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3,846,093
MIDDLE DISTILLATE FUEL CONTAINING ADDITIVE COMBINATION PROVIDING IMPROVED FILTERABILITY
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No Drawing. Continuation-in-part of abandoned application Ser. No. 157,615, June 28, 1971, which is a continuation-in-part of application Ser. No. 807,953, Mar. 17, 1969, now Patent No. 3,660,058. This application June 4, 1973, Ser. No. 366,538
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ABSTRACT OF THE DISCLOSURE

The low temperature filterability of a middle distillate petroleum fuel boiling within the range of about 250° and about 700° F. at atmospheric pressure is improved by adding to the fuel an essentially saturated amorphous normally solid hydrocarbon fraction that is substantially free of normal paraffin hydrocarbons, and that has an average molecular weight within the range of about 475 and about 3000, together with a wax-modifying additive selected from the group consisting of a polymer containing halogenated polymethylene segments and an N-aliphatic hydrocarbyl succinamic acid or a derivative thereof.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 157,615, filed June 28, 1971, now abandoned, which in turn was a continuation-in-part of application Ser. No. 807,953, filed Mar. 17, 1969, now U.S. Pat. 3,660,058.

FIELD OF THE INVENTION

Heating oils and other middle distillate petroleum fuels, e.g., diesel fuels, contain normal paraffin hydrocarbon waxes which, at low temperatures, tend to precipitate in large crystals in such a way as to set up a gel structure which causes the fuel to lose its fluidity. The lowest temperature at which the fuel 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 for depressing the pour point of the fuel oil. One function of such pour point depressants has been to change the nature of the crystals that precipitate from the fuel oil, thereby reducing the tendency of the wax crystals to set into a gel. Small size crystals are desirable so that the precipitated wax will not clog the fine mesh screens that are provided in fuel transportation, storage, and dispensing equipment. The pour point of a petroleum fuel oil is not the only measure of the flowability of that fuel at low temperatures; an equally important factor is the low temperature filterability of the fuel, i.e., its ability to pass through a filter. It is thus desirable to obtain not only fuel oils with low pour points, but also oils that will form small wax crystals so that the clogging of filters will not impair the flow of the fuel at low operating temperatures.

DESCRIPTION OF THE PRIOR ART

It is known in the prior art to employ various polymeric and copolymeric materials as pour point depressants for wax-containing petroleum fractions. Chlorinated polymers

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of ethylene are taught for this purpose in U.S. Pat. 3,337,313. The use of an alkenyl succinamic acid that is disubstituted on the nitrogen atom, or of the amine salts of such acids, and the use of such acids or their salts in combination with a low molecular weight ethylene-olefin copolymer are taught in U.S. Pat. 3,444,082. The use of a combination of a petroleum microcrystalline wax and certain pour point depressant additives including copolymers of olefins and styrene, condensation products of naphthalene and sperm oil, or copolymers of ethylene and vinyl acetate is taught in U.S. Pats. 3,250,599 and 3,288,577. The surprisingly effective combinations of substantially normal paraffin-free hydrocarbons with the additives used in the present invention are not disclosed in the prior art.

DESCRIPTION OF THE INVENTION

In accordance with the present invention, the low temperature filterability properties of a middle distillate fuel can be improved by incorporating a combination of an amorphous hydrocarbon fraction, substantially free of normal paraffinic hydrocarbons, more specifically defined hereinafter and either a polymer containing halogenated polymethylene segments or an N-aliphatic hydrocarbyl succinamic acid or a derivative thereof. More specifically there are added to a waxy middle distillate petroleum fuel from about 0.05 to about 2.5 wt. percent of the substantially normal-paraffin-hydrocarbon-free hydrocarbon fraction and from about 0.005 to about 0.5 wt. percent of a fuel-soluble additive component selected from the group consisting of a halogenated ethylene-containing polymer with a halogen content of from about 1 to 40 wt. percent and an alkenyl succinamic acid material, both of which are more fully described below.

The distillate fuel oils that can be improved by this invention include those having atmospheric boiling ranges within the limits of about 250° F. to about 700° F. The distillate fuel oil can comprise straight run or virgin gas oil or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates.

The most common petroleum middle distillate fuels are kerosene, diesel fuels, jet fuels and heating oils. Since jet fuels are normally refined to very low pour points, there will generally be no need to apply the present invention to such fuels. The low temperature flow problem is most usually encountered with diesel fuels and with heating oils. A representative heating oil specification calls for a 10% distillation point no higher than about 440° F., a 50% point no higher than about 520° F., and a 90% point of at least 540° F. and no higher than about 640° F. to 650° F., although some specifications set the 90% point as high as 675° 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. This invention is particularly applicable to use with diesel fuels, which must be capable of passing through very fine filters at low temperatures. A representative specification for a diesel fuel includes a minimum flash point of 100° F. and 90% distillation point between 540° F. and 640° F. (See ASTM Designations D-396 and D-975).

The fractions of essentially saturated hydrocarbons that are used in the present invention in conjunction with the wax-modifying additives are generally amorphous normally 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 475 to about 3000. This molecular weight range is above the highest molecular weight of any hydrocarbons that are naturally present in a fuel oil with a final boiling point of 700° F. These fractions are characterized by being generally isoparaffinic or cycloparaffinic in nature and by being sub-

stantially free of normal paraffin hydrocarbons, that is to say, they contain no more than about 5 wt. percent, preferably 3 wt. percent or less, and most preferably no more than about one wt. percent of normal paraffin hydrocarbons. The active components of these fractions can be either isoparaffins or cycloparaffins (i.e., naphthenes) or mixtures of both types.

An amorphous hydrocarbon fraction that is useful in this invention can be obtained by deasphalting a residual petroleum fraction and then adding a solvent such as propane, lowering the temperature of the solvent-diluted residuum, and recovering the desired solid or semi-solid amorphous product by precipitation, followed by filtration. The residual oil fractions from which the desired amorphous 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, by deasphalting a residual oil from certain Texas coastal crudes and then propane treating the residual fraction, a high molecular weight fraction can be obtained which has only a trace of normal paraffins, about 5% of isoparaffins, about 73% of cycloparaffins and about 22% 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 or other complexing agents. Other techniques known to the art can also be used such as solvent extraction, but complexing techniques are usually preferable.

Vacuum distillation can also be used for the removal of normal paraffin hydrocarbons from a high molecular weight paraffinic fraction, but such a procedure requires a very high vacuum, i.e., less than 5 mm. Hg, absolute pressure, preferably a pressure below 3 mm. Hg, absolute, e.g., 2 mm. or 120 microns. If the pressure used is 5 mm. or higher, the necessary temperature for the distillation is high enough to cause cracking of the constituents, which is undesirable.

Suitable amorphous substantially non-normal-paraffin fractions in the molecular weight range of about 475 to 600 or so can be obtained as by-products in the dewaxing of solvent-extracted heavy paraffin distillates as will be shown in one of the examples in this specification.

As already stated, one type of wax-modifying or pour point depressant additive that is employed in conjunction with the substantially normal-paraffin-free fraction in the practice of the present invention comprises an oil-soluble polymer containing halogenated polymethylene segments. This polymer is an oil-soluble, halogenated, predominantly hydrocarbon material having an average molecular weight of from about 200 to about 500,000, more preferably from about 500 to 50,000. Most advantageously molecular weights are within the range of about 500 and 10,000. The average molecular weights of the polymers may be conveniently determined by means of an ebullioscope or by means of an osmometer.

The polymers that are halogenated for use in this invention are polymers of ethylene or copolymers of ethylene with other monoolefins of from 3 to 6 carbon atoms, although higher olefins in the copolymers are not excluded. Preferably, the polymer or copolymer contains from 5 to about 100 wt. percent of ethylene.

Preferably the halogenated polymers used in this invention are chlorinated polymers. The chlorination produces chlorine substituents on the polymer chain. The chlorination can be carried out by any one of several procedures, the chlorination progressing until the desired content of chlorine is reached. The optimum chlorine contents will be dependent somewhat upon the particular polymer being chlorinated. Usually the chlorinated mate-

rials will contain from about 0.2 to about 40% by weight, preferably 1 to 35% by weight and most preferably 1.5 to about 25 wt. percent of chlorine.

In one process for chlorinating a polymer, chlorine is bubbled through the molten polymer under temperature conditions within the range of about 150° to 400° F. A second process involves bubbling chlorine through the polymer suspended in an inert solvent, such as carbon tetrachloride (or other chlorinated methanes, chlorinated ethanes, and the like) under temperature conditions of at least 75° F. The rate of reaction may be accelerated by using an actinic light source. In a third process chlorine is bubbled through an aqueous suspension of the polymer. The first two processes are preferred since it is believed that in their use the chlorine contacts a greater portion of the inner polymer chain. It is to be understood that the chlorine addition includes the use of known chlorinating compounds such as sulfuryl chloride, oxalyl chloride, phosgene and the like.

In general, the polymers and techniques of chlorination most preferred are similar to those used in and described in U.S. Pat. No. 3,337,313, which is incorporated herein by reference in its entirety. One significant difference in the description in that patent is that polymers made by the Ziegler process are equally applicable for use in the present composition. Descriptions of polymerizations and polymers resulting from Ziegler type catalysts suitable for use in this invention will be found in the profuse publications in the art. U.S. 3,389,087 and U.S. 3,474,157 are representative examples of these.

Polymers for chlorination as described above are well-known in the art and are readily available commercially. Many of the usable polymers for chlorination 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.

Suitable polyethylenes for chlorination are advantageously products or by-products from the peroxide catalyzed polymerization of ethylene. 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 pressures 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.

As stated earlier, a second type of pour point depressant additive employed with the hydrocarbon fraction in the practice of the present invention comprises an aliphatic hydrocarbyl succinamic acid or a derivative thereof. The hydrocarbyl succinamic acid can for the most part be represented by the following formula:

$$R-CH-COX$$
$$CH_1-COX^1$$
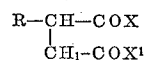
wherein R is a straight chain aliphatic hydrocarbon group having either 0 or 1 site of olefinic unsaturation (alkyl or alkenyl) attached at a secondary carbon atom to the succinyl group and is of at least 14 carbon atoms, generally in the range of 15 to 40 carbon atoms and more usually in the range of 15 to 30 carbon atoms. One of X and X^1 is hydroxyl and the other is:
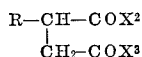
$$-NYY^1$$

wherein N has its normal meaning of nitrogen and Y and Y^1 are aliphatic hydrocarbyl groups of from 14 to 40 carbon atoms, more usually of from 15 to 30 carbon atoms, the total of Y plus Y^1 being from about 30 to 52 carbon atoms, more usually from 32 to 48 carbon atoms, and preferably, from 32 to 40 carbon atoms.

Y and Y^1 can be aliphatically saturated or aliphatically unsaturated, generally free of acetylenic unsaturation (i.e., either alkyl or alkenyl). There can be from 1 to 2 sites

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of olefinic unsaturation. Y and Y^1 may be the same or different and may be straight chain or branched chain, preferably straight chain. The branches will normally be not greater than 1 carbon atom, i.e., methyl. The position of attachment to nitrogen can be at a terminal or at an internal carbon atom.

As is evidenced from the above formula, it is not important which position the alkyl or alkenyl group has in relation to the carboxamide or carboxyl group. Because of the bulky nature of the amine, the usual method of preparation through the succinic anhydride will provide the alkenyl group β to the carboxamide as the major product. To the extent that this is the more easily accessible derivative, this derivative is preferred. However, as far as operability is concerned, either isomer or a mixture of the two isomers can be used. Individual compounds or mixtures of compounds may be used. Mixtures of different C- and/or N-substituents, both as to homologs and isomers, will frequently be employed when the individual precursors to the succinamic acid product are not readily available. Illustrative succinamic acids include: N,N-dihexadecyl hexadecylsuccinamic acid; N-hexadecyl, N-octadecyl octadecylsuccinamic acid; N,N-dihexadecenyl, C_{15-20} alkenylsuccinamic acid; N-hexadecenyl; N-eicosenyl octadecylsuccinamic acid; N,N-dioctadecenyl C_{16-18}-alkenylsuccinamic acid; etc.

As indicated previously, the succinamic acid may be used as its amine salt, preferably as a mixture of acid and amine salt. The acid or the amine salt or mixtures thereof can be represented by the following formula:

$$R—CH—COX^2$$
$$|$$
$$CH_2—COX^3$$

wherein R is as previously defined, and one of the X^2 and X^3 is $—NYY^1$ wherein Y and Y^1 are as previously defined. The other of X^2 and X^3 is of the formula:

$$—OH(NHY^2Y^3)_n$$

wherein Y^2 and Y^3 may be hydrogen, aliphatic hydrocarbon of from 1 to 30 carbon atoms or oxaliphatic hydrocarbon of from 3 to 30 carbon atoms, there being 1 ethereal oxygen atom present in the radical bonded to nitrogen at least β to the nitrogen atom. Y^2 and Y^3 may be taken together to form a heterocyclic ring of from 5 to 7 members having nitrogen and oxygen as the only heteromembers. The value of n varies from 0 to 1, preferably from 0.1 to 0.9; that is, from 10 to 90 mole percent of the succinamic acid present is in the form of its salt.

The aliphatic hydrocarbon groups are preferably saturated and if unsaturated will usually have no more than 2 sites of ethylenic unsaturation. The total number of carbon atoms for HNY^2Y^3 will be from 0 to 60, usually 1 to 40.

The groups indicated for Y and Y^1 may also be used for Y^2 and Y^3. Usually, where an amine other than the one used to prepare the succinamic acid is used to form the salt, as will be explained subsequently, there will be a mixture of salts; both the added amine and the secondary amine employed to prepare the succinamic acid will be involved in salt formation. Primary amines may be used as well as secondary amines to form the salt. Illustrative amines that can be used to form salts include di-sec-butyl amine, heptyl amine, dodecyl amine, octadecyl amine, tert-butyl amine, morpholine, diethyl amine, methoxybutylamine, methoxyhexylamine, etc.

The hydrocarbyl succinamic acids of this invention are readily prepared by reacting an alkyl or alkenyl succinic anhydride with the desired secondary amine at a temperature in the range of about 150° to 250° F. in approximately equimolar amounts, either neat or in the persence of an inert solvent. The time for the reaction is generally in the range of 15 minutes to 1 hour. This reaction is well known in the art and does not require extensive discussion here.

The alkyl or alkenyl succinic anhydride that is used

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may be an individual compound or may comprises mixtures of compounds; that is, various alkyl or alkenyl groups of differing number of carbon atoms or different positions of attachment to the succinic anhydride group may be used. Alternatively, a single isomer may be used. Since mixtures are generally more readily available, to that degree they are preferred. Frequently, use will be made of mixtures of aliphatic hydrocarbyl substituted succinic anhydrides wherein no single homolog is present in amount greater than 25 mole percent, each homolog being present in at least 5 mole percent.

Various secondary amines, both those having the same aliphatic hydrocarbon groups and those having different aliphatic hydrocarbon groups, can be used in making the succinamic acid. Either alkyl or alkenyl substituents may be present on the nitrogen, each having at least 14 carbon atoms. The range of difference between the two aliphatic hydrocarbon groups bonded at the nitrogen is not critical, but will generally be fewer than 8 carbon atoms, more usually fewer than 6 carbon atoms. For the most part, the aliphatic hydrocarbon groups will be straight chain, i.e., normal, with the amino nitrogen bonded either to internal, or to terminal carbon atoms.

It has been found that when using approximately a 1:1 mole ratio of amine to succinic anhydride, depending on the reaction conditions, a significant amount of amine may be unreacted and remain to form the salt of the succinamic acid that is formed. In some instances, as much as 30 percent of the amine may remain unreacted, forming a significant amount of salt. Thus, the salt will frequently be from 10 to 30 mole percent of the total succinamic acid present.

Also, in situations where significant amounts of water are present during the course of the reaction, the water may react with a succinic anhydride to form succinic acid. If the temperature is not high enough to regenerate the succinic anhydride, the succinic acid will probably remain unreacted or form the amine salt with available unreacted amine. Therefore, the mixtures of amic acid salts may be conveniently prepared merely by using a 1:1 mole ratio of amine to succinic anhydride, and not attempting to drive the reaction to completion, or up to a mole excess of amine.

The amine salts are readily prepared by adding the amine to the succinamic acid either as such or in an inert solvent. Mild heating may facilitate the reaction.

An optional aspect of this invention is to use, in combination with the succinamic acid component, one or more olefin polymers, particularly ethylene-olefin copolymers of from about 1000 to 100,000 molecular weight, preferably from about 1500 to 20,000 molecular weight wherein the mole ratio of ethylene to its comonomer is from about 6:1 to about 12:1.

The polymers employed in this aspect of the invention should have polyethylene segments in the polymer approximating the chain length of the wax. That is, the polyethylene segments should have from about 6 to 30 monomers on the average.

Thus the major function of the other monomer is to act as a divider between the polyethylene segments. For this reason, various monomers may be used that can be conveniently copolymerized with the ethylene. Such olefins include hydrocarbon terminal olefins and mixtures thereof of from about 3 to 30 carbon atoms, more usually of from about 10 to 30 carbon atoms and various heteroatom-containing addition polymerizable terminal olefins such as the acrylates, methacrylates, vinyl ethers, vinyl ketones, vinyl esters, dicarboxylic acids and esters, etc.
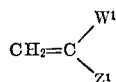
The hydrocarbon olefins that find use in the copolymers will have the following formula:

$$CH_2=C\begin{smallmatrix}W\\\\Z\end{smallmatrix}$$
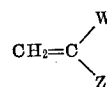
wherein W is hydrogen or methyl and Z is hydrocarbon

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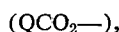of from 1 to 30 carbon atoms, more usually alkyl, Z is free of aliphatic unsaturation.

For the most part, the heteroatom-containing olefins will have the following formula:

$$CH_2=C\diagdown^{W^1}_{Z^1}$$

where W^1 is hydrogen, alkyl of from 1 to 3 carbon atoms or Z^1, and Z^1 is hydrocarbyloxycarbonyl

$$\left(\overset{O}{\underset{QO\,\overset{\|}{C}-}{}}\right)$$

where Q has from 1 to 20 carbon atoms and is aliphatically saturated hydrocarbyl, hydrocarbyloxy, acyloxy

$$(QCO_2-),$$

or hydrocarbyl carbonyl. Z^1 is free of aliphatic unsaturation.

The preferred Z^1 is acyloxy or hydrocarbyloxycarbonyl. The heteroatom-containing monomer will generally be of from 4 to 24 carbon atoms, more usually of from 4 to 20 carbon atoms, have from 1 to 2 oxygen heteroatoms, and have only one site of olefinic unsaturation as its only aliphatic unsaturation.

The method of preparation of the polymer or copolymer used with the succinamic acid component is not critical to this invention. Any convenient method for obtaining polymers of the desired molecular weight may be used. In preparing the hydrocarbon copolymers, usually non-stereospecific catalysts will be employed. Illustrative of such catalysts are triethylaluminum with vanadium oxychloride or titanium tetrachloride. These catalysts are in the category known as "Ziegler-type" catalysts. Alternatively, free radical, high pressure polymerizations may also be used.

The ratio of alkenyl succinamic acid component to other polymers will generally be about 0.25 to 10 parts of the succinamic acid or salt to 1 part of the polymer, more usually from about 2 to 8 parts of the succinamic acid component per part of polymer, preferably 3 to 6 parts of acid component to polymer.

The fuel compositions of this invention will contain from about 0.05 to about 2.5 wt. percent of the substantially normal-paraffin-free material and from about 0.005 to about 0.5 wt. percent of the other additive, i.e., the halogenated ethylene-containing polymer or the hydrocarbyl succinamic acid or its amine salt or combination of hydrocarbyl succinamic acid component and olefin polymer or copolymer as hereinabove described. The weight ratio of the two components in the combination can range from about 20:1 to 1:20, more usually from about 10:1 to 1:10 and most preferably from about 5:1 to 1:5. Although the separate components can be blended directly into the fuel by simple mixing it will frequently be found desirable to prepare a concentrate by first associating each component with a separate solvent or by dissolving the two components in a common solvent. For example, heavy solvent naphtha or a similar solvent of aromatic character can be employed. The concentrates can contain from 5 to 60 wt. percent of total additives.

This invention will be further understood when reference is made to the following examples which include preferred embodiments.

EXAMPLE 1

In this Example and in Examples 2, 3 and 4, the essentially saturated hydrocarbon substantially normal-paraffin-free fraction that was used was an amorphous solid hydrocarbon fraction having a melting point of 111° F. that had been obtained by propane precipitation from a deasphalted residuum of a Texas coastal crude oil. This hydrocarbon fraction was found by mass spectrographic analysis, and by gas chromatography, to contain 5 wt. percent of isoparaffins, 22 wt. percent of aromatic hydro-

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carbons, 73 wt. percent of cycloparaffins, and no more than a trace of normal paraffin hydrocarbons. The number average molecular weight of this material was about 775 as determined by osmometry. The distillation characteristics of this solid amorphous hydrocarbon fraction were as follows:

(ASTM D–1160)	Vapor temp. at 5 mm. Hg., ° F.	Vapor temp. converted to atmospheric pressure, ° F.
Initial B.P.	442	754
5%	590	926
10%	636	978
20%	686	1,034
24%	689	1,037

Only 24% would distill over. There were 75% bottoms, and 1% loss.

To evaluate the additive combinations of this invention, blends were prepared in a diesel fuel having the following inspection data:

ASTM Cloud Point	° F.	+7
API Gravity at 60° F.		32.1
Flash Point	° F.	182
10% Distillation at	° F.	460
50% Distillation at	° F.	526
FBP Distillation at	° F.	643

The diesel fuel and blends of additives in the fuel were evaluated for their low temperature flow properties by testing them in a low temperature filterability test called the Imperial Filterability Test (IFT). The IFT is carried out as follows:

A 200 milliliter sample of the oil is cooled at a controlled rate of 4° F. per hour until a temperature of −10° F. is reached, this being the temperature at which the flow test is conducted. The oil is then filtered through a U.S. 270 mesh screen at the test temperature, and the volume percentage of oil that passes through the screen at the end of 25 seconds is then measured. If at least 90% of the oil has gone through the screen in more than 25 seconds, the oil is considered to pass the test. The composition of each blend and the low temperature filterability test results are given in Table I.

TABLE I

Blend Tested	Percent Oil Passing Through at −10° F.
Diesel Fuel Alone	0
Fuel +0.75% Amorphous Hydrocarbon [1]	1
Fuel +0.5% Tolad 33 [2]	1
Fuel + 0.2% Amorphous Hydrocarbon +0.15% Tolad 33	95

[1] The substantially normal-paraffin-free hydrocarbon fraction described above.

[2] Substantially ethylene-containing polymer having a number average molecular weight of 2500 and a chlorine content of 21 wt. percent. Supplied by Tretolite Division of Petrolite Co. as a 50 wt. percent concentrate in hydrocarbon oil.

It will be seen from the results given in Table I, that neither the diesel fuel alone, nor the blends containing either the chlorinated ethylene polymer alone nor the substantially normal-paraffin-free amorphous hydrocarbon fraction alone passed the IFT with a 270 mesh screen (53 micron openings) at −10 F., whereas the diesel fuel blend containing a mixture of the two additives successfully passed the test. Moreover, when the test was repeated at −10° F. with a finer screen (325 mesh; 44 micron openings) the test was again successfully passed with 95% of the oil flowing through the screen in 25 seconds.

EXAMPLE 2

Using the same diesel fuel as in Example 1, additional blends were prepared wherein instead of the chlorinated

polymer (Tolad) there was used an additive known as Oronite 301 (OR–301) which was an additive concentrate (70% active component) in which the active component was a mixture of one part of ethylene-propylene copolymer of about 1500 number average molecular weight (C_2/C_3 mole ratio of about 9 to 1) and two parts of alkenyl succinamic acid obtained from di(hydrogenated tallow) amine and alkenyl succinic anhydride from C_{15}–C_{20} alpha olefins. See Example 1 of U.S. Pat. 3,444,-082.

The diesel fuel blends were subjected to the IFT test described in Example 1, using both 270 mesh and 325 mesh screens. The results are shown in Table II which follows:

TABLE II

Blend tested	Percent oil through screen at −10° F.	
	270 mesh	325 mesh
Fuel plus 0.3% O R–301	1	
Fuel plus 0.2 wt. percent amorphous hydrocarbon	1	
Fuel plus 0.2% wt. percent amorphous hydrocarbon plus 0.1% O R–301		100

The results given in Table II show that neither the fuel blend containing only the mixed ethylene-propylene copolymer and alkenyl succinamic acid nor the fuel blend containing only the substantially normal-paraffin-free hydrocarbon fraction could pass the IFT at −10° F. with a 270 mesh screen. On the other hand the fuel blend containing the two types of additives in combination successfully passed the test even when using the finer 325 mesh screen.

The above test results demonstrate that when a diesel fuel must be used in equipment utilizing a filter which has a porosity of about 50 microns, it will still be usable at temperatures below its cloud point because the wax crystal size can be effectively reduced with the additive combinations of the invention in order to enable the resulting wax-containing oil to pass through even very, very fine filters.

EXAMPLE 3

The following test results show that the alkenyl succinamic acid alone in the absence of the ethylene-propylene copolymer is effective in combination with the substantially normal-paraffin-free amorphous hydrocarbon fraction of this invention.

Using conventional dialysis separation techniques, the alkenyl succinamic acid/ethylene-propylene polymer concentrate (OR–301) described in Example 2 was separated into alkenyl succinamic acid and ethylene-propylene polymer fractions.

Blends utilizing the same diesel fuel base that was used in the blends of Example 1 were prepared and subjected to the IFT test. The results are summarized below in Table III.

TABLE III

Blend tested	Percent recovery in IFT with 270 mesh screen	
	−10° F.	−15° F.
Fuel plus 0.2 wt. percent amorphous hydrocarbon [1] plus 0.05 O R–301 [2]	100	100
Fuel plus 0.2 wt. percent amorphous hydrocarbon plus 0.05% succinamic acid [3]	100	100
Fuel plus 0.2 wt. percent amorphous hydrocarbon plus 0.05% copolymer [4]	0	0

[1] The essentially saturated substantially normal-paraffin-free hydrocarbon fraction described in Example 1.
[2] The concentrate containing both the succinamic acid and the copolymer.
[3] Separated from O R–301 as described.
[4] The ethylene-propylene copolymer separated from O R–301 as described.

The data in Table III show that the succinamic acid portion of the OR–301 concentrate worked very effectively in combination with the substantially normal-paraffin-free hy-

drocarbon fraction even though the ethylene-propylene copolymer was not present. They also show that the copolymer was not the active component of OR–301 concentrate.

EXAMPLE 4

An additive combination of this invention was tested under actual field conditions in five diesel-engine-powered trucks during an eleven-week season when the average weekly ambient temperatures ranged from +19° F. to −9° F. and where the lowest weekly temperatures during the same period stayed between −4° F. and −42° F. In keeping with standard practice each truck was fitted with an electrical water jacket heater to maintain the crankcase oil at sufficiently high temperatures to permit adequate cranking speeds for cold weather starting. The refueling of each truck was conducted in a heated garage in order to make sure that the temperature of the fuel would be above its cloud point at the start of the test. This procedure simulated refueling at a truck stop where the fuel would be pumped from underground storage and be free of separated wax. The fuel tanks of each truck were filled with a test fuel and the trucks were parked outside overnight with their water jacket heaters plugged into an outdoor electrical outlet. In the early morning after an overnight cold soak period of approximately 16 hours each truck was started with the aid of an ether spray and the trucks were idled for approximately 20 minutes to warm up. If this sequence of testing proved successful the truck was hitched to a loaded trailer and taken over the road for 45 or 60 minutes. Fuel temperature and fuel line pressure readings were regularly monitored and reached during each test sequence. A test run was considered a pass if the truck operated satisfactorily under fuel load conditions. If the truck could not be started or the engine stalled at any time, or if the truck could not be operated under full load conditions with adequate power, or even if the truck operation appeared to be satisfactory but fuel line pressure readings indicated incipient wax plugging at the filters, the run was recorded as a fail. Runs were conducted at different ambient temperatures and operability limits were determined as the lowest "pass temperature" of the fuel that occurred above the highest "fail temperature." In most cases ambient temperatures were about 6 to 12° F. below the measured fuel temperatures.

The test fuel was a commercial diesel fuel having an API gravity of 34° at 60° F., an ASTM cloud point of +6° F., an ASTM pour point of −5° F. and an ASTM D–86 distillation range of 361° F. initial boiling point, 50% point of 515° F. and a final boiling point of 645° F. Satisfactory operation in any of the trucks with the diesel fuel containing no additives did not extend below a fuel temperature that equalled the cloud point of the fuel. With a blend prepared by adding to that same diesel fuel 0.1% of the OR–301 concentrate described in Example 2 along with 0.3 wt. percent of the substantially normal-paraffin-free hydrocarbon fraction described in Example 1, the fuel temperature operability limit was lowered to −10° F., i.e., 16° F. below the cloud point of the original fuel, this result being obtained in the truck that was found to be most severe with respect to lowering of operability temperatures. In other words, even lower operability temperatures were obtained with the blended fuel in the other trucks used in the tests.

EXAMPLE 5

Using the same base fuel as in Example 1, additional blends were prepared wherein in place of the hydrocarbon fraction described in Example 1 there was employed another amorphous hydrocarbon fraction identified as Hydrocarbon B having a melting point of about 115° F., and a number average molecular weight of about 513. Analysis by a silica gel separation method showed that the aromatic hydrocarbon content of this material was 7.4% and the total of normal paraffins plus isoparaffins plus naphthenic hydrocarbons was 91.6%. The total n-paraffin hydrocar-

bon content of this hydrocarbon fraction was 1.6 wt. percent. Blends were prepared using this hydrocarbon fraction in combination with the Tolad additive of Example 1 or the OR–301 additive described in Example 2. The blends were subjected to the low temperature flowability test (IFT) described in Example 1, runs being made at both —5° F. and —10° F. using a 325 mesh screen. The results obtained are given in Table IV which follows.

TABLE IV

Blend tested—diesel fuel plus indicated percentage of additive	Percent of oil through 325 mesh screen at—	
	—5° F.	—10° 0
0.2 wt. percent hydrocarbon B	0	F
0.4 wt. percent hydrocarbon B	0	0
0.3% Tolad 33	30	15
0.2% O R–301	55	20
0.2 wt. percent hydrocarbon B plus 0.15 wt. percent Tolad 33	100	95
0.2 wt. percent hydrocarbon B plus 0.10 O R–301	100	100

As shown by the data in Table IV the combinations of hydrocarbon B with either the chlorinated polymer (Tolad) or the alkenyl succinamic acid (OR–301) were very effective in improving the low temperature filterability of the diesel fuel whereas satisfactory performance was not obtained when only the individual additives were blended into the fuel.

The amorphous hydrocarbon B was obtained as a by-product in the dewaxing of a heavy vacuum gas oil from a paraffinic crude oil, the gas oil having an approximate atmospheric boiling range of about 875 to 950° F. and equivalent in lubricant viscosity range to what is known as a 400 neutral. The gas oil was phenol extracted and the raffinate was subjected to ketone dewaxing with mixed methyl ethyl ketone and methyl isobutyl ketone to a target pour point in the range of +5° to 20° F., separating wax from the mixture of oil and ketones on a rotary filter. The separated wax at this stage had an oil content of 15%. It was reslurried with additional mixed ketones at the same dewaxing temperature and refiltered, yielding more usable lubricating oil and reducing the oil content of the wax to about 5 to 8%. This wax of reduced oil content was slurried with more ketone mixture, warmed to about 80° F. and filtered. The amorphous hydrocarbon B was recovered from the filtrate by distilling off the ketones which were recovered for reuse. The wax that remained on the filter was a refined hard paraffin wax. This procedure yielded from the starting raffinate about 75 percent of lubricating oil of the desired pour point, about 10 percent of paraffin wax and about 12–15% of hydrocarbon B.

The combinations of amorphous hydrocarbon fraction and pour point depressants herein described and claimed may constitute the sole additives that are incorporated in the fuel oil compositions, or they can be employed in conjunction with other additives commonly used in distillate fuels, including rust inhibitors, antioxidants, sludge dispersants, demulsifying agents, dyes, haze suppressors, etc.

What is claimed is:

1. A petroleum distillate fuel having a boiling range within the limits of about 250° F. and about 700° F. which has been improved with respect to its low temperature flow properties by adding thereto:

(a) about 0.05 to 2.5 wt. percent of an essentially saturated amorphous normally solid petroleum hydrocarbon fraction having a melting point in the range of about 80° to 140° F. and a number average molecular weight within the range of about 475 to 3000, said hydrocarbon fraction being substantially free of normal paraffin hydrocarbons, and

(b) about 0.005 to 0.5 wt. percent of a fuel-soluble additive component selected from the group consisting of:

(i) a halogenated ethylene-containing polymer having a halogen content of from 1 to 40 wt. percent, and

(ii) a hydrocarbyl succinamic acid material of the formula:

$$R-CH-COX_2$$
$$CH_2-COX_3$$
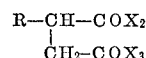
wherein R is a straight chain aliphatic hydrocarbon having from 0 to 1 site of olefinic unsaturation of from 14 to 40 carbon atoms and attached at a secondary carbon atom to the succinyl group; one of X^2 and X^3 is —NYY^1, wherein Y and Y^1 are aliphatic hydrocarbyl groups of from 14 to 40 carbon atoms, the other of X^2 and X_3 is of the formula:

$$-OH(NHY^2Y^3)_n$$

wherein n varies from 0 to 1, Y^2 and Y^3 are hydrogen, aliphatic hydrocarbon of from 1 to 30 carbon atoms or oxyaliphatic hydrocarbon of from 1 to 30 carbon atoms, and may be taken together with the nitrogen to which they are attached to form a heterocyclic ring of from 5 to 7 annular members.

2. A fuel composition as defined by claim 1 wherein the proportion of (a) and (b) is within the weight ratio range of from about 20:1 to about 1:20.

3. A fuel composition as defined by claim 1 wherein (b) is a chlorinated homopolymer of ethylene.

4. A fuel composition as defined by claim 1 wherein (b) is a chlorinated copolymer of ethylene and a C_3 to C_6 monoolefin.

5. A fuel composition as defined by claim 1 wherein (b) is a hydrocarbyl succinamic acid material wherein R is derived from mixed C_{15}–C_{20} cracked wax olefins.

6. A fuel composition as defined by claim 1 wherein, when component (b) is a hydrocarbyl succinamic acid, there is also present a copolymer of ethylene with another monomer of from 3 to 30 carbon atoms, selected from the group consisting of terminal olefins, acrylates, methacrylates, vinyl ethers, vinyl ketones, vinyl esters, dicarboxylic acids and dicarboxylic acid esters, said copolymer having a molecular weight within the range of about 1000 to 100,000 and a mole ratio of ethylene to other monomer of about 6:1 to 12:1, the ratio of succinamic acid to copolymer being about 0.25 to 10 parts of alkenyl succinamic acid or salt to one part by weight of copolymer.

7. A fuel composition as defined by claim 1 wherein said —NYY^1 group is derived from amines selected from the group consisting of:

(a) di(hydrogenated tallow) amine (C_{16}–C_{18});

(b) di(behenyl-arachidyl) amine (C_{22}–C_{24});

(c) mixtures of the foregoing.

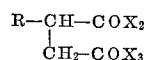8. A fuel composition as defined by claim 1 wherein said distillate fuel is a diesel fuel.

9. An additive combination having the property of improving the low temperature filterability of a petroleum distillate fuel when added thereto which comprises:

(a) an essentially saturated amorphous normally solid petroleum hydrocarbon fraction having a melting point in the range of about 80° to 140° F. and a number average molecular weight within the range of about 475 and 3000, said hydrocarbon fraction being substantially free of normal paraffin hydrocarbons, and

(b) a fuel soluble additive selected from the group consisting of:

(i) a halogenated ethylene-containing polymer having a halogen content of from 1 to 40 wt. percent, and

(ii) a hydrocarbyl succinamic acid material of the formula:

$$R-CH-COX_2$$
$$CH_2-COX_3$$

wherein R is a straight chain aliphatic hydrocar-

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bon having from 0 to 1 site of olefinic unsaturation of from 14 to 40 carbon atoms and attached at a secondary carbon atom to the succinyl group; one of X^2 and X^3 is —NYY^1, wherein Y and Y^1 are aliphatic hydrocarbyl groups of from 14 to 40 carbon atoms, the other of X^2 and X^3 is of the formula:

$$-OH(NHY^2Y^3)_n$$

wherein n varies from 0 to 1, Y^2 and Y^3 are hydrogen, aliphatic hydrocarbon of from 1 to 30 carbon atoms or oxyaliphatic hydrocarbon of from 1 to 30 carbon atoms, and may be taken together with the nitrogen to which they are attached to form a heterocyclic ring of from 5 to 7 annular members, the weight ratio of component (a) to component (b) ranging from about 20:1 to about 1:20.

10. An additive concentrate comprising from about 5 to about 60 wt. percent of the additive combination of claim 9 in an aromatic hydrocarbon solvent.

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44—63, 70, 71, 72, 80; 208—15