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JET FUEL COMPOSITIONS

Frederick M. Fowkes, Orinda, Calif., and Francis G. Bollo, Alton, Ill., assignors to Shell Oil Company, a corporation of Delaware

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This invention relates to hydrocarbon fuels, particularly to so-called jet fuels for use in jet aircraft engines.

In our copending application, Serial No. 560,867, filed January 23, 1956, now abandoned, of which the present application is a continuation-in-part, it has been shown that conventional foam inhibitors such as silicone polymers are ineffective foam inhibitors for jet fuels, but that certain hydrocarbon-insoluble perfluorocarbons are effective foam inhibitors for jet fuels. However, the perfluorocarbon foam inhibitors tend to separate out of solution during storage. Therefore, caution must be taken to thoroughly mix stored fuels containing a perfluorocarbon foam inhibitor to redisperse it otherwise the fuel will not be sufficiently foam resistant.

Solubilization of the perfluorocarbon anti-foam agent in the jet fuel can be obtained by the use of solubilizers such as oil-soluble alcohols and oil-soluble amines, but they are unsuitable because they interfere with the foam inhibiting properties of the perfluorocarbons in the hydrocarbon fuel.

It has now been discovered that storage stable and improved foam resistant hydrocarbon jet fuels are provided by addition to the jet fuels of a minor amount of from about 0.0001% to about 1%, preferably from about 0.01% to about 0.1% by volume, of a hydrocarbon-insoluble perfluorocarbon (containing only carbon and fluorine) having at least 12 carbon atoms and mixtures thereof, and as anti-foam enhancers and emulsifiers for the perfluorocarbons, a minor amount of from about 0.01% to about 10%, preferably from about 0.1% to about 5%, of a polyfluoroamide containing a hydrocarbon-insoluble perfluorohydrocarbyl group and an oil-solubilizing aliphatic group in the molecule.

The perfluorocarbon foam inhibiting agents are prepared by the method described in the articles by Fowler et al. and Burford et al. in the March 1947 issue of Ind. and Eng. Chem. (vol. 39, No. 3, pages 292 and 319). The perfluorocarbons are essentially aliphatic perfluorocarbons, containing only carbon and fluorine and may be obtained by completely fluorinating a light hydrocarbon distillate fraction, such as a fraction in the kerosene and/or light lubricating oil distillate range. Preferably the hydrocarbon material to be fluorinated should contain only a minor amount of aromatic and/or alicyclic hydrocarbons, i.e., it should be composed predominately of aliphatic, open-chain hydrocarbons.

Typical perfluorocarbons which are useful in the practice of the invention are set forth in Table I.

Perfluorocarbons such as composition F (Table I) or fractions thereof, such as fractions F_1, F_2, F_3, F_4, and F_5 (Table I) are suitable foam inhibitors for hydrocarbon jet fuels. They are essentially aliphatic compounds which contain carbon atoms arranged in a normal (straight-chain) or branched chain-structure.

TABLE I

Properties of various perfluorocarbons

Description	Empirical Formula	Identification Symbol	Molecular Weight (approx.)	Boiling Point, °C.	Density 20° C. (approx.)	Index of Refraction (approx.)	Solubility, wt. Percent at 27° C.		Benzene
							CCl_4	CH_3OH	
Perfluorokerosene (FCX-329)	$C_{12}F_{26}$	C	645	20–65 at 10 mm. Hg	1.922	1.3082	------	<1	<1
Perfluorokerosene (FCX-30)	$C_{14}F_{30}$	D	738	65–130 at 10 mm. Hg	1.994	1.3171	3.4	<1	<1
Perfluorolube oil (FCX-512)	$C_{20}F_{42}$	E	1,038	70–240 at 10 mm. Hg	2.059	1.3369	2.7	<1	<1
Perfluorolube oil (FCX-412)	$C_{21}F_{44}$*	F	1,126	130–240 at 10 mm. Hg	----------	1.3430	<1	<1	<1

* This material may be further fractionated into 5 different fractions having the following boiling point ranges at 10 mm. Hg abs. pressure and identified as:

	°C.
F_1—Fraction No. 1	130–150
F_2—Fraction No. 2	150–170
F_3—Fraction No. 3	170–190
F_4—Fraction No. 4	190–210
F_5—Fraction No. 5	210–240

Mixtures of perfluorocarbons boiling above 130° C. at 10 mm. Hg pressure and having more than 12 carbon atoms with lower boiling perfluorocarbons (130° C. at atmos. pressure) of not less than 12 carbon atoms in the ratio of from 4:1 to 1:4, from 4:1 to 2:1 respectively, can be used. Thus mixtures of perfluorocarbons such as C and F or D and F (Table I) in the mole ratio of 1:4 respectively, can be used as the anti-foam inhibitors.

The polyfluoroamide anti-foam enhancing and emulsifying agents for the perfluorocarbon foam inhibitors in the jet fuel are suitably and readily prepared by reacting perfluorocarboxylic acid, preferably a perfluoroaliphatic monocarboxylic acid having from 4 to 22 (better 8 to 18) carbon atoms in the molecule with a hydrocarbon-soluble amine, preferably an aliphatic monoamine or an N-alkyl polymethylene diamine where the aliphatic radical contains from 8 to 22, preferably 12 to 18, carbon atoms. Also the perfluoroamide can be prepared by reacting an organic carboxylic acid preferably a hydrocarbon-soluble aliphatic monocarboxylic acid having from 8 to 18 carbon atoms in the molecule with a perfluoroalkylamine.

The perfluoro acids include perfluoro mono- and polycarboxylic acids. The C_8–C_{18} perfluoroaliphatic monocarboxylic acids are preferred. Examples of such acids are perfluorobutyric acid, perfluorocaproic acid, perfluoroheptanoic acid, perfluorocaprylic perfluorocapric acid, perfluorolauric acid, perfluorostearic acid and mixtures thereof. Other suitable perfluoroalkyl substituted carboxylic acids include perfluoroalkyl aryl carboxylic acids such as C_4–C_{18} perfluoroalkylbenzoic or salicylic acid; perfluoroalkyl substituted polycarboxylic acids such as perfluorooctyl, perfluorodecyl or perfluorododecyl succinic, adipic or sebacic acids.

Amines for use in amidizing the above acids include oil-soluble mono- or polyamines containing at least one alkyl radical of at least 8 carbon atoms. Monoamines

of this type include octyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl monoamines. In the secondary amines the alyl radicals can be the same or different. Aliphatic polyamines include N-alkyl substituted alkylene polyamines wherein the alkylene radical contains from 2 to 10 carbon atoms, such as N-alkyl substituted ethylene diamine, propylene diamine, butylene diamine, diethylene tetramine, tetraethylene pentamine and the alkyl substituent group(s) can be attached to the same or different nitrogen atoms in the molecule and should generally have from 8 to 22 carbon atoms. Preferred N-alkyl substituted methylene polyamines include N-C_{12-18} alkyl trimethylene diamine, N-C_{17}-alkyl trimethylene diamine, N-C_{13}-alkyl trimethylene diamine, N-C_{11} trimethylene diamine, and the like.

Also the above corresponding non-fluorinated acids such as C_8–C_{18} aliphatic monocarboxylic acids e.g., caprylic acid, lauric acid or stearic acid can be amidized with perfluoroalkylamines such as perfluorooctylamine, perfluorododdecylamine, perfluorooctadecylamine, N-perfluoro C_{12-18} alkyl trimethylene diamine and the like.

Examples of perfluoroamides are decyl perfluorocaprylamide, dodecyl perfluorocaprylamide, octadecyl perfluorocaprylamide, octyl perfluorolaurylamide, octalperfluorostearylamide, N-C_{12-18} alkyl trimethylene perfluorocaprylamide, octadecyl perfluorododecyladipylamide, perfluoro-octyl caprylamide, perfluoro-octadecyl caprylamide, perfluorododecyl stearylamide and mixtures thereof.

The jet fuels for aircrafts are commonly known by the JP-designation such as JP–1, JP–3, JP–4 or JP–5 under MIL–F–5624 B specification, the properties of which are given in Table II.

TABLE II

[MIL–F–5624 B.]

	JP–1	JP–3	JP–4	JP–5
Reid Vapor Pressure, lb. per sq. in.		5–7	2–3	
ASTM Distillation:				
10% Distillation	410			
20% Evaporation at ° F.		240	270	
90% Evaporation at ° F.	490	470	470	
End Point ° F.	572	600	550	550
Total Sulfur, Percent wt.	0.2	0.4	0.4	0.4
Mercaptan sulfur, percent wt.	0.005	0.005	0.005	0.005
Aromatics, vol. percent	20	25	25	25
Freezing Point, ° F.	−76	−76	−76	−40
Gravity, °API	35	50–60	45–55	35–45

Jet fuels with the above characteristics upon being subjected to a rapid decrease in ambient pressure tend to boil vigorously and to foam as a result thereof. It is considered that foaming is caused by the vigorous boiling of the jet fuel (due to its volatile low boiling constituents) in the presence of and/or aggravated by the presence of relatively high boiling hydrocarbons, e.g. those hydrocarbons boiling in the range of from about 450° F. to about 600° F. and higher. Accordingly, due to the presence of a greater amount of low boiling hydrocarbons, as evidenced by the higher Reid Vapor Pressure, and also due to the presence of a greater proportion of high boiling hydrocarbons, a JP–3 jet fuel boils and foams much more than a JP type of jet fuel. Jet fuels which have Reid Vapor Pressure between about 0.5 and about 10 lbs. per sq. in at 100° F. and especially between about 2 and 7 lbs. per sq. in. are most susceptible to foam upon boiling and are advantageously improved in this respect, i.e., foaming is essentially eliminated by addition to such jet fuels (JP–3 fuels), of perfluorocarbons and are rendered storage stable by addition thereto of polyfluoroamides.

In order to demonstrate the effectiveness of compositions of this invention for their stability and resistance to foaming, a number of tests were carried out. The test apparatus for measuring foaming consisted of a long vertical 1½ inch diameter glass tube, representing a fuel tank, charged with 100 ml. of a representative type of jet fuel (JP–3). The air space above the test mixture was evacuated at a rate representative of the change in atmospheric pressure (ratio-of-climb performance) which would be experienced by a typical jet aircraft in a rapid climb. The foaming tendency was judged by the height of foam column produced in the tube above the fuel liquid level. The stability was measured by noting the time it took for separation of the perfluorocarbon from the fuel compositions at room temperature. The results of the various tests are set forth in Table III.

TABLE III

[Base: JP–3 Fuel.]

Foam Inhibitor	Percent Vol.	Emulsifier	Percent wt.	Height of Foam, in.	Separation Time
1. None		None		30	
2. Dow Corning Silicone No. 200 [a]	0.02	do		29	
3. Dow Corning Silicone No. 500	0.01	do		34	
4. 1,3 bis (trifluoromethyl) benzene	0.01	do		30	2 hours.
5. Perfluorodimethylcyclohexane	0.1	do		28	Do.
6. Perfluorocaprylic acid	0.1	do		30	Do.
7. F [b]	0.02	do		2	Do.
8. F_1	0.02	do		3	Do.
9. F_2	0.02	do		3	Do.
10. F_3	0.02	do		3	Do.
11. F_3		N-C_{12-18} alkyl trimethylene fluorocaprylamide.	0.5	30	2 days.
12. F_2		octadecylperfluorocaprylamide	0.5	30	Do.
13. F_2	0.02	N-C_{12-18} alkyl trimethylene fluorocaprylamide.	0.5	1	5 days.
14. F_1	0.02	N-C_{12-18} alkyl trimethylene fluorocaprylamide.	0.5	1	Do.
15. F_2	0.02	octadecylperfluorocaprylamide	0.5	3	Do.

[a] Dow Corning silicones are methyl silicone polymers described in the Jour. of Ind. Hygiene and Toxicology No. 1948, pp. 332–352 and in Dow Corning Bulletin entitled "New Engineering Materials DC Silicones" (1947).

[b] Note Table I for identification of compounds.

From the above data it can be noted that conventional foam inhibitors such as silicone polymers (compositions 2 and 3) or certain fluorine-containing compounds (compositions 4–6) are ineffective as foam inhibitors in jet fuel and are unstable. Perfluorocarbons which are effective foam inhibitors are unstable separating out of the fuel (JP–3) in about 2 hours (compositions 7–10). The polyfluoroamides are ineffective as foam inhibitors, but the fuel containing them is storage stable (compositions 11 and 12). However, when the two additives are used together in the fuel, foaming is inhibited and the stability is greatly improved (compositions 13, 14 and 15). This

patent application is a continuation-in-part of copending patent application Serial No. 560,867, filed January 23, 1956, which is, in turn, a continuation-in-part of patent application Serial No. 204,834, filed January 6, 1951, now abandoned.

We claim as our invention:

1. A stable, non-foaming petroleum hydrocarbon jet fuel composition consisting essentially of a major amount of a petroleum hydrocarbon jet fuel having a boiling range from about 240° F. to about 600° F. and containing from about 0.001% to about 1% by volume of a hydrocarbon-insoluble saturated perfluorocarbon having from 12 to 21 carbon atoms and having a boiling point range of from about 20° C. to about 240° C. at 10 mm. Hg and from about 0.01% to about 10% of a hydrocarbon dispersible polyfluoroamide of a saturated perfluoroaliphatic monocarboxylic acid having from 4 to 22 carbon atoms and an alkyl amine having 8 to 22 carbon atoms in the alkyl chain.

2. A stable, non-foaming petroleum hydrocarbon jet fuel composition consisting essentially of a major amount of a petroleum hydrocarbon jet fuel having a boiling range from about 240° F. to about 600° F. and a Reid Vapor Pressure above 0.5 lb. per sq. in. at 100° F. containing from about 0.01% to about 0.1% by volume of a hydrocarbon-insoluble saturated perfluorocarbon having from 12 to 21 carbon atoms and having a boiling point range of from about 20° C. to about 240° C. at 10 mm. Hg and from about 0.01% to about 10% of a hydrocarbon dispersible polyfluoroamide of an oil-soluble saturated perfluoroaliphatic monocarboxylic acid having from 12 to 18 carbon atoms and an oil-soluble amine having an alkyl radical of from 8 to 22 carbon atoms.

3. A stable, non-foaming petroleum hydrocarbon jet fuel composition consisting essentially of a major amount of a petroleum hydrocarbon jet fuel having a boiling range from about 240° F. to about 600° F. and a Reid Vapor Pressure above 0.5 lb. per sq. in. at 100° F. containing from about 0.01% to about 0.1% by volume of a hydrocarbon-insoluble saturated perfluorocarbon having from 12 to 21 carbon atoms and having a boiling point range of from about 20° C. to about 240° C. at 10 mm. Hg and from about 0.1% to about 10% of a hydrocarbon dispersible polyfluoroamide of an oil-soluble saturated aliphatic monocarboxylic acid having from 12 to 18 carbon atoms and an oil-soluble perfluoroalkylamine the perfluoroalkyl radical having from 8 to 22 carbon atoms.

4. A stable, non-foaming petroleum hydrocarbon jet fuel composition consisting essentially of a major amount of a petroleum hydrocarbon jet fuel having a boiling range from about 240° F. to about 600° F. and a Reid Vapor Pressure of 5–7 lbs. per sq. in at 100° F. containing from about 0.01% to about 0.1% by volume of an aliphatic perfluorocarbon having at least 21 carbon atoms and a boiling point of at least 130° C. at 10 mm. Hg and from about 0.5% to about 5% of N-C_{12-18} alkyl trimethylene fluoro caprylamide.

5. A stable, non-foaming petroleum hydrocarbon jet fuel composition consisting essentially of a major amount of a petroleum hydrocarbon jet fuel having a boiling range from about 240° F. to about 600° F. and a Reid Vapor Pressure of 5–7 lbs. per sq. in. at 100° F. containing from about 0.01% to about 0.1% by volume of a mixture of $C_{21}F_{44}$ aliphatic perfluorocarbon having a boiling point of 130–240° C. at 10 mm. Hg and $C_{12}F_{26}$ aliphatic perfluorocarbon having a boiling point of 20–65° C. at 10 mm. Hg in the mole ratio of from 4:1 to 2:1 respectively, and from about 0.5% to about 5% of N-C_{12-18} trimethylene fluorocaprylamide.

6. A stable, non-foaming petroleum hydrocarbon jet fuel composition consisting essentially of a major amount of a petroleum hydrocarbon jet fuel having a boiling range from about 240° F. to about 600° F. and a Reid Vapor Pressure of 5–7 lbs. per sq. in. at 100° F. containing from about 0.01% to about 0.1% by volume of a mixture of $C_{21}F_{44}$ aliphatic perfluorocarbon having a boiling point at 130–240° C. at 10 mm. Hg and $C_{14}F_{30}$ aliphatic perfluorocarbon having a boiling point of 65–130° C. at 10 mm. Hg in the mole ratio of from 4:1 to 2:1 respectively, and from about 0.5% to about 5% of N-C_{12-18} trimethylene fluorocaprylamide.

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