United States Patent Office

2,992,083

Patented July 11, 1961



2,992,083

# LIQUID HYDROCARBON POWER FUEL CONTAINING CYANOALKYLPOLYSILOXANES AS FOAM DEPRESSORS

Ben A. Bluestein, Schenectady, and Harold F. Sober, Troy, N.Y., assignors to General Electric Company, a corporation of New York

No Drawing. Filed Nov. 12, 1959, Ser. No. 852,219

5 Claims. (Cl. 44—72)

The present invention relates to fuel compositions and more particularly to hydrocarbon fuel compositions having reduced foaming properties. Specifically, the present invention relates to the incorporation of certain cyanoalkyl-substituted siloxanes as foam inhibitors in hydrocarbon power fuel compositions to reduce the foaming tendency of such compositions and to the resulting fuel compositions containing such foam inhibitiors.

It has been known that liquid hydrocarbons, particularly low vapor pressure fuels, have a tendency to froth and foam when agitated in the presence of air or gases. Under some conditions the volume of foam or froth produced is many times the initial volume of the liquid hydrocarbon. Heretofore, various conventional antifoam agents, such as polyglycols and morpholine, have been used in hydrocarbons with varying degrees of success and liquid organopolysiloxanes have been used in liquid hydrocarbons including oils with good results. However, neither the conventional antifoam agents nor the liquid polysiloxanes heretofore used have been effective in stabilizing low vapor pressure hydrocarbon fuels, particularly the special low vapor pressure hydrocarbon fuels which have been developed for the jet aircraft industries, and which have produced peculiar foam problems. Conventional foam inhibitors including the hydrocarbon-substituted polysiloxanes of Patnode have been found to be ineffective in use in these specially developed jet fuels, and particularly under the conditions often presented in measuring jet fuel flow.

It has now been discovered that certain cyanoalkyl polysiloxanes impart effective and spectacular antifoaming properties to liquid hydrocarbon power fuels. This is most unexpected in view of the fact that while conventional polysiloxanes generally have been effective in reducing the foaming tendencies of hydrocarbon oils, these standard commercially available silicone antifoaming agents were found to increase rather than decrease the amount of foam formed in such power fuels.

In accordance with the present invention it has been found that cyanoalkyl polysiloxanes corresponding to the following average formula are highly effective as foam inhibitors when added to hydrocarbon power fuel compositions, such as internal combustion and jet fuel compositions:

$$(1) \qquad [NC(C_mH_{2m})]_a(R)_bSiO_{\frac{4-a-b}{2}}$$

wherein R is a monovalent hydrocarbon group and a halogenated monavalent hydrocarbon group such as aryl, particularly phenyl, chlorophenyl, tolyl, diphenyl, naphthyl, etc.; aliphatic such as alkyl, chloroalkyl, alkenyl and alkynyl, particularly methyl, ethyl, propyl, butyl, chlorobutyl, pentyl, vinyl, allyl, butenyl, propynyl, butynyl, and wherein R is preferably a lower alkyl, such as methyl, and wherein "*m*" is an integer equal to from 1 to 5 and is preferably 2, and wherein "*a*" is equal to 0.001 to 1.0, and "*b*" is equal to 1.001 to 2.000, and the sum of "*a*" and "*b*" is equal to 2.001 to 3.000. A particularly preferred group of the above described cyanoalkyl polysiloxane antifoam agents of the present invention comprises polysiloxanes wherein the range of cyanoalkyl groups or "*a*" is between about .05 to .99 and "*b*" is between about 1.01 to 1.98.



In addition to being highly effective as foam inhibitors for specially developed jet fuels, the cyanoalkyl polysiloxanes of the present invention have also proved to be superior to the conventional organopolysiloxane fluids as foam depressors for hydrocarbon power fuels, including spark ignition fuels, such as aviation fuels, and jet ignition fuels. While it is not known what causes the antifoam effectiveness of the particular class of cyanoalkyl polysiloxanes, a possible explanation may lie in the fact that the cyanoalkyl substituent apparently modifies the solubility characteristics of the siloxane chain so that the resulting molecule is of quite limited and low solubility compared to the conventional methyl or phenyl silicone fluids. Thus, the cyanoalkyl-substituted siloxanes have been found to be especially valuable and highly effective as a foam depressor when dispersed in low vapor pressure hydrocarbon fuels or the type characterized by the following data, taken from the Department of Defense Bulletin MIL–J–5624D.

Classification: JP–4—low vapor pressure type, wide cut gasoline type. JP–5—high flash point, kerosene type.

CHEMICAL AND PHYSICAL PROPERTIES

| | JP-4 | JP-5 |
|---|---|---|
| Distillation: | | |
| Fuel Evaporated— | | |
| 10 percent min.....° C. | ---------- | 204.4 |
| 20 percent min.....° C. | 143.3 | ---------- |
| 90 percent min.....° C. | 243.3 | ---------- |
| End Point, max.....° C. | ---------- | 287.8 |
| Freezing Point.....° C. | —60 | —48 |
| Aromatics, vol. percent max. | 25.0 | 25.0 |

Accordingly, the present invention results in hydrocarbon fuel compositions having markedly reduced foaming properties by the production of a mixture of a hydrocarbon power fuel and a cyanoalkyl-substituted polysiloxane corresponding to Formula 1 wherein the cyanoalkyl-substituted polysiloxane is present in a range of at least 10 parts to 10,000 parts by weight per million parts of the fuel.

The cyanoalkyl polysiloxane compounds that are employed in the practice of the present invention can be further defined as polysiloxane fluids that include one or more of the following cyanoalkyl-silicon linked units:

$$NC(C_mH_{2m})SiO_{3/2};\ NC(C_mH_{2m})RSiO$$
$$NC(C_mH_{2m})R_2SiO_{1/2}$$

intercondensed with one or more of the following hydrocarbons-substituted silicon linked units:

$$RSiO_{3/2};\ R_2SiO;\ R_3SiO_{1/2}$$

wherein *m* and R have been previously defined. More particularly, the fluids employed in the practice of the present invention can be exemplified by condensation products of cyanoethyl siloxane, cyanopropyl siloxane, cyanoethylmethyl siloxane, cyanoethyldimethyl siloxane, cyanoethylethyl siloxane, cyanoethylphenyl siloxane, cyanopropylmethyl siloxane, with hydrocarbon-substituted siloxanes like dimethyl siloxane, methyl siloxane, trimethyl siloxane, diphenyl siloxane, methylphenyl siloxane, diethyl siloxane and dimethylphenyl siloxane.

In the practice of one form of the invention, therefore, a cyanoalkyl-substituted polysiloxane is initially added at the desired concentration to a suitable hydrocarbon fuel either directly or dissolved in an organic solvent. The mixture can then be agitated to uniformly disperse the defoamer throughout the mixture according to methods known in the art. Another satisfactory procedure is to add the defoamer to the fuel while the latter is being agitated with an inert gas so as to suppress foam

rise or, if desired, completely to eliminate foam according to the concentration of the defoamer added. Although the amounts of the added cyanoalkyl-substituted siloxane can vary over wide limits, it is advisable to employ at least 10 parts by weight of inhibitor per million parts of fuel, adequately to insure against subsequent foam build-up. Amounts in excess of 10,000 parts of inhibitor per million of fuel can be safely tolerated without seriously altering the desirable fuel characteristics of the resulting modified hydrocarbon composition but it would be desirable to avoid excessive amounts of inhibitor in view of economic considerations. Suitable organic solvents that can be employed with the cyanoalkylsiloxane defoamers of the present invention include, for example, gasoline, naphtha, toluene and benzene.

In order that those skilled in the art may be better able to practice the present invention, the following examples illustrate the preparation of a cyanoalkyl silane and a cyanoalkyl polysiloxane.

A. *Preparation of a hydrolyzable β-cyanoalkyl silane*

β-Cyanoethyltrichlorosilane was prepared by slowly adding 106.0 grams (2.00 moles) of acrylonitrile to a solution of 18.9 grams (0.1 mole) of tri-n-butylamine in 271.0 grams (2.00 moles) of trichlorosilane. The solution was then refluxed for 24 hours and the reaction mixture was distilled until the boiling point of the residue reached 100° C. The residue was then vacuum distilled and 267.2 grams of a fraction distilling at 72 to 102° C. at 10 to 11 mm. was collected. Most of this fraction boiled between 87 and 91° C. This fraction solidified at room temperature and an upper liquid layer of 11.5 grams was decanted off. The remainder was rectified and there was obtained 212.3 grams of β-cyanoethyltrichlorosilane boiling at 92.5° C. at 13 mm. to 83° C. at 7 mm. Analysis of the product showed it to contain 7.44 percent nitrogen; and 56.4 percent chlorine. (Theoretical: 7.43 percent nitrogen and 56.53 percenit chlorine.)

B. *Preparation of a β-cyanoalkyl polysiloxane*

An oil was prepared by adding a solution of 387.0 grams (3.00 moles) of dimethyldichlorosilane, 81.4 grams (0.75 mole) of trimethylchlorosilane, and 81.0 grams (0.42 mole) of β-cyanoethyltrichlorosilane to 2 liters of water in 25 minutes and the mixture was stirred for an additional 2 hours. An emulsion formed and about 1000 ml. benzene was added to aid the separation. The benzene solution was washed with water several times, dried over calcium chloride, and the benzene was evaporated off. The oil was then filtered and devolatilized at 200 to 215° C. at 1.5 mm. for 2 hours. Analysis of this oil showed it to contain 3.05 percent nitrogen which corresponds to a ratio of about 5.9 silicon atoms per β-cyanoethyl radical.

A series of cyanoalkyl-substituted polysiloxane fluids were made according to the above procedure for use in the examples below, to illustrate the practice of the invention. The fluids prepared, designated A, B and C, corresponded to the following average range of composition, where in each substituted siloxane grouping the cyano-substituted polysiloxane chain is expressed in mole percent:

| Fluids | Composition mole percent | | |
|---|---|---|---|
| | $NCCH_2CH_2SiO_{3/2}$ | $(CH_3)_2SiO$ | $(CH_3)_3SiO_{1/2}$ |
| A | 10 | 77 | 13 |
| B | 15 | 67 | 18 |
| C | 20 | 59 | 21 |

The following examples of the effective results obtained in accordance with the present invention are given by way of illustration and not by way of limitation. All parts are by weight.



EXAMPLE 1

Nitrogen was bubbled into a cylinder containing JP–4, a low vapor pressure hydrocarbon fuel. The nitrogen flow was regulated so that about a 50 percent build-up of foam resulted which was equivalent to about 1½" to 2". Fluid A prepared above, was added at a concentration of 100 parts of defoamer per million parts of fuel. The height of the foam dropped immediately to ¼ to ½ inch and completely disappeared when the nitrogen flow was stopped.

EXAMPLE 2

The procedure of Example 1 was repeated except Fluid B was substituted at the same concentration, as shown in Example 1. The foam dropped immediately and then built up to about ⅛ inch. There was no build-up of foam with time.

EXAMPLE 3

A similar procedure was employed with Fluid C as in Example 1, and the concentration of fluid was also 100 parts of inhibitor per million parts of fuel. As soon as the defoamer was added the foam dropped completely, and there was no rebuild of foam over an extended period of time.

EXAMPLE 4

Nitrogen was bubbled into a cylinder containing JP–4, as in Exmaple 1, and a 1 percent solution of Fluid B in toluene was added in amounts approximating 100 parts of fluid per million parts of fuel. The foam fell immediately and completely disappeared although the nitrogen flow continued for over thirty minutes.

EXAMPLE 5

A similar procedure was employed as in Example 4, but the amount of the 1 percent solution of Fluid B in toluene that was added was decreased to one half. The foam gradually rose to about ⅛ inch but there was no perceptible increase in height with time.

In addition to the above examples, a similar procedure was employed with the more conventional foam inhibitors, along with the standard hydrocarbon-substituted polysiloxane defoamers known to the trade. As illustrated in the following table, the more conventional variety of foam depressors tended to stabilize and build up the foam instead of inhibiting it. All defoamers were employed at concentrations of 100 parts of defoamer per million parts of fuel.

TABLE I.—CONVENTIONAL DEFOAMERS ADDED TO JP–4

| Defoamer | Height of Foam, in. | Remarks |
|---|---|---|
| Dimethylpolysiloxane | 2–3 | Foam built up, and tended to stabilize with time. |
| Glycerine | 3–4 | Foam built up with time. |
| Morpholine | 3–4 | Foam fell when $N_2$ stopped. |

The above results clearly illustrate the unexpected and valuable utility of cyanoalkyl-substituted polysiloxane fluids as foam inhibitors for low vapor pressure hydrocarbon fuels. The cyanoalkyl-substituted polysiloxane fluids have also been found to be eminently effective in checking foam build-up in hydrocarbon fuels generally, particularly in those fuels known to the art as "power fuels." Power fuels are described in the Encyclopedia of Chemical Technology, vol. 10, p. 164 (1953), by the Interscience Encyclopedia Inc. of New York. These fuels include hydrocarbons derived from both petroleum processing and coal hydrogenation and can be particularly designated as spark ignition fuels such as aviation fuels, compression ignition fuels, such as diesel fuels, and jet ignition fuels containing blends of naphthas, paraffins and kerosene respectively.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A hydrocarbon fuel composition having reduced foaming properties comprising (1) a major proportion of a hydrocarbon power fuel selected from the class consisting of spark ignition fuels, compression ignition fuels, and jet ignition fuels, and (2) a cyanoalkyl-substituted polysiloxane corresponding to the following formula:

$$[NC(C_mH_{2m})]_a(R)_bSiO_{\frac{4-a-b}{2}}$$

wherein R is a member selected from the group consisting of monovalent hydrocarbon groups and halogenated monovalent hydrocarbon groups and $m$ is an integer equal to from 1 to 5, $a$ is from 0.001 to 1, and $b$ is from 1.001 to 2, and the sum of $a$ and $b$ is equal to 2.001 to 3, said polysiloxane being present in the range of 10 parts to 10,000 parts by weight per million parts of fuel.

2. A hydrocarbon fuel composition in accordance with claim 1, wherein the hydrocarbon power fuel is a jet ignition fuel having a minimum evaporation of about 20 percent at about 140° C. and a minimum evaporation of about 90 percent at about 245° C.



3. A hydrocarbon fuel composition in accordance with claim 1, wherein the hydrocarbon power fuel is a jet ignition fuel having a minimum evaporation of about 10 percent at about 200° C. and a maximum evaporation of about 290° C.

4. A composition in accordance with claim 1, wherein R in said cyanoalkyl substituted polysiloxane is methyl.

5. A hydrocarbon fuel composition in accordance with claim 1, wherein said cyanoalkyl-substituted polysiloxane is a β-cyanoethyl-substituted polysiloxane.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,724,698 | Kittleson | Nov. 22, 1955 |
| 2,837,551 | Jex et al. | June 3, 1958 |
| 2,860,153 | Saam | Nov. 11, 1958 |
| 2,906,767 | Sommer | Sept. 29, 1959 |