

1

2,886,423

HYDROCARBON FUELS CONTAINING BETAINE
ANTIFREEZE COMPOSITIONS

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The present invention relates to liquid fuel compositions having improved low temperature characteristics and more specifically is concerned with kerosene, gasoline, diesel and turbo-jet fuel compositions having lower freezing points and wherein the formation of ice crystals and the separation of wax and other solids is prevented until substantially lower temperatures are reached.

Petroleum hydrocarbons have been established as the presently preferred fuels for spark-ignition engines, compression-ignition engines and jet-propulsion engines, the latter including the gas-turbine type of power plant, particularly employed for aircraft propulsion purposes. As used herein, these petroleum hydrocarbons fall into several loosely-defined classes of which the following are pertinent to the present invention: (1) aviation gasoline, the petroleum fraction boiling between about 100° and about 330° F.; (2) motor gasoline, the petroleum fraction boiling between 100° F. and about 430° F.; (3) kerosene and diesel fuel, the fraction boiling between about 300° and 625° F.; and (4) jet fuel, the fraction boiling between about 100° and about 600° F. and preferably between about 150° and about 550° F. All these products may be made up of straight run, thermally cracked and/or catalytically cracked components. With particular reference to kerosene and jet fuels which are illustrative but not limitative of the present invention, such products possess desirable characteristics of flammability, engine power requirements, freezing points, flash points, vapor loss, cost and availability which have rendered them most suitable for the fuel for jet aircraft.

Aviation kerosene is a blend of petroleum fractions and is made to meet a variety of specifications. The following data are presented to illustrate one particular commercial product:

Distillation (20% evap.)	degrees F. max.	392
End point	degrees F. max.	572
Residue, percent volume	max.	2.0
Loss, percent	max.	1.5
Sulfur, percent wt. max.		0.2
Freezing point	degrees F.	-40
B.t.u./lb. net, min.		18,300
Flash point	degrees F.	100

Similarly, turbo-jet fuels are blends of petroleum fractions and are made to meet a variety of specifications. The following data are presented to illustrate one particular product, namely, JP-4, which is a wide-cut petroleum fraction covering the boiling point range of both gasoline and diesel fuels.

Distillation:		
(20% evap.)	degrees F. max.	270
(50% evap.)	degrees F. max.	370
(90% evap.)	degrees F. max.	470
Residue, percent volume	max.	1.5
Loss, percent	max.	1.5
Sulfur, percent wt. max.		0.4
Freezing point	degrees F.	-76
B.t.u./lb. net, min.		18,400
Flash point	degrees F.	10

2

Low temperature characteristics, ice crystal and solid wax formation and freezing points of liquid fuels, and particularly jet fuels, are important factors leading to the acceptance thereof and this is especially so in military service and cold weather operations wherein the requirements are rigorous and varied.

Low freezing point values have been required in order to provide maximum pumpability of the liquid fuel in the aircraft or like fuel systems under extremely frigid conditions or at very high altitudes and to avoid the formation of ice crystals in the fuel whereby its low temperature behavior is seriously affected. At certain temperatures, fuels may contain up to 0.015 percent by weight of water dissolved in the fuel which, as the fuel temperature is reduced and its water solubility decreased, could lead to the separation of water and the undesirable formation of ice crystals. The possibility of blockages, such as in fuel filters, carburetors, and other operational equipment, is created with resulting engine failure.

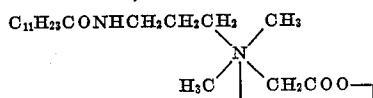
The principal object of the present invention is the provision of liquid fuel compositions of the type described above wherein improved low temperature characteristics as indicated by a reduced cloud point are obtained by incorporating therein both a surface-active acylamidoalkyl glycine betaine wherein the acyl group is the radical of a higher fatty acid and a monohydric alkanol of the type hereinafter defined. We have found that mixtures of glycine betaine surface-active agents of the above type with either a monohydric alkanol of from 2 to 3 carbon atoms or a 2-alkoxyethanol containing an alkoxy radical of from 1 to 4 carbon atoms in suitable ratios are soluble in the volatile liquid hydrocarbon fuels and possess the property of reducing materially the cloud points thereof.

The acylamidoalkyl glycine betaines used in practicing our invention are members of a relatively new class of organic compounds that are described and claimed in the copending application of Frank M. Cowen et al., Serial No. 547,845, filed November 18, 1955. The particular materials which we have found to be useful in antifreeze compositions for hydrocarbons are the acylamidoalkyl glycine betaines in which each acyl group is derived from a higher fatty acid which preferably contains from 12 to about 18 or more carbon atoms. Either the monoacylamidoalkyl or the bis-acylamidoalkyl glycine betaines may be used, typical compounds of these classes being hereinafter described in detail. They are preferably prepared by first forming the monoamide or bis-amide of an aliphatic diamine which is then reacted with a halogenated acetic acid such as chloroacetic acid to form the glycine betaine. The preparation of N-(lauramidopropyl)-N,N - dimethyl - N-carboxymethylammonium inner carboxylate is typical and is as follows.

A reaction flask fitted with a thermometer, stirrer, water trap and reflux condenser was charged with three kilograms (15 mols) of commercial lauric acid, 1920 grams (15 mols) of N,N-dimethyl-N-(3-aminopropyl)-amine and 500 ml. of benzene and the mixture was refluxed in a nitrogen atmosphere for eleven and one-half hours at 130° to 175° C. A titration at this time indicated 1.2% of free acid. The reaction product was stripped by heating to 150° C. at 3 mm. of mercury pressure, whereupon the N-lauramidopropyl-N,N-dimethylamine was obtained in a yield of 4240 grams. It was mixed with an equimolecular amount (1380 grams) of chloroacetic acid and 2900 ml. of isopropyl alcohol and the mixture was heated to reflux in the same equipment. A solution of 596 grams (14.6 mols) of sodium hydroxide in 1460 ml. of water was added to the refluxing mixture over a one hour period and refluxing was continued for an additional 8.5 hours. The mixture was then filtered free of salt and stripped of

3

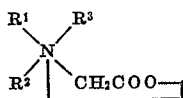
solvent and the product was dried at 90°–110° C. The betaine, a soft tan wax, has the formula



It will be understood that any saturated or unsaturated fatty acid of about 12–18 or more carbon atoms may be substituted for the lauric acid in the above preparation or that fatty acid mixtures may be used. Typical fatty acids are stearic acid, oleic acid, commercial stearic acids obtained from tallow or hydrogenated tallow, partially or completely hydrogenated fish oil acids, coconut fatty acids, cottonseed oil acids and the like and tall oil fatty acids such as the mixture containing about 48% oleic acid and 43% linoleic acid that is sold as "Acintol FA-1." Other secondary or tertiary diamines such as bis-(3-amino-propyl)-amino, bis-(3-aminopropyl)-methylamine, bis-(3-aminopropyl)-butylamine, diethylenetriamine, N,N-dimethyl - N - (2-aminooctyl)-amine, bis-(2-aminoethyl)-amine or -methylamine and the like may be used. Amides formed by reacting the above and similar reagents are converted into inner carboxylates or betaines by reaction with a halogenated acetic acid and alkali as illustrated above. Typical compounds that can be used in admixture with alcohols to reduce the cloud points of volatile hydrocarbon fuels are the following:

- N - (lauramidopropyl) - N,N-dimethyl-N-carboxymethyl-ammonium betaine.
- N - (stearamidopropyl) - N,N-dimethyl-N-carboxymethyl-ammonium betaine.
- N - (oleylamidoethyl) - N,N - dimethyl-N-carboxymethyl-ammonium betaine.
- N,N-bis - (stearamidoethyl) - N-methyl-N-carboxymethyl-ammonium betaine.
- N,N-bis-(oleylamidopropyl) - N-methyl-N-carboxymethyl-ammonium betaine.
- N,N - bis - (lauramidoethyl) - N-butyl-N-carboxymethyl-ammonium betaine.

It will be seen therefore that the cationic compounds used in practicing the invention are higher fatty acid amidoalkyl N-carboxymethylammonium betaines, which can also be defined by the formula



in which R¹ is the amidoalkyl radical of a fatty acid containing at least 12 carbon atoms, R² is hydrogen or an alkyl radical of from 1 to about 10 carbon atoms, which is hereinafter sometimes referred to as a lower alkyl radical, and R³ is either the same as R¹ or is hydrogen or an alkyl radical as in R².

The glycine betaines of the above class are incorporated into volatile petroleum fractions together with a monohydric alcohol capable of a synergistic action therewith resulting in improved low temperature characteristics in the fuel. We have found that the monohydric alkanols of from 2 to 3 carbon atoms, i.e., ethanol, propanol and isopropanol or mixtures thereof, or 2-alkoxyethanols such as the monomethyl, monoethyl, monopropyl or monobutyl ethers of ethylene glycol, are capable of such synergistic action. Our invention in its broadest aspects therefore consists in the provision of normally liquid and volatile petroleum fuels wherein a hydrocarbon-soluble mixture of one or more of these monohydric alkanols is present in admixture with a glycine betaine of the type described above in cloud point-reducing quantities. The quantities of these mixtures to be used will depend somewhat on the results desired; when only a slight reduction in cloud point is necessary small quantities on the order of about 0.1% of the weight of the hydrocarbon fuel may

4

be used. Larger quantities of the mixture can of course be used to reduce still further the cloud points of the liquid fuel compositions up to maximum quantities within the range of about 3% to 5% on the weight of the fuel.

- 5 Larger amounts are not recommended as some of the additive may tend to separate out of the fuel at very low temperatures. The term "cloud point-reducing quantities" as used herein is therefore intended to designate quantities within the range of about 0.1% to 3% on the weight of the hydrocarbon fuel with slightly larger amounts up to about 5% being permissible in special cases.

- 10 The monohydric alkanols are used in admixture with the glycine betaine surface-active agents in weight ratios within the range of from 1:4 to 4:1; i.e., from about 25% by weight of the alcohol and 75% by weight of the surface-active agent to 25% of the surface-active agent and 75% of the alcohol. In order to reduce cost we prefer to use as much of the alcohol and as little of the surface-active agent as is consistent with the degree of cloud point-reduction desired in the fuel.

- 20 A remarkable reduction in the cloud points of volatile petroleum fractions is obtained when the above mixtures are added thereto in the quantities indicated. After adding the surface-active agent and the alcohol, individually or jointly, the liquid fuel is slowly cooled with constant stirring and is observed for the development of cloudiness or haziness due to the appearance of small ice or wax crystals. The fuel is then allowed to warm slowly and the temperature at which the cloudiness or haziness disappears due to the remelting of the crystals is noted. A sample of the JP-4 fuel described above, containing no antifreeze, became turbid at +32° F. under the test conditions and cleared at +40° F.; after adding 0.5% by weight of a mixture containing 25% by weight of N-(lauramidopropyl)-N,N-dimethyl-N-carboxymethyl-ammonium inner carboxylate the corresponding temperatures were -30° F. and -28° F. The same temperatures were obtained with other samples of the same fuel in which 2-ethoxyethanol was substituted for the isopropanol. When N-stearoyloxyethyl-N,N-dimethyl-N-carboxymethylammonium betaine was used instead of the lauric acid derivative, together with isopropanol, the fuel became turbid at -30° F. but cleared on warming to -10° F. The bis-compounds gave approximately the same test results; N,N-bis-(oleylamidoethyl)-N-methyl-N-carboxymethylammonium betaine in conjunction with isopropanol, added as a 25%–75% mixture in a quantity of 0.5% on the weight of the fuel, showed turbidity at -32° F. which cleared on warming to -28° F.

- 50 The acylamidoalkyl glycine betaines, being cationic surface-active agents, also impart antistatic properties to the hydrocarbon fuels, and this is another important advantage of the invention. Explosion hazards due to the development of static charges when the fuels are transported or otherwise agitated are diminished by this antistatic action.

What we claim is:

1. A liquid fuel of improved low temperature characteristics consisting essentially of a petroleum fraction boiling between about 100° F. and 625° F. containing cloud point-reducing quantities within the range of 0.1% to about 5% by weight of a hydrocarbon oil-soluble mixture of (1) a 12–18 carbon atom fatty acid amido-lower alkyl glycine betaine and (2) a member of the group consisting of monohydric alkanols of from 2 to 3 carbon atoms and 2-alkoxyethanols containing an alkoxy radical of from 1 to 4 carbon atoms, the weight ratio of (1) to (2) being within the range of from 1:4 to 4:1.

2. A liquid fuel of improved low temperature characteristics consisting essentially of a petroleum fraction boiling between about 100° F. and 625° F. containing cloud point-reducing quantities within the range of 0.1% to about 5% by weight of a hydrocarbon oil-soluble mixture of (1) a bis-acylamido-lower alkyl glycine betaine in which the acyl groups are the radicals of fatty acids of 12

5

to 18 carbon atoms and (2) a member of the group consisting of monohydric alkanols of from 2 to 3 carbon atoms and 2-alkoxyethanols containing an alkoxy radical of from 1 to 4 carbon atoms, the weight ratio of (1) to (2) being within the range of from 1:4 to 4:1.

3. A liquid fuel of improved low temperature characteristics consisting essentially of a petroleum fraction boiling between about 100° F. and 625° F. containing cloud point-reducing quantities within the range of 0.1% to about 5% by weight of (1) a lauramido-lower alkyl glycine betaine and (2) a member of the group consisting of monohydric alkanols of from 2 to 3 carbon atoms and 2-alkoxyethanols containing an alkoxy radical of from 1 to 4 carbon atoms, the weight ratio of (1) to (2) being within the range of from 1:4 to 4:1.

4. A liquid fuel of improved low temperature characteristics consisting essentially of a petroleum fraction boiling between about 100° F. and 625° F. containing cloud

6

point-reducing quantities within the range of 0.1% to about 5% by weight of (1) an oleyl-lower amidoalkyl glycine betaine and (2) a member of the group consisting of monohydric alkanols of from 2 to 3 carbon atoms and 2-alkoxyethanols containing an alkoxy radical of from 1 to 4 carbon atoms, the weight ratio of (1) to (2) being within the range of from 1:4 to 4:1.

5. A liquid fuel according to claim 4 in which the betaine is a bis-oleylamido-lower alkyl glycine betaine.

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