United States Patent [19]

Feldman

[11] **3,910,776**

[45] **Oct. 7, 1975**

[54] **ADDITIVE COMBINATION FOR COLD FLOW IMPROVEMENT OF DISTILLATE FUEL OIL**

[75] Inventor: **Nicholas Feldman,** Woodbridge, N.J.

[73] Assignee: **Exxon Research and Engineering Company,** Linden, N.J.

[22] Filed: **Aug. 9, 1974**

[21] Appl. No.: **496,004**

Related U.S. Application Data

[63] Continuation of Ser. No. 283,548, Aug. 24, 1972, abandoned.

[52] **U.S. Cl.** **44/62;** 44/70; 44/71

[51] **Int. Cl.**[2] **C10L 1/22**

[58] **Field of Search** 44/62, 70, 71, 79, 66

[56] **References Cited**

UNITED STATES PATENTS

3,245,766	4/1966	Lifson et al.	44/62
3,337,313	8/1967	Otto	44/79 X
3,444,082	5/1929	Kautsky	44/71 X
3,449,251	6/1969	Tunkel et al.	44/66 X
3,475,321	10/1929	Henselman et al.	44/62 X
3,544,467	12/1970	Kautsky	44/71 X
3,639,226	2/1972	Henselman et al.	44/62 X

FOREIGN PATENTS OR APPLICATIONS

993,744	6/1965	United Kingdom	44/80

Primary Examiner—Daniel E. Wyman
Assistant Examiner—Y. Harris-Smith
Attorney, Agent, or Firm—Frank T. Johmann; Roland A. Dexter

[57] **ABSTRACT**

Additive combinations of (A) alkyl aromatics, e.g., the condensation product of chlorinated wax and naphthalene, with: (B) ethylene-containing polymers, e.g., copolymers of about 4 to 30 molar proportions of ethylene copolymerized with an unsaturated ester, and/or (C) N-aliphatic hydrocarbyl succinamic acids and/or their amine salts, are cold flow improvers for distillate petroleum fuels.

11 Claims, No Drawings

ADDITIVE COMBINATION FOR COLD FLOW IMPROVEMENT OF DISTILLATE FUEL OIL

This is a continuation of application Ser. No. 283,548 filed Aug. 24, 1972, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a combination of an alkyl aromatic with an ethylene-containing polymer and/or a succinamic acid material for improving the cold flow properties of distillate fuel oil.

2. Description of the Prior Art

Kerosene, which is a solvent for wax, has traditionally been a component of distillate fuel oils, e.g., diesel fuels, home heating oils, etc. With the demands for kerosene for use in jet fuels, the amount of kerosene used in distillate fuel oils has decreased over the years. This, in turn, has frequently required the addition of wax crystal modifiers, e.g., pour point depressant additives, to the fuel oil to make up the lack of kerosene.

One class of such pour point depressant additives are alkylated aromatics, particularly the wax-naphthalene pour point depressants. These materials have been used in various petroleum oils, such as lubricating oils, e.g., see U.S. Pat. Nos. 1,815,022 and 2,297,292; as dewaxing aids, including use with other co-additives, e.g., see U.S. Pat. Nos. 3,417,010 and 3,475,321; and as pour depressants for middle distillate fuels, e.g., see U.S. Pat. No. 3,245,366.

Another class of pour point depressant additives are ethylene containing polymers. The more effective of these polymers for distillate fuel oil are copolymers of ethylene with other monomers, e.g., copolymers of ethylene and vinyl esters of lower fatty acids such as vinyl acetate (U.S. Pat. No. 3,048,479); copolymers of ethylene and alkyl acrylate (Canadian Pat. No. 676,875); terpolymers of ethylene with vinyl esters and alkyl fumarates (U.S. Pat. No. 3,304,261 and 3,341,309); polymers of ethylene with other lower olefins; etc. Also, homopolymers of ethylene (British Pat. Nos. 848,777 and 993,744) and chlorinated polyethylene (Belgium Pat. No. 707,371) are now known as distillate pour depressants.

Still another class of pour point depressants are N-aliphatic hydrocarbyl succinamic acid disubstituted on the nitrogen, and its amine salts as taught in U.S. Pat. Nos. 3,444,082 and 3,544,467.

SUMMARY OF THE INVENTION

The present invention is based upon finding that the combinations of (A) alkylated aromatics with: (B) ethylene-containing polymeric pour point depressants and/or (C) said N-aliphatic hydrocarbyl succinamic acid and its amine salts, are particularly effective as flow improvers in distillate fuel oils.

Many of the aforedescribed prior art materials, while very effective in lowering the pour point of distillate fuel oil, sometimes do not sufficiently reduce the particle size of the wax crystals that form. These large wax particles tend to be filtered out by the screens and other filter equipment normally used on trucks and in fuel oil storage systems, etc., with a resulting plugging of these screens and filters even though the temperature of the oil is substantially above its pour point. In general, the combinations of the invention can control

the wax crystal size more effectively then either material alone.

Because of this increased effectiveness in regulating wax crystal size, the additive combination of the invention is particularly useful in diesel fuels in view of the current tendency and desire to increase the cloud point by raising the distillation temperature. One advantage of increasing the cloud point is that the resulting fuel will then contain a larger proportion of higher molecular weight hydrocarbons which in turn, increases the BTU value of the fuel. The greater BTU value gives economies during the operation of diesel engines, for example, diesel trucks.

The wax crystal size of these fuels will frequently need to be controlled. For example, in the normal operation of diesel trucks, the diesel engine is usually provided with a fine mesh filter of about 50 microns, e.g., about equivalent to a 270 mesh screen, ahead of the engine. In cold weather when the ambient temperature is below the cloud point, it becomes especially essential that the wax crystals that form are sufficiently fine so that they will pass through any filters. As previously indicated, the present invention provides an additive combination which can be used to reduce or regulate the wax crystal size to thereby obtain improved cold flow properties.

In general, the compositions of the invention will comprise a major amount of a distillate fuel oil improved in flow characteristics by a minor, flow improving amount of: (A) an alkyl aromatic with either (B) an ethylene polymeric pour point depressant and/or (C) an N-aliphatic hydrocarbyl succinamic acid or amine salt, usually in relative ratios of 0.3 to 10, preferably 0.5 to 5, parts by weight of (A) per part by weight of (B) and/or (C).

THE DISTILLATE FUELS

In general the distillate fuel oils of the invention will boil in the range of 250° to 900°F., and will have cloud points usually from about −20°F. to about 45°F. The fuel oil can comprise straight run, or cracked gas oil, or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates, etc. 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 with heating oils.

A typical 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°F. to 650°F., although some specifications set the 90 percent point as high as 675°F.

A typical specification for a diesel fuel includes a minimum flash point of 100°F., and a 90 percent distillation point (ASTMD-1160) between 540°F. and 640°F., (See ASTM Designations D-496 and D-975).

An example of a high cloud diesel fuel is a 40°F. cloud point fuel having an initial boiling point of about 350°F., a 90 percent distillation point of about 733°F. and a final boiling point of about 847°F. (ASTM-D-1160).

(A) — THE ALKYL AROMATICS

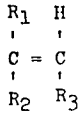
These materials are usually made by the Friedel-Crafts condensation of a halogenated paraffin or an olefin with an aromatic hydrocarbon. They are well

known in the art, primarily as lube oil pour depressants and as dewaxing aids as previously mentioned. Usually, the halogenated paraffin will contain from about 15 to about 60, e.g., 16 to about 50 carbons, and from about 5 to about 25 wt. percent, e.g., 10 to 18 wt. percent, chlorine. Typically, the halogenated paraffins are prepared by chlorinating to the above recited chlorine content a paraffin wax having a melting point within the range of about 100° to 200°F. The aromatic hydrocarbon used usually contains a maximum of three substituent groups and/or condensed rings. It may be a hydroxy compound such as phenol, cresol, xylenol, or an amine such as aniline, but is preferably naphthalene, phenanthrene or anthracene.

(B) — THE ETHYLENE CONTAINING POUR DEPRESSANT

In general, these polymeric pour depressants have a polymethylene backbone which is divided into segments by hydrocarbon or oxy-hydrocarbon side chains. These oil-soluble polymers will generally have a number average molecular weight in the range of about 500 to 50,000, preferably about 1,000 to about 5,000, as measured for example, by Vapor Pressure Osmometer, such as using a Mechrolab Vapor Pressure Osmometer Model 310A. Generally, they will comprise about 3 to 40, preferably 4 to 20, molar proportions of ethylene per molar proportion of a second ethylenically unsaturated monomer, which latter monomer can be a single monomer or a mixture of such monomers in any proportion.

The unsaturated monomers, copolymerizable with ethylene, include unsaturated 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_{16}, preferably 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 and R_3 are hydrogen and R_2 is $-OOCR_4$ includes vinyl alcohol esters of C_2 to C_{17} monocarboxylic acids, preferably C_2 to C_5 monocarboxylic acid. 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 methyl acrylate, isobutyl acrylate, methyl methacrylate, lauryl acrylate, C_{13} Oxo alcohol esters of methacrylic acid, etc. Examples of monomers where R_1 is hydrogen and R_2 and R_3 are $-COOR_4$ groups, include mono and diesters of unsaturated dicarboxylic acids such as: mono C_{13} Oxo fumarate, di-C_{13} Oxo fumarate, di-isopropyl maleate; di-lauryl fumarate; ethylmethyl fumarate; etc.

Another class of monomers that can be copolymerized with ethylene include C_3 to C_{16} alpha monoolefins, which can be either branched or unbranched, such as propylene, isobutene, n-octene-1, isooctene-1, n-decene-1, dodecene-1, etc.

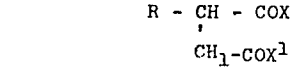
Still other monomers include vinyl chloride, although essentially the same result can be obtained by polyethylene chlorinated to contain about 5 to 35 wt. percent chlorine. Even branched polyethylene can be used per se as the pour depressant.

These polyethylene and ethylene copolymer pour depressants are generally formed using a free radical promoter, or in some cases they can be formed by thermal polymerization, or they can be formed by Ziegler type polymerization in the case of ethylene with other olefins. The polymers produced by free radical polymerization appear to be the more important and can be formed as follows: Solvent, and 0–50 wt. percent, of the total amount of monomer other than ethylene, e.g., an ester monomer, used in the batch, are charged to a stainless steel pressure vessel which is equipped with a stirrer and cooling coil. The temperature of the pressure vessel is then brought to the desired reaction temperature, e.g., 70° to 250°C., and pressured to the desired pressure with ethylene, e.g. 800 to 10,000 psig., usually 900 to 6,000 psig. Then promoter, usually diluted with the reaction solvent, and additional amounts of the second monomer, e.g., unsaturated ester, are added to the vessel continuously, or at least intermittently, during the reaction time, which continuous addition gives a more homogeneous copolymer product as compared to adding all the unsaturated ester at the beginning of the reaction. Also during this reaction time, as ethylene is consumed in the polymerization reaction, 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, usually a total reaction time of ¼ to 10 hours will suffice, the liquid products are withdrawn from the pressure vessel, and the solvent removed by stripping, leaving the polymer as residue.

(C) — THE SUCCINAMIC ACID MATERIALS

A description of these materials is given in U.S. Pat. Nos. 3,444,082 and 3,544,467, which description is as follows:

The alkenyl succinamic acids preferably (n-aliphatic hydrocarbyl) succinamic acids will, for the most part, have the following formula:



wherein R is a straight chain aliphatic hydrocarbon group having from 0 to 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, having a total of from about 30 to 52 carbon atoms, more usually of from 32 to 48 carbon atoms, and, preferably, of from 32 to 40 carbon atoms.

Y and Y^1 can be aliphatically saturated or aliphatically unsaturated, generally free of acetylenic unsaturation (alkyl or alkenyl). There may be from 1 to 2 sites 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 may be at a terminal or 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 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 may be used.

Individual compounds or mixtures of compound 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 amine salt or the acid or mixtures thereof can be represented by the following formula:

$$R - \underset{\displaystyle CH_2\text{-}COX^3}{\overset{\displaystyle |}{CH}} - COX^2$$

wherein R is as previously defined, one of the X^2 and X^3 is $-NYY^1$ wherein Y and Y^1 have been 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 (there being 1 ethereal oxygen atom present in the radical bonded to nitrogen at least β to the nitrogen atom) of from 3 to 30 carbon atoms. 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, 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 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. However, as already indicated, primary amines may be used as well as secondary amines to form the salt. 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.

Illustrative amines which may be used to form salts are di-sec-butyl amine, heptyl amine dodecyl amine, octadecyl amine, tert-butyl amine, morpholine, diethyl amine, methoxybutylamine, methoxyhexylamine, etc.

The alkyl or alkenyl 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 presence 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 anhydrides that are used may be individual compounds or 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, mixtures will be used of aliphatic hydrocarbyl substituted succinic anhydrides wherein no single homolog is present in amount greater tha **25** mole percent, each homolog being present in at least 5 mole percent.

Various secondary amines may be used, both those having the same aliphatic hydrocarbon groups and those having different aliphatic hydrocarbon groups. 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 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 is 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 which 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, conveniently as prepared, or in an inert solvent. Mild heating may facilitate the reaction.

The fuel compositions of the invention will comprise a major amount of the petroleum distillate fuel, and about 0.005 to 3 wt. percent, preferably 0.01 to 1.0 wt. percent of the additive combination of the invention. The additive combination, in turn, will comprise about 0.3 to 10, preferably 0.5 to 5 parts by weight of Component (A), i.e. the alkyl aromatic per part by weight of Component (B) and/or Component (C). Component

(B) is the ethylene polymer and Component (C) is the succinamic acid material. Concentrates of the aforesaid additive combination can also be prepared containing 3 to 60 wt. percent of the combination in a mineral oil, e.g., a distillate fuel.

The additive combination of the invention may be used alone as the sole oil additive, or in combination with other oil additives such as corrosion inhibitors; antioxidants; sludge inhibitors; etc.

The invention will be further understood by reference to the following examples which include preferred embodiments of the invention.

In carrying out the Examples, the following materials were used:

Additive A — This was a concentrate of about 50 wt. percent of a light mineral oil and about 50 wt. percent of a wax-naphthalene made from 100 parts by weight of n-paraffin wax having a melting point of about 163°F. chlorinated to about 12 wt. percent chlorine and condensed with about 8.8 parts naphthalene (Friedel-Crafts).

Additive B — This was a concentrate of about 50 wt. percent light mineral oil and about 50 wt. percent of wax-naphthalene made by Friedel-Crafts condensation of about 100 parts by weight of n-paraffin wax having a melting point of about 125°–129°F. chlorinated to about 14.5 wt. percent chlorine based on the weight of chlorinated wax, and about 12 parts by weight of naphthalene.

Additive C — This consisted of about 55 wt. percent light mineral oil and about 45 wt. percent of an ethylene-vinyl acetate random copolymer having a number average molecular weight of about 1900 as determined by Vapor Pressure Osmometry, having about 1.5 methyl terminated branches (exclusive of the methyl groups in the vinyl acetate) per 1,000 molecular weight of polymer and about 38 wt. percent vinyl acetate. The copolymer was prepared by copolymerizing ethylene and vinyl acetate with dilauroyl peroxide at a temperature of about 105°C., under about 1050 psig ethylene pressure in cyclohexane solvent. A typical laboratory preparation of this polymer is as follows:

A three liter stirred autoclave is charged with about 1000 ml. of cyclohexane as solvent and about 100 ml. of vinyl acetate. The autoclave is then purged with nitrogen and then with ethylene. The autoclave is then heated to 105°C. while ethylene is pressured into the autoclave until the pressure is raised to about 1050 psig. Then, while maintaining a temperature of 105°C. and said 1050 psig. pressure, about 160 ml/hour of vinyl acetate and about 80 ml/hour of solution consisting of 9 wt. percent di-lauroyl peroxide dissolved in 91 wt. percent cyclohexane are continuously pumped into the autoclave at an even rate. A total of 320 ml. of vinyl acetate and 11 gm. of peroxide are injected into the reactor over a period of about 2 hours. After the last of said peroxide is injected, the batch is maintained at 105°C. for an additional 10 minutes. Then, the temperature of the reactor contents is lowered to about 60°C., the reactor is depressurized, and the contents are discharged from the autoclave. The emptied reactor is rinsed with 1 liter of warm benzene (about 50°C.) which is added to the product. The product is then stripped of the solvent and unreacted monomers on a steam bath overnight by blowing nitrogen through the product.

Further examples of this class of polymers are described in Canadian Pat. No. 882,194. Details of measuring the branching on this type of polymer are given in Journal of Applied Polymer Science, Vol. 15, pp. 1737–1742 (1971).

Additive D — This was a concentrate in mineral oil of about 60 wt. percent of chlorinated polyethylene having a number average molecular weight of about 5100 and a chlorine content of 21 wt. percent.

Additive E — This was a concentrate of about 35 wt. percent mineral oil and about 65 wt. percent of active ingredient which was a mixture of (1) an ethylene-isobutyl acrylate random copolymer, having a molecular weight (VPO) of about 2000, and a relative mole ratio of ethylene to isobutyl acrylate of about 7 to 1, and (2) a succinamic acid prepared according to U.S. Pat. No. 3,544,467 — Example 1, which is the reaction product of a molar amount of a di-hydrogenated tallow amine with a molar amount of alkenyl succinic anhydride wherein the alkenyl groups are isomerized C_{15-20} monoolefins. The weight ratio of said copolymer to said succinamic acid is about 1:4.

Fuel A — This was a diesel fuel oil having a cloud point of +6°F., a pour point of −5°F., an API gravity at 60°F. of 33.9, and ASTM distillation (D-86) of 10 percent at 440°F. and 95 percent at 625°F.

Fuel B — This was a diesel fuel oil having a +10°F. cloud point, an API gravity at 60°F. of 30.7, and ASTM-D-86 distillation of 10 percent at 470°F. and 95 percent at 621°F.

Flow Test A — In this test a 200 ml. sample of oil is cooled at a rate of 4°F./hr. from 10°F. above the cloud point of the oil to either −5 or −10°F. at which temperature the oil is allowed to pass under 36 inches of water vacuum through a 270 mesh screen of 1 cm. diameter. The percent of the sample that passes through in 25 seconds is reported.

Flow Test B — This flow test was carried out in a similar manner as Flow Test A except that a 30 mesh screen was used.

Examples — Various blends of the above-noted Additives were made in said Fuels by simple mixing, followed by testing according to Flow Tests A and B. The specific blends prepared and their cold flow characteristics are summarized in the following Tables:

TABLE I

Wt. % Additive in Fuel A	% Fuel Recovery, Flow Test A with 270 mesh Screen	
	−5°F.	−10°F.
0.4% A	0	—
0.4% C	16	—
0.2% C + 0.2% A	100	—
0.6% A	—	0
0.6% C	—	12
0.5% A + 0.1% C	—	100
0.6% B	0	—
0.3% D	30	—
0.3% B + 0.15% D	100	—
0.5% A	0	—
0.25% A + 0.15% D	100	—
0.6% A	—	0
0.15% E	—	0
0.2% A + 0.06% E	—	100
None	0	0

TABLE II

Wt. % Additive in Fuel B	% Recovery in Flow Test B through 30 mesh screen at −10°F.
.10% D	100
.075% D	1
.10% C	100
.075% C	65
.006% C	3
.20% B	1
0.10% B + 0.05% D	100
0.10% B + 0.05% C	91
None	0

As seen by Tables I and II, the combinations of the invention of the wax-naphthalene lube oil pour depressant (A and B), with either the ethylene backbone pour depressants (C and D) or the succinamic acid material (E), were synergistic and more effective improving the cold flow characteristics of these fuels which were made by distillation at atmospheric pressure (i.e., atmospheric distillate oils) by attaining smaller wax crystals (as determined by the Flow Tests) than the single components alone.

What is claimed is:

1. A fuel oil improved in its cold flow characteristics comprising a major proportion of an atmospheric distillate petroleum fuel oil, and a flow improving combination of:

A. wax-aromatic lubricating oil pour point depressant which is the Friedel-Crafts condensation product of wax having a melting point of about 100° to 200°F. chlorinated to about 5 to 25 wt. percent chlorine and condensed with an aromatic in a relative weight ratio of about 5 to 15 parts of chlorinated wax per part of said aromatic, and a middle distillate fuel oil pour depressant selected from the group consisting of:

B. an ethylene backbone pour point depressant of about 500 to 50,000 number average molecular weight selected from the group consisting of:

1. branched polyethylene,
2. ethylene polymer chlorinated to contain about 5 to 35 wt. percent chlorine,
3. copolymers of 3 to 40 molar proportions of ethylene with a C_3 to C_{16} alpha monoolefin, or a monoethylenically unsaturated mono- or dialkyl ester having about 1 to 16 carbon atoms in said alkyl groups, and

C. succinamic acid composition of the formula

$$R - CH(CH_2 - COX_3) - COX_2$$

wherein R is a straight chain aliphatic hydrocarbon having from 0 to 1 sites of olefinic unsaturation 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 28 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 oil according to claim **1**, wherein said composition contains a major amount of a diesel fuel oil and said wax aromatic is wax-naphthalene.

3. A fuel oil according to claim **2**, wherein said middle distillate fuel oil pour depressant is said ethylene backbone pour point depressant, and is a copolymer of ethylene with said unsaturated ester.

4. A fuel oil according to claim **3**, wherein said unsaturated ester is a vinyl ester of a C_2 to C_{16} fatty acid.

5. A fuel oil according to claim **4**, wherein said vinyl ester is vinyl acetate.

6. A fuel oil composition according to claim **2**, wherein said middle distillate fuel oil pour depressant is said chlorinated ethylene polymer.

7. A fuel oil composition according to claim **2**, wherein said middle distillate pour point depressant is said succinamic acid composition.

8. An additive blend useful for improving the cold flow characteristics of petroleum fuel oil comprising a mixture of:

A. wax-aromatic lubricating oil pour point depressant which is the Friedel-Crafts condensation product of wax having a melting point of about 100° to 200°F. chlorinated to about 5 to 25 wt. percent chlorine and condensed with an aromatic in a relative weight ratio of about 5 to 15 parts of chlorinated wax per part of said aromatic, and a middle distillate fuel oil pour depressant selected from the group consisting of:

B. an ethylene backbone pour point depressant of about 500 to 50,000 number average molecular weight selected from the group consisting of:

1. branched polyethylene,
2. ethylene polymer chlorinated to contain about 5 to 35 wt. percent chlorine,
3. copolymers of 3 to 40 molar proportions of ethylene with a C_3 to C_{16} alpha monoolefin, or a monoethylenically unsaturated mono- or dialkyl ester having about 1 to 16 carbon atoms in said alkyl groups, and

C. succinamic acid composition of the formula

$$R - CH(CH_2 - COX_3) - COX_2$$

wherein R is a straight chain aliphatic hydrocarbon having from 0 to 1 sites of olefinic unsaturation from 14 to 40 carbon atoms and attached at a secondary carbon atoms 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 28 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 in a relative weight ratio of 0.3 to 10 parts of (A) per part by weight of (B) and/or (C).

9. An additive blend according to claim 8 which is an oil concentrate containing about 3 to 60 wt. percent total of said (A), (B) and/or (C).

10. A fuel oil improved in its cold flow characteristics comprising a major proportion of an atmospheric distillate petroleum fuel oil, and a flow improving combination of:

A. wax-aromatic lubricating oil pour point depressant which is the Friedel-Crafts condensation product of paraffin wax having a melting point of about 100° to 200°F. chlorinated to about 5 to 25 wt. percent chlorine and condensed with an aromatic in a relative weight ratio of about 5 to 15 parts of chlorinated wax per part of said aromatic, and a middle distillate fuel oil pour depressant selected from the group consisting of:

B. an ethylene backbone pour point depressant of about 500 to 50,000 number average molecular weight selected from the group consisting of:

1. ethylene polymer chlorinated to contain about 5 to 35 wt. percent chlorine, and

2. copolymers of 3 to 40 molar proportions of ethylene with a vinyl ester of a C_2 to C_5 fatty acid,

C. succinamic acid composition of the formula

$$R - \underset{|}{CH} - COX_2$$
$$CH_2 - COX_3$$

wherein R is a straight chain aliphatic hydrocarbon of from 14 to 40 carbon atoms having from 0 to 1 site of olefinic unsaturation 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 28 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, and mixtures of (B) and (C);

there being present from 0.3 to 10 parts of (A) by weight for each part by weight of (B), (C) or mixtures of (B) and (C).

11. An additive blend useful for improving the cold flow characteristics of petroleum fuel oil comprising a mixture of:

A. wax-aromatic lubricating oil pour point depressant which is the Friedel-Crafts condensation product of paraffin wax having a melting point of about 100° to 200°F. chlorinated to about 5 to 25 wt. percent chlorine and condensed with an aromatic in a relative weight ratio of about 5 to 15 parts of chlorinated wax per part of said aromatic, and a middle distillate fuel oil pour depressant selected from the group consisting of:

B. an ethylene backbone pour point depressant of about 500 to 50,000 number average molecular weight selected from the group consisting of:

1. ethylene polymer chlorinated to contain about 5 to 35 wt. percent chlorine, and

2. copolymers of 3 to 40 molar proportions of ethylene with a vinyl ester of a C_2 to C_5 fatty acid,

C. succinamic acid composition of the formula

$$R - \underset{|}{CH} - COX_2$$
$$CH_2 - COX_3$$

wherein R is a straight chain aliphatic hydrocarbon of from 14 to 40 carbon atoms having from 0 to 1 site of olefinic unsaturation 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 28 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 of 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 and mixtures of (B) and (C); there being a relative weight ratio of 0.3 to 10 parts of (A) per part by weight of (B), (C) or mixtures of (B) and (C).

* * * * *