(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 220 892
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 86308059.4

(22) Date of filing: 17.10.86

(51) Int. Cl.⁴: **C 10 L 1/22**
C 07 C 103/44, C 07 C 93/187

(30) Priority: 21.10.85 US 789815 18.12.85 US 810115

(43) Date of publication of application:
06.05.87 Bulletin 87/19

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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(54) Cold flow improving fuel additive compound and fuel composition containing same.

(57) The product of reaction between a branched chain monocarboxylic acid amide or ester, an epoxide and a carboxylic acid when added to a hydrocarbyl distillate fuel in minor effective amounts provides a fuel composition having improved cold flowability.

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Description

COLD FLOW IMPROVING FUEL ADDITIVE COMPOUND AND FUEL COMPOSITION CONTAINING SAME

The present invention is directed to cold flow improving fuel additive compound. More particularly, it is directed to an additive compound consisting of the reaction product of an amide or ester derivative of a branched-chain monocarboxylic acid having at least one tertiary-amine group, an epoxide and a carboxylic acid and to said additive compounds. It is further directed to hydrocarbyl fuel compositions containing such cold flow improving fueld additive compounds.

It is well known that distillate fuels such as diesel fuels are subject to poor flowability at low temperatures and have relatively high cold filter plugging points. Many expedients have been attempted in the prior art to overcome these adverse cold temperature properties.

U.S. Patent 4,108,613 teaches the use of a mixture of (1) the reaction product of an epoxidized alpha-olefin with a nitrogen-containing compound selected from ammonia, an amine, a polyamine or a hydroxyamine and (2) an ethylene-olefin copolymer as an additive to depress the pour point of hydrocarbonaceous fuels and oils.

U.S. Patent 3,962,104 discloses lubricating oil compositions containing minor amounts of quaternary ammonium salts useful as oil improving additives. The quaternary ammonium salts utilize a cation derived from the reaction product of one molar proportion of a tertiary amine with one or more molar proportions of an olefin oxide and an amount of water in excess of stoichiometric. The anion is derived from an organic acid and the tertiary amine has substituents which are alkyl, alkenyl, substituted alkyl, substituted alkenyl, aromatic or substituted aromatic groups.

None of these prior art materials utilize the specific branched chain acid reaction products as described below or provide a breakthrough in cold flow plugging point (CFPP) and pour point depression of distillate fuels to ensure the desired performance at low temperatures. Additionally, the materials in accordance with the invention are applicable to a wide variety of distillate (diesel) fuels whereas presently commercially available additive materials are more specific and generally work for only one or two particular fuels, not over a broad range of available fuels.

The present invention provides novel fuel additive compounds useful in improving the low temperature characteristics of distillate fuel compositions comprising the reaction product of (1) an amide or ester derivative of a branched chain monocarboxylic acid having at least one tertiary amine group, (2) an epoxide and (3) additional carboxylic acid.

This invention also provides liquid hydrocarbyl distillate fuels having improved low temperature characteristics comprising a major proportion of a liquid hydrocarbyl distillate fuel and a minor proportion, effective to improve low temperature characteristics of the fuel, of the reaction product of (1) an amide or ester derivative of a branched chain monocarboxylic acid having at least one tertiary amine group, (2) an epoxide and (3) additional carboxylic acid.

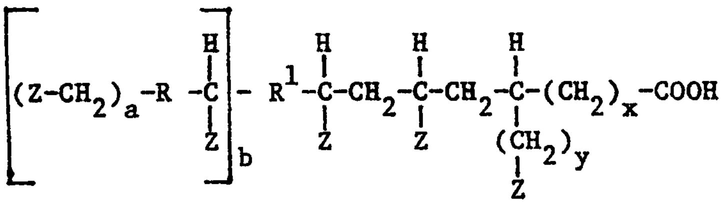
This invention further provides a method of reducing the pour point and cold flow plugging point of liquid distillate fuels, which method comprises additin to the fuel an effective amount of the reaction product of (1) an amide or ester derivative of a branched chain monocarboxylic acid having at least one tertiary amine group, (2) an epoxide and (3) additional carboxylic acid.

According to the present invention, the low temperature distillate fuel additive product or compound when added to the fuel in cold flowability effective amounts, significantly decreases the cold flow plugging point, cloud point, filterability as well as the pour point of the fuel to which it is added. Suitable fuels include, but are not limited to, diesel fuel, home heating oil, airplane jet fuel and the like.

The additive providing these properties is a product of reaction formed by the reaction of (1) an amide or ester derivative of a branched chain monocarboxylic acid having at least one t-amine group, (2) an epoxide and (3) additional carboxylic acid. The additional carboxylic acid may be the same branched chain carboxylic acid or a different branched chain acid or a linear carboxylic acid. When added to a hydrocarbyl distillate fuel, these additive products significantly decrease the fuel's pour point as well as its cold flow plugging point below the temperatures obtained by additives utilized in the prior art.

The preferred branched chain carboxylic acids are telomer acids which may be prepared by the free radical addition of one mole of acetic anhydride to at least 3 moles of hexene and/or a higher olefin having up to about 30 or more carbon atoms (C_{30}^{+}) in the presence of a trivalent manganese compound. This invention is not, however, limited to any specific method of preparing the telomer acids. Any method known in the art may be used. Preferred telomer acids are those made from C_{10}-C_{20} alpha olefins and manufactured under the trade name Kortacid through Akzo Chemie, Chicago, Illinois. Specific acids are identified for example as Kortacid T-1801, Kortacid T-1001 and the like. The first two digits give the number of carbon atoms in at least one side chain of the acid. More specifically it is noted that the monocarboxylic acid having the below structural formula is known and further identified as a telomer acid and may be formulated in accordance with a procedure provided in U.S. Patent 4,283,314 in which a compound having the same structural formula and meanings is disclosed. U.S. Patent 4,283,314 is incorporated herein by reference.

Independent of the molecular weight, it is particularly preferred that the branched chain monocarboxylic acid have the structural formula



$$\left[(Z\text{-}CH_2)_a\text{-}R\text{-}\underset{Z}{\overset{H}{C}}\right]_b\text{-}R^1\text{-}\underset{Z}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{Z}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{\underset{Z}{(CH_2)_y}}{\overset{H}{C}}\text{-}(CH_2)_x\text{-}COOH \qquad (I)$$

where Z is $-(CH_2)_nCH_3$ where n is an integer of from about 3 to about 42; x and y are different and are either 0 or 2; a is 0 or 1, if a is 0, R is hydrogen but if a is 1, R is $-CH_2$; and b is 0 or 1, if b is 0, R^1 is hydrogen but if b is 1, R^1 is $-CH_2$.

The amide or ester derivative of a branched chain monocarboxylic acid having at least one tertiary amine group has the general formula:

$R^2COXR^4N(R^5)(R^6)$

where R^2 is a branched chain monocarboxylic acid radical having a molecular weight of between 300 and 1,000; X is O or NR^3 in which R^3 is hydrogen or C_1-C_{25} alkyl; R^4 is a hydrocarbyl group of 1 to 25 carbon atoms; and R^5 and R^6 are the same or different and are C_1-C_{25} alkyl.

The amide derivative reaction product may be classified by the general formula:

$R^2CON(R^3)R^4N(R^5)(R^6)$

wherein R^2, R^3, R^4, R^5, and R^6 have the definitions given above.

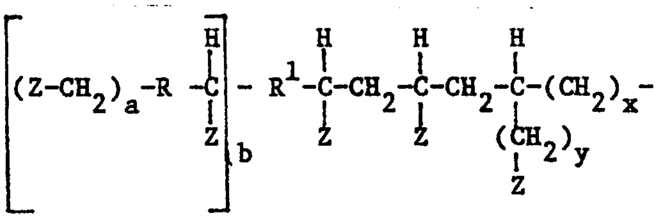
Generally speaking, the branched chain monocarboxylic acid having a molecular weight of about 300 to 1,000 may be reacted as disclosed below with a suitable diamine to produce the above described amide derivative. In a more preferred embodiment of the present invention, the branched chain monocarboxylic acid has a molecular weight of 400 to 900. Still more preferably, the molecular weight of the branched chain monocarboxylic acid is in the range of between 500 and 800.

The amide derivatives may be formed by a simple reaction between the acid and a suitable diamine such as

$RCO_2H + H_2N\text{-}CH_2CH_2CH_2N(CH_3)_2 \rightarrow$

$RCO\text{-}NH_2\text{-}CH_2CH_2CH_2N(CH_3)_2$

where R is a telomer acid radical. Any suitable diamine may be used and any conventional process known to the art may be used to provide the amide derivative. The amide derivative is thereafter reacted with an epoxide and additional carboxylic acid and is further defined by the branched chain hydrocarbyl having a molecular weight of between about 300 and 1,000. R^2, in a preferred embodiment for both amide and ester derivatives, has the structural formula



$$\left[(Z\text{-}CH_2)_a\text{-}R\text{-}\underset{Z}{\overset{H}{C}}\right]_b\text{-}R^1\text{-}\underset{Z}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{Z}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{\underset{Z}{(CH_2)_y}}{\overset{H}{C}}\text{-}(CH_2)_x\text{-}$$

where Z, R, R^1, n, a, b, x and y have the meanings given for structure (I).

Some of the useful diamines include but are not limited to N-(3-aminopropyl) morpholine, N-(2-aminoethyl) morpholine, N-(2-aminopropyl) morpholine, N,N'-bis(3-aminopropyl) piperazine, N,N-diethylethylenediamine, 3-dimethylaminopropylamine, unsymmetrical (unsym.) dimethylethylenediamine, N,N-dimethyl-N'-ethylethylenediamine and the like and mixtures of two or more of these. Especially preferred is 3-dimethylaminopropylamine. All the R groups mentioned are alkyl, nevertheless, others can be alkenyl, aryl, alkaryl, aralkyl or cycloalkyl. If aryl the group will contain 6 to 14 carbon atoms. The amines may be obtained as articles of commerce or prepared in any convenient manner.

The epoxides useful herein generally contain from 2 to about 18 carbon atoms. The epoxides may be substituted with an aromatic or a saturated or unsaturated aliphatic group. Among the preferred epoxides that may be used in the present invention are ethylene oxide, propylene oxide, styrene oxide, 1,2-epoxybutane, decene epoxide, tetradecene epoxide and octadecene epoxide and the like. It is emphasized that the above list is non-limiting. Any other epoxides, within the preferred group of epoxides having 2 to 18 carbon atoms may be advantageously used.

The ester derivatives may be formed by a simple reaction between the branched chain monocarboxylic acid (preferably telomer) and a suitable hydroxy amine such as

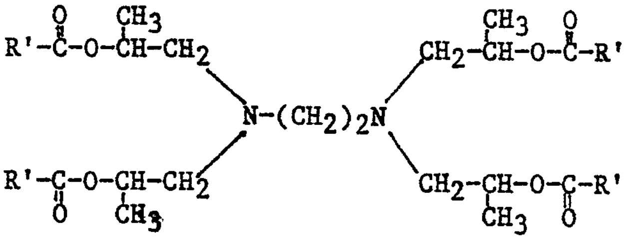
$RCO_2H + HO\text{-}CH_2CH_2CH_2N(CH_3)_2 \rightarrow$

$RCO\text{-}O\text{-}CH_2CH_2CH_2N(CH_3)_2$

where R is a telomer acid radical. Any suitable amino alcohol or hydroxy compound may be used and any conventional process known to the art may be used to provide the ester derivative. The ester derivative is thereafter reacted with an epoxide and additional carboxylic acid.

The ester derivative reaction product may be classified by the general formula
$R^2COO(R^3)N(R^5)(R^6)$ (II)
where R^2, R^3, R^5 and R^6 have the meanings given above.

Structural formula II is limited to those derivatives having only one ester group and only one tertiary amine group. However, the invention is also directed to derivatives having more than one (multiple) ester groups and more than one (multiple) tertiary amine groups. An example is:



with 4 ester groups and 2 tertiary amine groups where at least one R′ is a telomer acid radical and the remaining R′ groups may be the same or different or may be linear or branched and are from C_1 to about C_{25} hydrocarbyl or hydrogen.

Generally speaking, the branched chain monocarboxylic acid having a molecular weight of about 300 to 1,000 may be reacted as disclosed above with a suitable hydroxy amine or amino alcohol to produce the described ester derivative. In a more preferred embodiment of the present invention, the branched chain monocarboxylic acid has a molecular weight of 400 to 900. Still more preferably, the molecular weight of the branched chain monocarboxylic acid is in the range of between 500 and 800.

Some of the useful amines include but are not limited to N,N′N′-tris-(2-hydroxypropyl)N-tallowalkyl-1,3-diaminopropane, N,N,N′,N′-tetrakis(2-hydroxypropyl) ethylenediamine, N,N,N′,N′-tetrakis (2-hydroxymethyl) ethylenediamine, 3-dimethylaminopropanol, N-methyldiethanolamine and the like and mixtures of two or more of these. Especially preferred is N,N,N′,N′ tetrakis (2-hydroxypropyl) ethylenediamine. All the R groups mentioned are alkyl, nevertheless, other useful groups can be alkenyl, aryl, alkaryl, aralkyl or cycloalkyl. If aryl, the group will contain 6 to 14 carbon atoms. The amines may be obtained as articles of commerce or prepared in any convenient manner.

The product of reaction of (1) an amide or ester derivative of a telomer acid, (2) an epoxide and (3) additional carboxylic acid has been surprisingly found to improve the cold temperature performance of distillate fuels such as diesel fuels, residential fuel oils, aviation jet fuels and the like. This improved performance is manifested by significantly decreased pour point and cold filter plugging point temperatures for fuels to which additives/compounds of the present invention are added.

The various reactants are usually reacted in substantially stoichiometric amounts or equimolar amounts, however, a slight molar excess of telomer acid to other reactants may be used if desired at temperatures ranging from about 50-175°C at pressures determined by the specific reaction, i.e., autogenous in 0.5 to about 3 hours or more. It is to be understood that when the amide derivative is reacted with the epoxide and additional carboxylic acid, the additional carboxylic acid may also be a branched chain acid which may be a telomer acid that is different or the same as the acid from which the amide derivative is prepared or a linear monocarboxylic acid. The additional carboxylic acid has up to 20 or more carbon atoms, preferably 10-20.

The improved cold flow effect manifested by the additives of the present invention to distillate fuels is accomplished by providing an effective cold flow improving amount of the additive compound of the present invention to a distillate fuel. More preferably, the amount added to the distillate fuel is in the range of between about 0.01 and 3-5 percent by weight, based on the total weight of the fuel composition. Still more preferably, the concentration of the flow improving product of reaction of the present invention to the distillate fuel is in the range of between 0.02 and 2 percent by weight. In certain cases, depending, inter alia, on the particular fuel and/or weather conditions, up to about 10 wt.% may be used. Up to about 10-20 wt.% of other additives for their known purposes may also be used.

The following examples are given to illustrate the present invention. Since these examples are given for illustrative purposes only, the invention embodied therein should not be limited thereto.

A. AMIDE DERIVATIVES

EXAMPLE 1

Preparation of Amine Compound From Branched Chain Monocarboxylic Acid

Kortacid (trademark) T-1801, a branched chain monocarboxylic telomeric acid (obtained from AKZO Chemie) was reacted with 3-dimethylaminopropylamine) as follows to produce the 3-dimethylaminopropylamide of Kortacid T-1801.

Equimolar amounts of Kortacid T-1801 (111.3g, 0.164 moles) and 3-dimethylaminopropylamine (16.7g, 0.164 moles) were heated in a stirred flask at 110-115°C in the presence of benzene solvent to azeotropically remove the water formed. After about two-thirds of the calculated amount of water was collected the solvent was distilled from the flask and the temperature was slowly raised to 150° C and held for one hour. The reaction was stripped of volatile materials at 150° C for one hour under full pump vacuum. The product was filtered through a bed of diatomite and solidified to a soft brown material on cooling.

EXAMPLES 2-7

Preparation of Cold Flow Improving Additive Products/Compounds

Example 2: 30.5g. of the amide derivative formed in Example 1 was charged into a pressure vessel with 2.3g. of propylene oxide and 27.0g of Kortacid T-1801, representing equimolar amounts of the three reactants, and heated at 70-100° C until all the propylene oxide was reacted. Completion of the reaction was evidenced by loss of pressure. The pressure is autogenous, from unreacted propylene oxide, and depends on the temperature, amounts of materials present and vessel size. When the Rx (reaction) is done, pressure drops to 0 if all the propylene oxide is consumed (actually, the Rx is run under N_2 for safety, 2-5 psi of N_2 is left in the vessel at all times).

Example 3: 23.9g of the compound of Example 1 was reacted with 4.9g of 1,2-epoxydecane and 21.3g of Kortacid T-1801.

Example 4: 24.4g of the compound of Example 1, 3.8g of styrene oxide and 21.7g of Kortacid T-1801 were reacted in a pressure vessel at a temperature of 90-100° C.

Example 5: 25.2g of the compound of Example 1, 2.4g of 1,2-epoxybutane and 22.4g of Kortacid T-1801 were reacted at a temperature of 70-100° C.

Example 6: 23.1g of the compound of Example 1, 6.4g of commercial grade tetradecene epoxide and 20.5g of Kortacid T-1801 were reacted at a temperature of 70-100° C.

Example 7: 22.3g of the compound of Example 1, 7.8g of commercial grade octadecene epoxide and 19.9g of Kortacid T-1801, were reacted at a temperature of 70-100° C.

Example 5 was otherwise run as Ex. 2. All the rest (Examples 3, 4, 6 and 7) have boiling points of about 125° C and were run in an open flask at 125° C until the reaction was complete (disappearance of epoxide band in infrared). This usually took from about 0.5-1.5 hours, depending on the reactivity of the epoxide.

EVALUATION OF ADDITIVE PRODUCTS

The products made in accordance with Examples 2-7 were each blended in a typical Diesel fuel (described in Table 1) in a concentration of 0.05% by weight, based on the total weight of the Diesel fuel composition. Each of the thus modified fuel compositions were tested to determine their pour point, in accordance with ASTM Test Procedure D-99, and filterability, in accordance with the Cold Filter Plugging Point (CFPP) test, IP 309/76.

In determining the Cold Filter Plugging Point of a distillate fuel, the fuel sample is cooled under prescribed conditions and, at intervals of 1° C, a vacuum of 200 mm water gauge is applied to draw the fuel through a fine wire mesh filter. As the fuel cools below its cloud point, increasing amounts of wax crystals will be formed. These will cause the flow rate to decrease and eventually complete plugging of the filter will occur. The Cold Filter Plugging Point is defined as the highest temperature (expressed as a multiple of 1° C) at which the fuel, when cooled under the prescribed conditions, either will not flow through the filter or requires more than 60 seconds for 20 ml to pass through.

TABLE 1

Typical:	Distillation	°C (°F)
Diesel	Initial	185 (366)
Fuel	50°C	253 (487)
	End	350 (663)

API Gravity	34.8
Sulfur	0.17%
Aniline Point	54°C (130°F)

COMPARATIVE EXAMPLE 1 (CE1)

The Diesel fuel with which the additive compounds of Examples 2-7 were blended was tested to determine its pour point and CFPP. The CE1 was tested in the absence of the additives of the present invention. The test was conducted in accordance with the procedures described above. The results of these tests are included in Table 2.

Table 2 clearly reveals that the additives in accordance with the invention dramatically lower both the pour point, and the cold filter plugging point.

TABLE 2

Diesel Fuel Composition of Example No.	Epoxide Employed	Pour Pt, °C(°F)	CFPP, °C(°F)
CE1	None	-23(-10)	-19(- 3)
2	Propylene Oxide	-32(-25)	-23(-10)
4	Styrene Oxide	-34(-30)	-24(-12)
5	1,2-Epoxybutane	-34(-30)	-22(- 8)
3	C_{10} Epoxide	-34(-30)	-22(- 8)
6	C_{14} Epoxide	-34(-30)	-23(-10)
7	C_{18} Epoxide	-34(-30)	-22(- 8)

The improved low temperature characteristics of compositions (additives) in accordance with the invention is readily apparent from Table 2.

B. ESTER DERIVATIVES

BASE A

A tetraester of telomer acids was prepared from 66g Kortacid (Trade name) T-1801 (Akzo Chemie, Chicago, Illinois, and 5.7g Quadrol (BASF Wyandotte: N,N,N',N'-tetrakis [2-hydroxypropyl] ethylenediamine) at 175°C with azeotropic removal of water. The material had an acid value of 10.1.

BASE B

A triester of telomer acids and Propoduomeen T/13 (Armak: N,N',N'-(2-hydroxypropyl)-N-tallowalkyl-1,3-diaminopropane) was prepared in a similar manner from 168.2g Kortacid T-1801 and 36.3g of the aminoalcohol.

BASE C

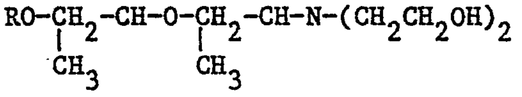
A monoester of the telomer acids was prepared from 174.5g Kortacid T-1801 and 37.6g DMAMP (Angus Chemical: an 80% aqueous solution of 3-dimethylaminopropanol) using toluene for azeotropic removal of water at 150°C.

BASE D

A diester was prepared from 188.5g Kortacid T-1801 and 16.5 N-methyldiethanolamine under similar conditions.

BASE E

A diester of Kortacid T-1801 and Texaco M-302 was prepared in a similar manner. Texaco M-302 is described as having the approximate composition:



$$\mathrm{RO{-}\underset{\displaystyle CH_3}{\underset{|}{CH_2}}{-}CH{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{CH_2}}{-}CH{-}N{-}(CH_2CH_2OH)_2}$$

$R = C_{10-12}$

EXAMPLES 8-12

Preparation of the epoxidized additives was as follows:

Equimolar amounts of the base (A through E), an epoxide as indicated in Table 3, and Kortacid (Tradename)

T-1801 were heated at 80-125°C until no free epoxide was noted by infrared analysis. For volatile epoxides, a sealed pressure vessel was used but in other cases simple stirring in an open flask was sufficient. The reaction was usually complete within two hours at 125°C; but it was often convenient to keep the propylene oxide pressure bottle reactions on a steam bath overnight. Where more than one tertiary amine group was present (Examples 8 and 9) equivalent amounts of epoxide and acid could be used for each amine. The additives were used as recovered from the reaction flask without further purification or workup.

EVALUATION

The materials described in Examples 8 to 12 were blended percent by weight) into a typical diesel fuel (Table 1) and tested for pour point (ASTM D-97), cloud point (ASTM D-2500) and filterability by the LTFT procedure described below with the results shown in Table 3. The mole ratio of tertiary amine/epoxide/acid is 1/1/1 except as otherwise noted. LTFT testing starts at -21°C (-6°F). A failure at this point indicates essentially no significant reduction from the control base oil test at 1°.

LTFT, Low Temperature Flow Test for Diesel Fuels, a filtration test under consideration by CRC (Coordination Research Council). LTFT Procedure: The test sample (200 ml) is gradually lowered to the desired testing temperature at a controlled cooling rate. After reaching that temperature the sample is removed from its cold box and filtered under vacuum through a 17 micrometer screen. If the entire sample can be filtered in less than 60 seconds it shall be considered as having passed the test. An F in this test indicates failure at the maximum acceptable temperature -21°C (-6°F). All test results are shown in Table 3.

Any suitable distillate fuel oil or diesel fuel oil may be used in accordance herewith. However, as mentioned hereinabove, fuels having an initial boiling point of about 350°F and an end point of about 675°F are preferred. The base diesel fuel used in these tests was a blend of 15% kerosene with 85% of a straight distillate having the following characteristics shown in Table 1.

TABLE 3

BASE	EPOXIDE	LTFT, °C(°F)	POUR POINT, °C(°F)	CLOUD POINT, °C(°F)
Unmodified Fuel (No Additive)		-17(1)	-23(-10)	-21(6)
A	Propylene	-22(-8)	-40(-40)	-18(0)
B	Propylene, 1/1/1	-21(-6)	-43(-45)	-18(0)
B	Propylene, 1/2/2	-22(-8)	-43(-45)	-
B	Dodecene	-22(-8)	-43(-45)	-17(-1)
C	Propylene	-22(-8)	-37(-35)	-
D	Propylene	-21(-6)	-40(-40)	-
E	Tetradecene	-21(-6)	-40(-40)	-18(0)

The data of Table 3 clearly show the improved results obtained over the unmodified when additive compositions in accordance with the invention are used.

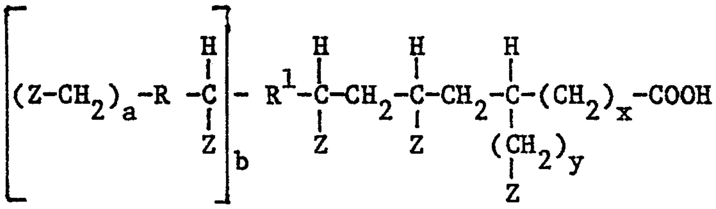
The important data is that with respect to the Low Temperature Flow Test. It is noted that the additives of the invention dramatically improved the low temperature characteristics of the base fuel oil.

Claims

1. A product of reaction useful for improving the low temperature characteristics of hydrocarbyl distillate fuels produced from the reaction of (1) an amide derivative of a branched chain monocarboxylic acid having at least one tertiary amine group, (2) an epoxide having from 2 to about 18 carbon atoms, and (3) an additional carboxylic acid selected from branched chain monocarboxylic acids or linear monocarboxylic acids and wherein said reactants are reacted in substantially stoichiometric or equimolar amounts at temperatures ranging from about 50 to about 175°C under autogenous pressure in 0.5 to about 3 hours or more.

2. The reaction product of claim 1 wherein said amide has the following generalized structure
$R^2CON(R^3)R^4N(R^5)(R^6)$
where R^2 is a branched chain monocarboxylic acid radical having a molecular weight of from about 300 to about 1,000, R^3 is hydrogen or C_1-C_{10} alkyl, R^4 is C_1-C_{25} hydrocarbyl and R^5 and R^6 are the same or different and are C_1-C_{25} alkyl.

3. The reaction product in accordance with Claim 2 wherein said branched chain monocarboxylic acid is a telomer acid in which at least a portion of said telomer acid has the following generalized structural formula



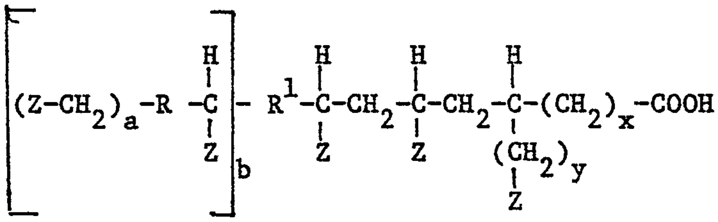
$$\left[(Z\text{-}CH_2)_a\text{-}R\text{-}\underset{Z}{\overset{H}{C}}\right]_b\text{-}\;R^1\text{-}\underset{Z}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{Z}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{\underset{Z}{(CH_2)_y}}{\overset{H}{C}}\text{-}(CH_2)_x\text{-}COOH$$

where Z is $-(CH_2)_nCH_3$; n is an integer of from 3 to 42; x and y are different and are 0 or 2; a is 0 or 1; if a is 0, R is hydrogen but if a is 1, R is $-CH_2$; and b is 0 or 1; if b is 0, R^1 is hydrogen but if b is 1, R^1 is $-CH_2$.

4. The reaction product in accordance with Claim 1 wherein said additional carboxylic acid is a telomer branched chain carboxylic acid.

5. The reaction product in accordance with Claim 4 wherein said additional carboxylic acid is the same telomer as said branched chain carboxylic acid.

6. An additive product useful for improving the low temperature characteristics of hydrocarbyl distillate fuels comprising the reaction produt of (1) a branched chain monocarboxylic acid amide having the following generalized structure
$R^2CON(R^3)R^4N(R^5)(R^6)$
where R^2 is a branched chain monocarboxylic telomer acid radical having a molecular weight of from about 300 to about 1,000, R^3 is hydrogen or C_1-C_{10} alkyl, R^4 is C_1-C_{25} hydrocarbyl and R^5 and R^6 are the same or different and are C_1-C_{25} alkyl; (2) an epoxide having 2 to about 18 carbon atoms with (3) a carboxylic acid selected from branched chain monocarboxylic and linear monocarboxylic acids and wherein at least a portion of said telomer acid has the following generalized structure.



$$\left[(Z\text{-}CH_2)_a\text{-}R\text{-}\underset{Z}{\overset{H}{C}}\right]_b\text{-}\;R^1\text{-}\underset{Z}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{Z}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{\underset{Z}{(CH_2)_y}}{\overset{H}{C}}\text{-}(CH_2)_x\text{-}COOH$$

where Z is $-(CH_2)_nCH_3$; n is an integer of from 3 to 42; x and y are different and are 0 or 2; a is 0 or 1; if a is 0, R is hydrogen but if a is 1, R is $-CH_2$; and b is 0 or 1; if b is 0, R^1 is hydrogen but if b is 1, R^1 is $-CH_2$.

7. The additive product of claim 6 wherein said telomer acid is further identified as a C_{18} telomer acid.

8. The additive product of claim 6 wherein said telomer acid is further identified as a C_{10} telomer acid.

9. The additive product in accordance with Claim 6 wherein said branched chain acid has at least one side chain of from about 8 to 18 carbon atoms.

10. The additive reaction product in accordance with Claim 6 wherein said branched chain acid has at least one side chain having about 18 carbon atoms.

11. The reaction product of claim 1 wherein the epoxide reactant is selected from the group consisting essentially of propylene oxide, styrene oxide, 1,2-epoxybutane, a C_{10} epoxide, a C_{14} epoxide and a C_{18}

epoxide.

12. The reaction product of claim 1 wherein the amide is derived from an amine selected from the group comprising the following amines N-(3-aminopropyl) morpholine, N-(2-aminoethyl) morpholine, N-(2-aminopropyl) morpholine, N,N'-bis(3-aminopropyl) piperazine, N,N-diethylethylenediamine, 3-dimethylaminopropylamine, unsymmetrical (unsym.) dimethylethylenediamine,N,N-dimethyl-N'-ethylethylenediamine and mixtures of two or more of these.

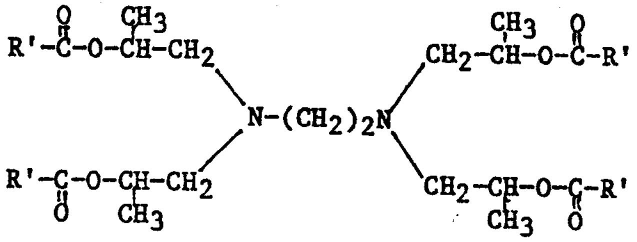
13. The reaction product of claim 12 wherein the amide is derived from the following amine: 3-dimethylaminopropylamine.

14. A product of reaction useful for improving the low temperature characteristics of hydrocarbyl distillate fuels produced from the reaction of (1) a branched chain monocarboxylic acid ester having at least on tertiary amine group and at least one branched chain acid ester group, (2) an epoxide having from 2 to about 18 carbon atoms and (3) an additional carboxylic acid selected from branched chain monocarboxylic acids or linear monocarboxylic acids and wherein said reactants are reacted in substantially stoichiometric or equimolar amounts at temperatures ranging from about 50 to about 175° C under autogenous pressure in 0.5 to about 3 hours or more.

15. The reaction product of claim 14 wherein said ester has the following generalized structure $R^2COO(R^3)N(R^5)(R^6)$

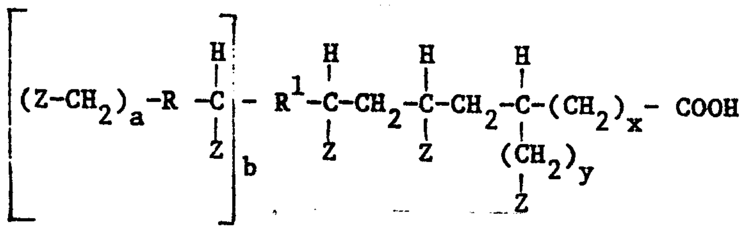
where R^2 is a branched chain monocarboxylic acid radical having a molecular weight of from about 300 to about 1,000, R^3 is hydrogen or C_1-C_{10} alkyl, R^5 and R^6 are the same or different and are C_1 to C_{25} alkyl or substituted alkyl and said branched chain monocarboxylic acid radical R_2 is a telomer acid radical.

16. The reaction product of claim 14 wherein said ester has the following generalized structural formula:



where at least one R' is a telomer acid radical and the remaining R' groups are the same or different, linear or branched and from C_1 to about C_{25} hydrocarbyl or hydrogen.

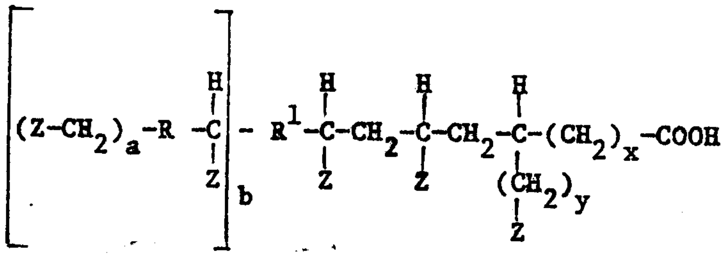
17. The reaction product in accordance with claim 15 wherein at least a portion of said telomer acid radical has the following generalized structure:



$$\left[(Z\text{-}CH_2)_a\text{-}R\text{-}\overset{H}{\underset{Z}{C}}\right]_b\text{-}R^1\text{-}\overset{H}{\underset{Z}{C}}\text{-}CH_2\text{-}\overset{H}{\underset{Z}{C}}\text{-}CH_2\text{-}\overset{H}{\underset{\underset{Z}{(CH_2)_y}}{C}}\text{-}(CH_2)_x\text{-}\ COOH$$

where Z is $-(CH_2)_nCH_3$; n is an integer of from 3 to 42; x and y are different and are 0 or 2; a is 0 or 1; if a is 0, R is hydrogen but if a is 1, R is $-CH_2$; and b is 0 or 1: if b is 0, R^1 is hydrogen but if b is 1, R^1 is $-CH_2$.

18. The reaction product in accordance with claim 16 wherein at least a portion of said telomer acid radical has the following generalized structure:



$$\left[(Z\text{-}CH_2)_a\text{-}R\text{-}\overset{H}{\underset{Z}{C}}\right]_b\text{-}R^1\text{-}\overset{H}{\underset{Z}{C}}\text{-}CH_2\text{-}\overset{H}{\underset{Z}{C}}\text{-}CH_2\text{-}\overset{H}{\underset{\underset{Z}{(CH_2)_y}}{C}}\text{-}(CH_2)_x\text{-}COOH$$

where Z is $-(CH_2)_nCH_3$; n is an integer of from 3 to 42; x and y are different and are 0 or 2; a is 0 or 1; if a is 0, R is hydrogen but if a is 1, R is $-CH_2$; and b is 0 or 1: if b is 0, R^1 is hydrogen but if b is 1, R^1 is $-CH_2$.

19. The reaction product in accordance with Claim 14 wherein said additional carboxylic acid is a telomer acid and said branched chain monocarboxylic acid ester is derived from the same telomer acid.

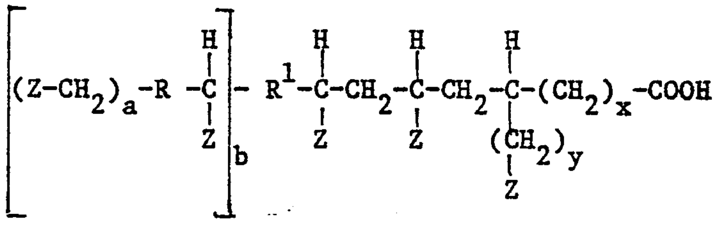
20. The reaction product in accordance with Claim 14 wherein said additional carboxylic acid is a telomer

acid and said branched chain monocarboxylic acid ester is derived from a different telomer acid.

21. An additive product useful for improving the low temperature characteristics of hydrocarbyl distillate fuels comprising the reaction product of (1) a branched chain monocarboxylic acid ester having the following generalized structure:

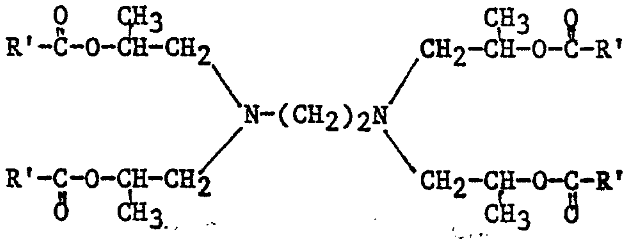
$R^2COO(R^3)N(R^5)(R^6)$

where R^2 is a branched chain monocarboxylic telomer acid radical having a molecular weight of from about 300 to about 1,000, R^3 is hydrogen or C_1-C_{10} alkyl, R^5 and R^6 are the same or different and are C_1-C_{25} alkyl or substituted alkyl; (2) an epoxide containing 2 to 18 carbon atoms with (3) a carboxylic acid and wherein at least a portion of said branched chain acid has the following generalized structure:



where Z is $-(CH_2)_nCH_3$; n is an integer of from 3 to 42; x and y are different and are 0 or 2; a is 0 or 1; if a is 0, R is hydrogen but if a is 1, R is $-CH_2$; and b is 0 or 1; if b is 0, R^1 is hydrogen but if b is 1, R^1 is $-CH_2$, said reactants being reacted in substantially stoichiometric or equimolar amounts at temperatures ranging from bout 50 to about 175°C under autogenous pressure in 0.5 to aout 3 hours or more and wherein said carboxylic acid is selected from branched chain monocarboxylic acids and linear monocarboxylic acids.

22. The additive product of claim 21 wherein said ester has the following generalized structural formula:



where at least one R′ is a telomer acid radical and the remaining R′ groups are the same or different, linear or branched and from C_1 to about C_{25} hydrocarbyl or hydrogen.

23. The additive product of claim 21 wherein said telomer acid is further identified as a C_{18} telomer acid.

24. The additive product of claim 21 wherein said telomer acid is further identified as a C_{10} telomer acid.

25. The additive product of claim 21 wherein said telomer acid is further identified as a C_{14} telomer acid.

26. The additive product of claim 21 wherein said telomer acid is further identified as a C_{20} telomer acid.

27. The additive product in accordance with Claim 21 wherein said branched chain acid has at least one side chain of from about 8 to 18 carbon atoms.

28. The additive reaction product in accordance with claim 27 wherein said branched chain acid has at least one side chain having about 18 carbon atoms.

29. The reacton product of claim 14 wherein the epoxide reactant is selected from the group consisting essentially of propylene oxide, dodecene oxide, and tetradecene oxide.

30. The reaction product of claim 14 wherein the ester derivative is derived from an amine selected from the group comprising the following amines N,N′N′-tris-(2-hydroxypropyl)N-tallowalkyl-1,3-diaminopropane,
N,N,N′,N′-tetrakis(2-hydroxypropyl) ethylenediamine,
N,N,N′,N′-tetrakis (2-hydroxyethyl) ethylenediamine,
3-dimethylaminopropanol, N-methyldiethanolamine and the like and mixtures of two or more of these.

31. The reaction product of claim 30 wherein said product is further identified as a tetraester of a C_{18} telomer acid, N,N,N′,N′-tetrakis(2-hydroxypropyl) ethylenediamine, propylene oxide and additional C_{18} telomer acid.

32. The reaction product of claim 30 wherein said product is further identified as a tetraester of a C_{14} telomer acid, N,N,N′,N′-tetrakis(2-hydroxypropyl) ethylenediamine, propylene oxide and additional C_{14} telomer acid.

33. The reaction product of claim 30 wherein said product is further identified as a tetraester of a C_{20} telomer acid, N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylenediamine, propylene oxide and additional C_{20} telomer acid.

34. The reaction product of claim 30 wherein the molar ratio of amine/epoxide/additional acid is 1/1/1.

35. The reaction product of claim 30 wherein the molar ratio of amine/epoxide/additional acid is 1/2/2.

36. The reaction product of claim 30 wherein the epoxide is decane oxide.

37. The reaction product of claim 30 wherein the epoxide is tetradecane oxide.

38. A distillate fuel composition comprising a major proportion of a hydrocarbyl distillate fuel and a minor cold flow improving amount of the additive reaction product defined in claim 1 or 14 effective to reduce the pour point and the Cold Filter Plugging Point of said fuel.

39. A distillate fuel composition comprising a major amount of a hydrocarbyl distillate fuel and a minor cold flow improving amount of the additive of claim 1 or 14.

40. A distillate fuel composition comprising a major proportion of a hydrocarbyl distillate fuel and a minor cold flow improving amount of the additive of claim 6 or 21.

41. A hydrocarbyl distillate fuel composition comprising a distillate fuel and between about 0.01 and 3% by weight, based on the total weight of the composition, of the additive of claim 1 or 14

42. A hydrocarbyl distillate fuel composition comprising a distillate fuel and between about 0.01 and 3% by weight, based on the total weight of the composition, of the additive of claim 6 or 21.

43. A method for lowering the pour point and the CFPP of hydrocarbyl distillate fuels which comprises adding a minor pour point depressant and CFPP lowering amount of a product /of reaction as defined in claim 1 or 14.

44. A method for lowering the pour point and the CFPP of hydrocarbyl distillate fuels which comprises adding a minor pour point depressant and CFPP lowering amount of a product of reaction as defined in claim 1 or 14.

45. A method for lowering the pour point and the CFPP of hydrocarbyl distillate fuels which comprises adding a minor pour point depressant and CFPP lowering amount of a product of reaction as defined in claim 6 or 21.