flow improver of the type comprising a copolymer of ethylene with another ethylenically unsaturated monomer, such as an unsaturated ester or another alpha olefin, wherein the ethylene forms a backbone along which there are randomly distributed side chains consisting of hydrocarbon groups or of oxy-substituted hydrocarbon groups of up to 16 carbon atoms. The use of copolymers of ethylene and polar monomers such as vinyl esters, acrylate esters or methacrylate esters, and the like to lower the pour point and improve the flowability of middle distillate fuels at low temperatures is well known in the art. See for example U.S. Pats. Nos. 3,037,850, 3,048,079, 3,069,245, 3,093,623, and 3,236,612.

REFERENCE TO CO-PENDING APPLICATION

It is taught in the application of Nicholas Feldman and Wladimir Philippoff, Ser. No. 807,953, having the same filing date as the present application, that an amorphous, normally solid, essentially saturated hydrocarbon fraction, obtained from a residual petroleum oil, said fraction being substantially free of normal paraffinic hydrocarbons and having a number average molecular weight within the range of about 600 to 3000, when added to a middle distillate petroleum fuel oil in a concentration of about 0.01 to about 3 wt. % will depress the pour point of the fuel oil to some extent and will also improve the low temperature flowability of the said petroleum fuel oil. It is that type of hydrocarbon that is used in lower concentrations as one component of the additive combination of the present invention.

DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has been found that the response of a petroleum middle distillate fuel oil, that contains constituents derived from a paraffinic crude oil, to a flow improver, particularly one of the type comprising a copolymer of ethylene and another unsaturated monomer, can be improved by incorporating into the fuel oil along with the said flow improver a small concentration of an essentially saturated hydrocarbon fraction that is substantially free of normal paraffin hydrocarbons, i.e., contains no more than about 5 wt. %, and preferably no more than about 1 wt. % of normal paraffin hydrocarbons, and that has a number average molecular weight in the range of about 600 to about 3,000. More specifically, there are added to a waxy middle distillate petroleum fuel from about 0.001 to about 1 wt. %, more generally about 0.01 to about 0.1 wt. %, of said copolymer flow improver and from about 0.001 to about 0.099 wt. %, preferably 0.01 to 0.099 wt. %, of said hydrocarbon fraction. These weight percents are based on the total fuel composition. Normally it is desired to add to said fuel oil sufficient of said hydrocarbon fraction so that said hydrocarbon fraction becomes insoluble in the fuel oil at a temperature higher than the temperature at which the paraffin wax that is originally present in the fuel oil normally begins to separate.

Usually the weight percent of added high molecular-weight normal-paraffin-free hydrocarbon fraction will not exceed the weight percent of added copolymer flow improver, and will

usually be less, e.g., from about one one-hundredth to about three-fourth of the amount of added flow improver.

The distillate fuel oils that can be improved by this invention include those having boiling ranges within the limits of about 250° to about 700° F. The distillate fuel oil can comprise straight run distillate or cracked distillate or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. These distillate fuels, before they are improved by the present invention, will contain normal paraffins within the range of about 10 and about 32 carbon atoms, although not necessarily all of the normal paraffins in that range.

The most common petroleum middle distillate fuels are kerosene, diesel fuels, jet fuels and heating oils. The low temperature flow problem is most usually encountered with diesel fuels and heating oils. A representative Number 2 heating oil specification calls for a 10 percent distillation point no higher than about 440° F., a 50 percent point no higher than about 520° F., and a 90 percent point of at least 540° F. and no higher than about 640° to 650° F. Heating oils are preferably made of a blend of virgin distillate, e.g., gas oil, naphtha, etc., and cracked distillates, e.g., catalytic cycle stock.

The pour point depressants or flow improvers that are employed in this invention are of the type comprising a copolymer of ethylene and at least one second unsaturated monomer. The second monomer can be another alpha olefin, e.g., a C₃ to C₁₆ alpha olefin, or it can be an unsaturated ester, as for example vinyl acetate, vinyl butyrate, vinyl propionate, lauryl methacrylate, ethyl acrylate, di-lauroyl fumarate, diethyl maleate, or the like. (See Canadian Patents 676,875 and 695,679.) Other monomers include N-vinyl pyrrolidone (See Canadian Patents 658,216). The second monomer can also be a mixture of an unsaturated mono or diester and a branched or straight chain alpha monoolefin. Mixtures of copolymers can also be used, as for example mixtures of a copolymer of ethylene and vinyl acetate with an alkylated polystyrene or acylated polystyrene (see U.S. Pats. Nos. 3,037,850 and 3,069,245).

Stated more generally, a copolymer pour depressant useful in this invention will consist essentially of about three to 40, and preferably three to 20, molar proportions of ethylene per molar proportion of the ethylenically unsaturated monomer, which latter monomer can be a single monomer or a mixture of such monomers in any proportion, said polymer being oil-soluble and having a number average molecular weight in the range of about 1,000 to 50,000, preferably about 1,500 to about 5,000 number average molecular weight. Molecular weights can be measured by vapor phase osmometry, for example, by using a Mechrolab Vapor Phase Osmometer Model 310A. Cryoscopic methods of molecular weight determination can also be used.

The monomers, copolymerizable with ethylene, include unsaturated esters of monocarboxylic acids with the double bonds being located either in the alcoholic or acidic moiety, unsaturated acids, acid anhydrides, and mono and diesters of dicarboxylic acids of the general formula:



wherein R₁ is hydrogen or methyl, R₂ is a —OOCR₄ or —COOR₄ group wherein R₄ is hydrogen or a C₁ to C₁₆, preferably a C₁ to C₄, straight or branched chain alkyl group and R₃ is hydrogen or —COOR₄. The monomer, when R₁ and R₃ are hydrogen and R₂ is —OOCR₄ includes vinyl alcohol esters of C₂ to C₁₇ monocarboxylic acids. Examples of such esters include vinyl acetate, vinyl isobutyrate, vinyl laurate, vinyl myristate, vinyl palmitate, etc. When R₂ is —COOR₄ such esters include C₈ Oxo alcohol acrylate, methyl acrylate,

methyl methacrylate, lauryl acrylate, isobutyl methacrylate, palmityl methacrylate, C₁₃ Oxo alcohol esters of methacrylic acid, etc. Examples of monomers where R₁ is hydrogen and R₂ and R₃ are —OOCR₄ groups, include mono C₁₃ Oxo alcohol fumarate, di-C₁₃ Oxo alcohol fumarate, di-isopropyl maleate, di-lauryl fumarate, ethyl methyl fumarate, etc.

Other unsaturated monomers copolymerizable with ethylene to prepare pour point depressants or flow improvers useful in this invention include C₃ to C₁₆ branched chain or straight-chain alpha monoolefins, as for example, propylene, n-octene-1, 2-ethyl decene-1, n-decene-1, etc.

Small proportions, e.g., about 1 to 20 mole percent, of a third monomer, or even of a fourth monomer, can also be included in the copolymers, as for example a C₃ to C₁₆ branched or straight chain alpha monoolefin, e.g., propylene, n-octene-1, n-decene-1, etc.

The copolymers that are formed are random copolymers consisting primarily of an ethylene polymer backbone along which are distributed side chains of hydrocarbon or oxy-substituted hydrocarbon.

The Oxo alcohols used in preparing the esters mentioned above are isomeric mixtures of branched chain aliphatic primary alcohols prepared from olefins, such as oligomers of C₃ to C₄ monoolefins, reacted with carbon monoxide and hydrogen in the presence of a cobalt-containing catalyst such as cobalt carbonyl, at temperatures of about 300° to 400° F., under pressures of about 1,000 to 3,000 psi., to form aldehydes. The resulting aldehyde product is then hydrogenated to form the Oxo alcohol, the latter being recovered by distillation from the hydrogenated product.

Any of the known methods for polymer preparation can be used in preparing the copolymer flow improver or pour depressants, including the techniques taught for ethylene-vinyl ester polymerizations in U.S. Pat. Nos. 3,048,479, 3,131,168, 3,093,623 and 3,254,063. However, a particularly useful technique is as follows: Solvent and a portion (e.g., 5 to 50 percent of the total amount to be reacted) of each of the unsaturated monomers, that is to be copolymerized with the ethylene are charged to a stainless steel pressure vessel which is equipped with a stirrer. The temperature of the pressure vessel is then brought to reaction temperature and pressured to the desired pressure with ethylene. Then an initiator, which can be dissolved in a solvent to aid in handling, and additional amounts of the co-monomer or co-monomers are added to the vessel periodically or continuously during the reaction time. Also during this reaction time, as ethylene is consumed in the polymerization, additional ethylene is supplied through a pressure controlling regulator so as to maintain the desired reaction pressure fairly constant at all times. Following the completion of the reaction, the solvent and other volatile constituents of the reacted mixture are stripped from the contents of the pressure vessel, leaving the polymer as residue. In general, based upon 100 parts by weight of polymer to be produced, about 100 to 600 parts by weight of solvent, and about one to 20 parts by weight of catalyst, will be used.

The initiator, or promoter, will generally be of the free radical type, including organic peroxide types such as benzoyl peroxide, diacetyl peroxide, ditertiary butyl peroxide, dicumyl peroxide, tertiary butyl perbenzoate, di-lauroyl peroxide, t-butyl hydroperoxide, and also such non-peroxy compounds as azo-bis-isobutyronitrile, and the like.

The solvent can be any non-reactive organic solvent for furnishing a liquid phase reaction, preferably a hydrocarbon solvent such as benzene, hexane, or the like. The solvent should, of course, be one that will not destroy radicals formed from the initiator or otherwise interfere with the reaction.

Temperatures and pressures employed may vary widely. For example, depending primarily on the half life time of the promoter, the temperature can range from 100° to 450° F., with pressures of 500 to 30,000 psig. However, usually the temperature will range between about 160° and about 350° F. Relatively moderate pressures of 700 to about 3,000 psig. will be used with vinyl esters such as vinyl acetate, whereas with

esters that have a lower reactivity to ethylene, such as methyl methacrylate, somewhat higher pressures, e.g., 3,000 to 10,000 psig. are more satisfactory. A superatmospheric pressure is employed which is sufficient to maintain the desired concentration of ethylene in solution in the solvent. In general, this pressure is attained by maintaining a continuous supply of high pressure ethylene into the reactor through a pressure regulator. The time of reaction will generally be within 1 to 10 hours, the reaction time being usually inter-related with the reaction temperature and pressure, and will also vary with the particular initiator used.

The specific copolymer of ethylene and vinyl ester used in the working examples of the invention, and referred to as flow improver A, consisted of about 65 wt. % of ethylene and about 35 wt. % of vinyl acetate, and the copolymer had a number average molecular weight of about 2,000 as measured by vapor phase osmometry. The copolymer was prepared by copolymerizing ethylene and vinyl acetate, using di-tertiary-butyl peroxide initiators, etc. (See Belgium Patent 673,566, and French Patent 1,461,008).

A typical preparation of this copolymer is as follows:

A 3-liter stirred autoclave is charged with 1,150 ml. of benzene as solvent and 40 ml. of vinyl acetate. The vapor space of the autoclave is first purged with a stream of nitrogen, followed by a stream of ethylene. The autoclave is heated to about 300° F. while ethylene is pressured into the autoclave until a pressure of 950 psig. is reached. Then, while maintaining a temperature of about 300° F. and 950 psig. pressure, 90 ml./hr. of vinyl acetate and 30 ml./hr. of a solution consisting of 23 vol. % t-butyl peroxide dissolved in 77 vol. % of benzene, are continuously pumped into the autoclave at an even rate. Vinyl acetate is injected over about 135 minutes, while the peroxide solution is injected into the reactor over a period of about 150 minutes from the start of the injection. After the last of the peroxide solution is injected, the batch is maintained at 300° F. for an additional 15 minutes. Then, the temperature of the reactor contents is lowered to about 140° F., the reactor is depressured, and the contents are discharged from the autoclave. The emptied reactor is rinsed with 1 liter of warm benzene (at about 120° F.) which is added to the product. The product mixture is then stripped of the solvent and unreacted monomers by blowing nitrogen through it while it is heated on a steam bath.

Flow improver B is a copolymer of 22 wt. % vinyl acetate, 8 wt. % of C₁₃ Oxo alcohol diesters of fumaric acid, and 70 wt. % of ethylene, the copolymer having a number average molecular weight of 2,400 as measured by vapor phase osmometry.

The copolymer pour point depressants or flow improvers can be employed in conjunction with other additives commonly used in distillate fuels, including rust inhibitors, antioxidants, sludge dispersants, demulsifying agents, haze inhibitors, dyes, etc.

The fractions of essentially saturated hydrocarbons that are used in accordance with the present invention in conjunction with the copolymer pour point depressants are generally amorphous solid materials having melting points within the range of about 80° to 140° F. and having number average molecular weights within the range of about 600 to about 3,000. This molecular weight range is above the highest molecular weight of any hydrocarbons that are naturally present in the fuel oil.

An amorphous hydrocarbon fraction that is useful in accordance with this invention can be obtained by deasphalting a residual petroleum fraction and then adding a solvent such as propane to the deasphalted residuum, lowering the temperature of the solvent-diluted residuum and recovering the desired solid or semi-solid amorphous material by precipitation at a low temperature, followed by filtration. The residual oil fractions from which the desired hydrocarbons are obtained will have viscosities of at least 125 SUS at 210° F. Most of these residual oils are commonly referred to as bright stocks.

In some instances products obtained by this procedure will be naturally low in normal paraffin hydrocarbons and can be used in the present invention without further treatment. For example, low temperature propane treatment of a deasphalted residual oil from certain Texas coastal crudes a precipitated high molecular weight amorphous fraction can be obtained which has only a trace of normal paraffins, about 5 percent of isoparaffins, about 73 percent of cycloparaffins and about 22 percent of aromatic hydrocarbons. In other instances it is necessary to treat the high molecular weight fraction in some manner to reduce its content of normal paraffins. Removal of normal paraffins from an amorphous hydrocarbon mixture can be effected by complexing with urea, as will be illustrated hereinafter in one of the examples. Solvent extraction procedures can also be used, but in many instances they are not as effective as complexing techniques. Thus the amorphous hydrocarbon mixture can be dissolved in a ketone, e.g., methyl ethyl ketone, at its boiling point and then when the solution is cooled to room temperature the normal paraffins will be predominantly precipitated and the resultant supernatant solution will give a mixture containing some normal paraffins but predominating in cycloparaffins and isoparaffins.

The nature of this invention and the manner in which it can be practiced will be more fully understood from the following examples, which include a preferred embodiment.

EXAMPLE 1

Fuel oil blends were prepared using as the base oils two separate distillate fuels identified as base fuel I and base fuel II. Base fuel I was a 100 percent straight run fuel whereas base fuel II consisted of 60 percent of straight run stocks and 40 percent of cracked stocks. More specifically, base fuel I consisted of 40 vol. % of kerosene and 60 vol. % of western Canadian virgin gas oil having a 95 percent distillation point of 635° F., while base fuel II consisted of 35 vol. % kerosene, 25 vol. % of virgin gas oil having a 95 percent distillation point of 655° F. and 40 vol. % of catalytically cracked gas oil. To each of these base fuels there were added either a small percentage of flow improver A described above, and which was a copolymer of ethylene and vinyl acetate, or a small quantity of high molecular weight hydrocarbon fraction, or both the latter fraction and the flow improver.

The added hydrocarbon fraction was an amorphous material having a melting point of 111° F. that had been obtained by propane precipitation from the deasphalted residuum of a Texas coastal crude oil. This hydrocarbon fraction was found by mass spectrographic analysis and gas chromatography to contain no more than a trace of normal paraffin hydrocarbons and consisted of 5 wt. % of isoparaffins, 22 wt. % of aromatic hydrocarbons and 73 wt. % of cycloparaffins. The number average molecular weight of this material was about 775 as determined by osmometry. The distillation characteristics of this solid hydrocarbon fraction were as follows:

Distillation

(ASTM D-1160	Vapor Temp. at 5 mm. Hg	Vapor Temp. Converted to Atmospheric Pressure
Initial BP	442° F.	754° F.
5%	590	926
10%	636	978
20%	686	1034
24%	689	1037
Only 24% would distill over		
There were 75% bottoms, and 1% loss		

Each of the blends that was prepared was subjected to a low temperature filterability test which was run as follows:

A 200 milliliter sample of the oil is cooled at a rate of 2° F. per hour until a temperature is reached that is 5° F. below the ASTM cloud point of the oil, this being the temperature at

which the flow test is conducted. The cooling rate of 2° F. per hour is the rate that is frequently encountered under natural climatic conditions. The oil is then filtered at the test temperature under a vacuum (12 inches of water below atmospheric) through a filter element that is provided with a screen. The quality of the oil is then measured in terms of the finest screen through which the 200 milliliter sample of oil will pass in no more than 25 seconds. Thus the finer the screen through which the oil will pass, the better is the oil in respect to its low temperature properties.

The composition of each blend and the low temperature filterability test results that were obtained are given in Table I which follows:

TABLE I

Filterability Test Results			
Blend	Wt. % Flow Improver A	Wt. % Amorphous Solid Hydrocarbon	Finest Screen Passing oil in 25 sec. or less
With Base Fuel I			
1	0.025	—	30 mesh
2	—	0.0125	10 mesh
3	0.0375	—	30 mesh
4	—	0.0375	30 mesh
5	0.025	0.0125	40 mesh
Blend	Wt. % Flow Improver A	Wt. % Amorphous Solid Hydrocarbon	Finest Screen Passing oil in 25 sec. or less
With Base Fuel II			
6	0.05	—	Fail 20 mesh
7	—	0.025	Fail 20 mesh
8	0.075	—	Pass 20 mesh
9	—	0.075	Fail 20 mesh
10	0.05	0.025	Pass 30 mesh

It will be noted from the data in Table I that the passage of a wax-cloudy fuel through screens as measured by the filterability test was greatly improved when a 2:1 blend by weight of flow improver A and solid hydrocarbon was incorporated in the fuel. Use of either of these two additives alone in a concentration equal to that of the mixture of the two additives resulted in a significantly lesser improvement.

Example 2

The low temperature flow properties of base fuel II, described above, are improved by adding thereto 0.06 weight percent of a 2,400 number average molecular weight copolymer of vinyl acetate, C₁₃ Oxo alcohol diesters of fumaric acid, and ethylene (flow improver B, described above), and 0.02 weight percent of the amorphous solid hydrocarbon fraction described in Example 1.

What is claimed is:

1. A wax-containing petroleum distillate fuel having a boiling range within the limits of about 250° and 700° F. which has been improved with respect to its low temperature flow properties by adding thereto:
- from about 0.001 to about 0.099 wt. % of a flow-improving amorphous, normally solid, essentially saturated hydrocarbon fraction obtained from a residual petroleum oil, said fraction being substantially free of normal paraffinic hydrocarbons and having a number average molecular weight within the range of about 600 to 3,000; and from about 0.001 to about 1 wt. % of an oil-soluble wax-modifying random copolymer of ethylene and at least one additional ethylenically unsaturated polymerizable monomer, said copolymer having an average molecular weight of from about 1,000 to 50,000 and comprising from about 3 to 40 molar proportions of ethylene per molar proportion of other monomers, said other monomers being selected from the group consisting of an alpha mono-olefin of three to 16 carbon atoms; N-vinyl pyrrolidone; and an unsaturated acid, unsaturated acid anhydride, unsaturated monoester, or unsaturated diester, of the general formula:



- wherein R₁ is hydrogen or methyl; R₂ is a —OOCR₄ or —COOR₄ group wherein R₄ is hydrogen or a C₁ to C₁₈ straight or branched chain alkyl group and R₃ is hydrogen or —COOR₄.
2. Improved petroleum distillate fuel as defined by claim 1 wherein said copolymer is a copolymer of ethylene and an unsaturated ester.
3. Improved distillate fuel as defined by claim 1 wherein said copolymer is a copolymer of ethylene and vinyl acetate.
4. Improved petroleum distillate fuel as defined by claim 1 wherein said copolymer is a terpolymer of ethylene, vinyl acetate, and aliphatic alcohol diester of fumaric acid.

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