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54 Middle distillate fuel.

57 A middle distillate fuel having added thereto deasphaltered residuum and a copolymer comprising ethylene and at least one other unsaturated monomer has improved low temperature flow properties as compared with either additive alone. The copolymer preferably is selected from the group consisting of ethylene vinyl acetate, ethylene vinyl chloride and mixtures thereof.

MIDDLE DISTILLATE FUEL

This invention is directed at the production of a fuel having improved low temperature flow properties. More specifically, the present invention is directed at improving the low temperature flow properties of a middle distillate fuel having an atmospheric boiling point ranging between about 120°C and about 450°C.

In the production of middle distillate fuels, one of the major problems encountered is the formation of relatively large wax-type crystals which may plug fuel lines and/or fuel filters. While the consumption of gasoline is projected to show little, if any, growth in most industrial countries, the consumption of middle distillate fuels, particularly diesel fuel, is expected to increase significantly. Therefore, it would be advantageous to broaden the range of middle distillates which could be utilized as fuels. However, one significant barrier to broadening the boiling range of middle distillates utilized as fuels has been the poor low temperature flow properties of the middle distillates. At low temperatures paraffinic compounds present in the middle distillates, particularly normal paraffins, tend to precipitate, forming waxy compounds which tend to plug fuel lines and fuel filters. These problems tend to be particularly acute in diesel fuel, where the fuel filters frequently have openings of about 5-50 microns in diameter.

Conventional pour depressants, such as those used in lube oils, may not be effective in fuels, since lubricating systems normally do not have filters with as fine a mesh as fuel systems.

Much work has been done on improving the low temperature flow properties of hydrocarbons, such as lubricating oils and middle distillates.

U. S. Patent No. 2,084,512 is directed at improving the pour point of a lubricating oil. This patent discloses the use of bright stocks in combination with a pour inhibitor, such as the low temperature aluminum chloride condensation of halogenated paraffin wax and naphthalene. However, it has been found that additives which are effective for pour point depression of a lube oil may not be effective for improving the low temperature flow properties of a middle distillate fuel. While acceptable pour point depression may be accomplished in a lube oil having relatively large wax crystals present, large wax crystals may plug the small pores of fuel filters.

Considerable work also has been done to develop additives for middle distillate fuels which will improve the low temperature flow properties of the fuels. U. S. Patent No. 3,660,057 discloses the addition to a middle distillate of an essentially saturated hydrocarbon fraction substantially free of normal paraffinic hydrocarbons having a number average molecular weight range of about 600 to 3,000 in combination with a copolymer of ethylene with an ethylenically unsaturated monomer, such as an unsaturated ester or an alpha-olefin. This patent

discloses in Table I that the finest screen through which the distillate fuel could be passed was a 40 mesh screen, which has openings of about 420 microns.

U. S. Patent No. 3,832,150 discloses the use of recycle cat cycle oil in combination with ethylene and vinyl acetate as a pour depressant for middle distillate fuel oil boiling in the range of about 250°F and about 670°F. While this combination of additives permits middle distillate fuel oil to flow through openings 2,250 microns in diameter, it is not believed that this combination will improve the cold flow of the distillate fuels by reducing the size of the wax crystals so as to enable them to flow through the fine mesh filters commonly found on diesel engines.

U. S. Patent No. 3,389,979 discloses the combination of ethylene vinyl acetate and a resin extracted from a hydrocarbon. While this combination is reported to improve the flow rate of hydrocarbon distillate fuels through a copper tubing it is not believed that this combination will improve the cold flow of distillates by reducing the size of the wax crystals formed to permit flow through the fine mesh filters associated with diesel engines.

U. S. Patent No. 3,640,691 discloses the use of ethylene vinyl acetate and a normal paraffinic hydrocarbon in the C₂₄-C₄₀ range for use as a flow improver in tests utilizing screens having 570 micron diameter openings. While the use of this combination may have enabled middle distillate fuel to pass through coarse screens several hundred microns in diameter, it is not believed that this combination will permit flow through the fine mesh screens of diesel engines.

Accordingly, it would be advantageous to provide an additive and a method for improving the low temperature flow properties of middle distillate fuels.

It also would be advantageous to utilize a petroleum based additive generally available at petroleum refineries for improving the low temperature flow properties of middle distillate fuels.

It also would be desirable to provide an additive which is relatively inexpensive and is readily available at many integrated refineries.

It also would be advantageous to provide an additive which could be added directly to the middle distillate product without utilizing elaborate heating and/or mixing systems.

It would be a further advantage to provide an additive which did not significantly affect the combustion properties of the fuel.

The present invention is directed at the addition to a middle distillate fuel of deasphalted residuum in combination with a copolymer to improve the low temperature flow properties of the fuel.

The present invention is directed at a wax-containing petroleum distillate fuel having a boiling range between about 120°C to about 450°C which has deasphalted residuum and a copolymer added thereto to improve its low temperature flow properties. The

copolymer preferably is selected from the group of copolymers consisting of ethylene and vinyl acetate, and ethylene and vinyl chloride.

The present invention also is directed at a method for improving the low temperature flow properties of a middle distillate fuel boiling in the range of about 120°C to about 450°C, preferably in the range of about 120°C to about 400°C, more preferably in the range of about 120°C to about 370°C, which comprises adding to the middle distillate fuel oil deasphalted residuum and a copolymer. The copolymer preferably is selected from the group of copolymers consisting of copolymers of ethylene and vinyl acetate and ethylene and vinyl chloride.

In a preferred embodiment the deasphalted residuum added to the distillate fuel comprises below about 5 weight percent of the fuel, and preferably ranges between about 1 weight percent and about 3 weight percent of the middle distillate fuel. The copolymer added to the middle distillate fuel preferably comprises below about 0.5 weight percent of the fuel and preferably ranges between about 0.02 and about 0.15 weight percent of the fuel.

The deasphalted residuum and the copolymer may be added to the distillate fuel at any point which will assure good mixing of the additive with the middle distillate fuel oil.

The present invention is directed at improvement in the low temperature flow properties of middle distillates by promoting the formation of relatively small wax crystals from the precipitated wax.

The present invention is directed at improving the cold flow properties of middle distillate fuels by the addition to the fuel of a deasphalted residuum, or deasphalted oil, and a copolymer. The copolymer preferably comprises a copolymer of ethylene and vinyl acetate and/or ethylene and vinyl chloride.

As used herein, the term "middle distillate fuels" refers to fuels having an atmospheric boiling point ranging between about 120°C and about 450°C, preferably between about 120°C and about 400°C, and more preferably between about 120°C and about 370°C. Commonly used middle distillate fuels comprise diesel fuel, Number 2 fuel oil, kerosene, and turbine fuel. The term "deasphalted residuum" or "deasphalted oil" refers to hydrocarbon bottoms from an atmospheric and/or vacuum pipestill which have had the asphaltenic components at least partially removed. Methods for producing a deasphalted residuum are well-known in the art and do not form a part of this invention. Deasphalting commonly is conducted by contacting the residuum with an alkane solvent selected from the group consisting of propane, butane, pentane and hexane. While the deasphalting process normally reduces the Conradson carbon content and the metals content of the deasphalted oil significantly, the actual degree to which these are removed by the deasphalting process will be a function of many factors, including the crude

processed, the Conradson carbon content and metals content of the residuum, the solvent utilized, the feed throughput rate and the solvent addition rate.

Although much work has been directed at the use of compounds to depress the pour point of middle distillate fuels, pour point depressant tests have not been particularly useful in predicting the performance of middle distillate fuels at low temperatures. While the pour point measures the lowest temperature at which a fuel may still flow, it has been found that this measure of a fuel is not a reliable indication of the degree to which the fuel will flow through the relatively small pores of a fuel filter. Since the openings in an automobile fuel filter typically may range between about 5 and about 50 microns, and the openings in screens of fuel heating systems may range between about 400 and about 1,000 microns, it is essential that the crystals of wax formed, if any, be relatively small so that they do not plug the openings in the filters.

A test has been devised which has been found to be a relatively accurate indicator of cold flow performance of fuels in passing through filter media. In this test, designated as the Low Temperature Filterability Test (LTFT), 200 ml of the test fuel is cooled at a rate of 2°F/hour to the desired test temperature and subsequently passed through a screen having openings of 17 microns diameter under a vacuum of 20 kPa. The fuel is determined to pass the test only if all of the test fuel that can pass through the screen, passes through the screen in one minute. If any of the of test fuel that should pass through the screen has not passed through the screen in one minute,

the test is designated a failure. This test procedure is described in more detail at page C-15 in CRC Report No. 528, entitled "CRC Diesel Fuel Low Temperature Operability Field Test", September, 1983, published by Coordinating Research Counsel, Atlanta, Georgia, the disclosure of which is incorporated herein by reference.

One measure of the effectiveness of an additive in improving the low temperature flow properties of a middle distillate fuel is the degree to which the fuel flows at temperatures below the cloud point, i.e., the lower the temperature below the cloud point at which the fuel passes the LTFT test, the better the additive in improving the low temperature flow properties of the fuel. As shown in Table I below, for a diesel fuel having a 0°F cloud point, the combination of 2 weight percent deasphalted residuum in combination with 0.06 weight percent copolymer of ethylene and vinyl acetate produces acceptable LTFT results at temperatures as low as -10°F, whereas the addition of 3 weight percent deasphalted residuum, or 0.2 weight percent of ethylene and vinyl acetate copolymer alone to fuel produced unacceptable test results at only -4°F.

The diesel fuel employed had a boiling range of 171 to 343°C. The ethylene vinyl acetate copolymer had a number average molecular weight of approximately 1800.

Table I

<u>Additive</u>	<u>LTFT Results</u>				
	<u>Wt. %</u>	<u>-4°F</u>	<u>-6°F</u>	<u>-10°F</u>	<u>-14°F</u>
Ethylene & Vinyl Acetate Copolymer	0.10	Fail	Fail	-	-
Ethylene and Vinyl Acetate Copolymer	0.20	Pass	Fail	Fail	-
Deasphalted Residuum	3.0	Fail	Fail	-	-
Ethylene and Vinyl Acetate Copolymer	0.06				
+	+				
Deasphalted Residuum	2.0	-	Pass	Pass	Fail

Similarly, as shown in Table II, for the same diesel fuel as above detailed, the combination of 2 weight percent deasphalted residuum and 0.10 weight percent of a copolymer of ethylene and vinyl chloride produced satisfactory LTFT results at -14°F, whereas the use of either 3.0 weight percent of the deasphalted residuum or 0.20 weight percent of the copolymer alone produced unsatisfactory results even at -4°F.

The ethylene vinyl chloride copolymer had a number average molecular weight of approximately 2500.

Table II

Additive	Wt.%	LTFT Result			
		<u>-4°F</u>	<u>-6°F</u>	<u>-10°F</u>	<u>-14°F</u>
Ethylene and Vinyl Chloride Copolymer	0.10	Fail	Fail	-	-
Ethylene and Vinyl Chloride Copolymer	0.20	Fail	Fail	-	-
Deasphalted Residuum	3.0	Fail	Fail	-	-
Deasphalted Residuum	2.0	-	Pass	Pass	Pass
+	+				
Ethylene and Vinyl Chloride Copolymer	0.10				

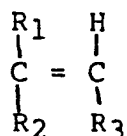
Thus, based on the data presented in Tables I and II it can be seen that the combination of the deasphalted residuum with a copolymer of ethylene and vinyl chloride and/or vinyl acetate produces a synergistic improvement in the cold flow properties of middle distillates.

The 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 unsaturated monomer can be another monoolefin, e.g., a C₃ to C₁₆ alpha-monoolefin, or it

can be an unsaturated ester, as for example vinyl acetate, vinyl butyrate, vinyl propionate, lauryl methacrylate, ethyl acrylate or the like. (See Canadian Patent Nos. 676,875 and 695,679). Other monomers include N-vinyl pyrrolidone. (See Canadian Patent No. 658,216). The second monomer can also be a mixture of unsaturated mono- or diester and a branched or straight chain alpha monoolefin. Mixtures of copolymers can also be used, as for example a mixture of a copolymer of ethylene and vinylacetate with an alkylated polystyrene or acylated polystyrene. (See U. S. Patent Nos. 3,037,850 and 3,069,245).

Stated more generally, the copolymer useful in this invention will consist essentially of about 3 to 40, and preferably 3 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 molecular weight. Molecular weights can be measured by vapor phase osmometry, for example by using a Mechrolab Vapor Phase Osmometer Model 310A.

The unsaturated monomers, copolymerizable with ethylene, include unsaturated acids, acid anhydrides, and mono- and diesters of the general formula:



wherein R_1 is hydrogen or methyl; R_2 is a ---OOCR_4 , or ---COOR_4 group wherein R_4 is hydrogen or a C_1 to C_{10} , more usually a C_1 to C_4 straight or branched chain alkyl group and R_3 is hydrogen or ---COOR_4 . The monomer, when R_1 to R_3 are hydrogen and R_2 is ---OOCR_4 includes vinyl alcohol esters of C_2 to C_{17} monocarboxylic acids. Examples of such esters include vinyl acetate, vinyl isobutyrate, vinyl laurate, vinyl myristate, vinyl palmitate, etc. When R_2 is ---COOR_4 such esters include C_8 Oxo alcohol acrylate, methyl acrylate, methyl methacrylate, lauryl acrylate, isobutyl methacrylate, palmityl alcohol ester of alpha-methyl-acrylic acid, C_{13} Oxo alcohol esters of methacrylic acid, etc. Examples of monomers wherein R_1 is hydrogen and R_2 and R_3 are ---OOCR_4 groups, include mono- C_{13} Oxo alcohol fumarate, di- C_{13} Oxo alcohol fumarate, diisopropyl maleate, dilauryl fumarate, ethyl methyl fumarate, fumaric acid, maleic acid, etc.

Other unsaturated monomers copolymerizable with ethylene to prepare pour point depressants or flow improvers useful in this invention include C_3 to C_{16} branched chain or straight-chain alpha monoolefins, as for example propylene, n-octene-1, 2-ethyldecene-1, n-decene-1, etc.

Small proportions, e.g., about 0 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 C_3 to C_{16} branched or straight chain alpha mono-olefin, e.g., propylene, n-octene-1, n-decene-1, etc. Thus, for example, a copolymer of 3 to 40 moles of ethylene with one mole of a mixture of 30 to 99 mole percent of unsaturated ester and 70 to 1 mole percent of olefin could be used.

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 concentration of each of the components added to the middle distillate fuel should be sufficiently low that it does not cause a significantly adverse effect on the combustion properties of the fuel oil. Moreover, since the cost of copolymer is substantially higher than the cost of the deasphalted residuum, the minimum quantity of copolymer should be utilized which will give the desired cold flow properties. The quantity of the deasphalted residuum added to the fuel should be maintained below about 5 weight percent, preferably within the range of about 1 weight percent to about 3 weight percent of the fuel. The quantity of the copolymer added to the fuel should generally be maintained below 0.5 weight percent, preferably within the range of about 0.02 to about 0.15 weight percent.

The point at which the deasphalted residuum and copolymer are added to the fuel is not critical. A preferred method would be to pre-mix both components and add this mixture during the final blending of the product, although it would be possible to add the components either singly or in combination at other points in the manufacture or distribution process. The preferred method would facilitate the relatively uniform distribution of the small quantity of copolymer in the fuel.

CLAIMS:

1. A wax-containing petroleum distillate fuel having a boiling range of about 120°C to about 450°C, characterized by containing, to improve its low temperature flow properties, deasphalted residuum and a copolymer comprising ethylene and at least a second unsaturated monomer, the deasphalted residuum comprising between about 1 and about 5 weight percent of the fuel.

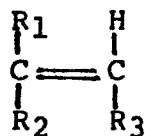
2. The fuel of claim 1 above further characterized by the deasphalted residuum content ranging between about 1 and about 3 weight percent of the fuel.

3. The fuel of either claim 1 or claim 2 above further characterized by the copolymer content being below about 0.5 weight percent of the fuel.

4. The fuel of any of claims 1-3 above further characterized by the concentration of copolymer in the fuel ranging between about 0.02 and about 0.15 weight percent of the fuel.

5. The fuel of any of claims 1-4 above further characterized by the copolymer comprising ethylene and at least one second unsaturated monomer.

6. The fuel of any of claims 1-5 above further characterized by the second unsaturated monomer being selected from the group consisting of unsaturated acids, acid anhydrides, mono- and diesters and mixtures thereof of the general formula:



wherein:

R_1 is hydrogen or methyl;

R_2 is a ---OOCR₄ or COOR₄ group wherein R_4 is hydrogen or a C₁-C₁₀ straight chain alkyl group; and

R_3 is hydrogen or COOR₄.

7. The fuel of any of claims 1-6 above further characterized by the second unsaturated monomer being selected from the group consisting of C₃-C₁₆ branched chain alpha monoolefins, C₃-C₁₆ straight chain monoolefins and mixtures thereof.

8. The fuel of any of claims 1-7 above further characterized by the copolymer being selected from the group of copolymers consisting of ethylene-vinyl acetate, ethylene-vinyl chloride, and mixtures thereof.

9. A method for improving the low temperature flow properties of middle distillate fuel boiling in the range 120 to 450°C, preferably 120 to 370°C, characterized by adding (i) between about 1 and about 5 weight percent deasphalted residuum and (ii) a copolymer comprising ethylene and a second unsaturated monomer to the fuel.

10. The method of claim 9 above wherein the copolymer added to the fuel ranges between about 0.02 and about 0.15 weight percent of the fuel.