United States Patent Office 3,361,545 Patented Jan. 2, 1968

3,361,545

SLUDGE INHIBITING JET FUEL ADDITIVES AND METHODS FOR THEIR USE

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No Drawing. Filed Jan. 15, 1962, Ser. No. 166,361
The portion of the term of the patent subsequent to Jan. 14, 1981, has been disclaimed.
18 Claims. (Cl. 44—70)

This invention relates to a method of protecting hydrocarbon distillate compositions from attack by microorganisms.

More particularly this invention concerns the addition of certain di-substituted naphthalene additives to the above hydrocarbon distillates to inhibit the growth of sludge or slime producing microorganisms.

These microorganisms include such classes as the bacteria, actinomycetes, algae, fungi, and yeasts.

These inhibitors are di-substituted naphthalenes in which the substituents pairs are selected from the group consisting of alkyl-alkyl ester, alkyl-formyl, alkyl-hydroxyalkyl, alkyl ester-formyl, alkyl ester-hydroxyalkyl, alkyl ester-alkyl ester, formyl-hydroxyalkyl, hydroxyalkyl-hydroxyalkyl, 1,8-dialkyl, 1,2-dialkyl, 1,6-dialkyl, and mixtures of 1,8-, 1,2-, and 1,6-dialkyl.

As used throughout this disclosure the alkyl and hydroxyalkyl are understood to be those radicals having at least 1 and no more than 6 carbon atoms, branched or unbranched, joined or conjoined.

Illustrative examples of the inhibitors intended to be within this invention include 1,8-dimethylnaphthoate, 1,6-diethylnaphthoate, 1,2-dipropylnaphthoate, 2,6-dihydroxymethylnaphthalene, 1,4-dihydroxyethylnaphthalene, 6-hydroxypropyl-2-methylnaphthalene, 2-hydroxyethyl-3-ethylnaphthalene, 6 - formyl - 2 - ethylnaphthoate, 8-formyl-1-propylnaphthoate, 6-formyl-2-methylnaphthalene, 1-formyl-2-ethylnaphthalene, 1-formyl-2-methylnaphthoate, 8-formyl - 1-propylnaphthoate, 4-hydroxymethyl-1-methylnaphthoate, 2-formyl-1-hydroxymethylnaphthalene, 6-formyl-1-hydroxyethylnaphthalene, 1,8-dimethylnaphthalene, 1,2-dimethylnaphthalene, and 1,6-dimethylnaphthalene, among others.

By "hydrocarbon distillates" is meant those cuts of petroleum distillates comprising mostly saturated aliphatic and cyclic hydrocarbons with little or no aromatic content. These include kerosene, straight run gasolines and heating oils. Particularly of interest are the kerosene type aviation fuels known as "jet fuels" or more properly referred to as turbine engine fuels. By "heating oils" and gasoline is meant those cuts of hydrocarbon distillates used for heating purposes or as fuels for an internal combustion machine in automobiles or aeroplanes.

The term "microorganisms" as used throughout this disclosure refers to those organisms of biological origin, of microscopic or ultra microscopic size, capable of metabolizing or feeding upon jet fuel substrates in the presence or absence of oxygen. These microorganisms include but are not limited to bacteria, fungi, yeasts, molds, algae, protozoa, and the like. Microorganisms particularly troublesome to jet fuels include among many others the following genera: Penicillium, Aspergillus, Spicaria, Helminthosporium, Pseudomonas, Aerobacter, Bacterium, Clostridium, Cladosporium, as well as certain gram-negative Diplococcus and Spirochaetes.

That certain types of microorganisms are able to utilize hydrocarbons as nutrient substrates has been known for many years but has aroused little but academic interest.

The reason for this lack of interest was that little hydrocarbon was consumed. The microorganism attack

took place over long periods of time and no perceptible change in the hydrocarbon fuels was noticed by the user.

Recently, however, with the much wider use of turbine type aircraft, large quantities of kerosene free from even trace amounts of contaminants are required. There have been increasing reports that the heretofore supposedly innocuous microorganism digestion of the hydrocarbons produces sludge, slime, and solid sediment which not only cause operational difficulties in the aircraft but induce more rapid corrosion of the aircraft parts, particularly the fuel tanks.

While the mechanism of this sludge and slime formation is not fully understood at this time, it appears as though the sludge-like contaminants are produced by the microorganism as a metabolic waste product. Whatever be the means by which the contaminating substances are produced, it is clear that during operational use the contaminated fuel clogs and plugs the aeroplane's fuel filters and coalescers and fouls the tank gauges to the point that they become unreliable. These malfunctions of aircraft parts interfere with efficient engine operation, and, it is suspected, have upon occasion caused operational turbine engine failure.

An indirect but no less costly problem caused by the sludge is the increased corrosion of the aeroplane fuel tanks. Apparently, this comes about by the microorganisms concentrating the small amounts of water present in the fuel so that small agglomerates of water are continuously held in contact with the walls of the metal tank, instead of being dispersed innocuously throughout the fuel.

With the recognition of the existence of the sludge problem many different solutions have been suggested and tried. Some of the proposed solutions to this problem have been dehydration and purification of the fuel, adding rust inhibitors, coating the tank sides with protective materials, adding bactericides or fungicides to the stored compositions, and better "housekeeping" procedures such as more frequent cleaning of the tanks and draining of the accumulated water. Unfortunately, all of these approaches appreciably raise the cost of the fuel and none has proved to be truly effective. Turbine engine fuel is already remarkably free from water and solid contaminants. For example, most commercial specifications call for less than 2 mg. of solid particles per gallon and less than 100 p.p.m. of water. To reduce these trace impurities further or to dehydrate the fuel more completely would be prohibitively expensive and would undoubtedly require better storage facilities than presently exist to maintain the fuels at their high level of purity. The use of bacteriostatic or fungistatic additives such as organic boron compound is promising, but up to now, none of the recommended compounds has proved to be completely satisfactory in so far as their activity or cost of application is concerned. For example, a recent report on the problem by the Gulf Research and Development Company (Development of the Microbiological Sludge Inhibitors) by Churchill and Leathen reveals that all of the recommended materials required concentrations of at least 500 p.p.m. to function effectively, and the majority required 1000–20,000 p.p.m. Furthermore, the cost of some of these inhibitors substantially increases the cost of the fuel. Another failing of many of these inhibitors is their exceedingly narrow spectrum of activity. Few if any of the recommended biocides would be effective against many of the 184 microorganisms disclosed (in the above report) to have been isolated from contaminated fuel samples. Thus, applicants' discovery that the presence of certain di-substituted naphthalenes in small concentrations inhibit the growth of the noxious microorganisms is a truly significant finding, advantageous in several respects. For example, these inhibitor compositions are

soluble in the fuel phase, unlike many conventional biocides which are derived from salts or contain heavy metals. Thus these inhibitors are suitable for operational turbine engine use. However, because of the extremely low concentrations required for inhibition, these inhibitors will not only protect the fuel composition but will also disperse in the interface between the fuel and water phases to keep this potentially favorable growth environment free from microorganisms.

Another advantage of the microorganism growth inhibitors of this invention is their low cost and ease of preparation. These inhibitors are well known compounds whose preparation and properties are presented among other places in Chemical Abstracts and in the exhaustive review by Donaldson, entitled "The Chemistry and Technology of Naphthalene Compounds," published by Edward Arnold, Ltd., 1958. Furthermore, applicants' inhibitors have a broad spectrum of activity against a variety of sludge-forming yeasts, fungi, and bacteria, including but not limited to the following genera: Aspergillus, Alternaria, Rhizopus, Fusarium, Proteus, Pseudomonas, Salmonella, Staphylococcus, Escherichia, Bacillus, Kloeckera, Saccharmyces.

This broad spectrum of activity against microorganisms is unusual in that many of the suggested biocides are highly active against a few microorganisms but are completely inactive against all others. For example, the applicants' inhibitors are advantageous over the recommended organic borates, in having a broader spectrum of inhibiting activity against many different types of microorganisms, and high activity at low concentrations. This combination of high activity at low concentrations and a broad spectrum of inhibitory activity permits the treatment of the fuels without causing a significant increase in their cost.

Finally the inhibitors of this invention possess good hydrocarbon solubility coupled with good inhibitory activity. Especially active are the alkyl esters of the mono- and dicarboxynaphthalenes, the formyl naphthoic acid esters, and the 1,8- and 1,2-dialkylnaphthalenes. This hydrocarbon solubility is especially important in the operational use of the inhibitors as turbine engine fuel additives. This operational use requires the control of microorganisms living within the hydrocarbon fuel, sustained by the small amounts of water present. While a water soluble inhibitor can effectively prevent the growth of microorganisms in the water phase, this effect is wasted if the microorganisms can continue to survive in the fuel itself. To effectively prevent the growth of the microorganisms in their fuel environment, an inhibitor must be able to enter and disperse in this environment sufficiently long to control their growth. This requires a hydrocarbon soluble inhibitor. Another requirement of a turbine engine fuel additive suitable for operational use is that the inhibitor must burn freely in the engine without leaving corrosive residues or forming corrosive gases. This latter requirement eliminates most of the potentially valuable conventional biocides of the prior art. These inhibitors are generally compounds having halogens or heavy metals in the molecule which upon ignition leave corrosive residues or produce corrosive gases. In contrast the inhibitors of this invention do not contain halogen or heavy metals and are therefore considered satisfactory for operational fuel use.

While all of the above compositions inhibit the formation of sludge or slime caused by microorganisms, as in any large group of compounds, there are certain considerations such as substantial differences of activity, commercial availability, ease of production, yield, solubility, cost, and the like, which cause some of the compositions to be favored over the others. Particularly important considerations in the choice of a particular inhibitory additive for operational use are low cost of treatment coupled with good activity. Thus, within the disclosed group of inhibitors, a smaller group consisting of the 1,8-, 1,6-, and the

1,2-dialkylnaphthalenes are favored. In this group the 1,8-, 1,6-, and 1,2-dimethyl and diethylnaphthalenes are especially attractive as inhibitors because they occur in the aromatic portion of catalytic gas oils and can be recovered therefrom. The major part of the unresolved aromatic portion is made up of larger amounts of the inactive dialkylnaphthalene isomers as well as other aromatics. The naphthalenes can be readily separated and can be used unresolved as an isomer mixture as long as a growth inhibiting amount of the three active isomers singly or in combination is present. Alternatively, the three active isomers can be separated from the naphthalene fraction and from each other and used as the individual inhibitors.

However, on the basis of their higher inhibitor activity and good hydrocarbon solubility, the preferred inhibitor embodiments for turbine engine fuel, gasoline, and fuel oil use, particularly for operational use, are the alkylnaphthoates, the dialkylnaphthoates, and the hydroxyalkyl-alkylnaphthoates.

To more fully set forth the detailed workings of this invention, the following illustrative examples of this invention are submitted:

EXAMPLE I

Determining fungicidal activity of representative compounds of this invention against test organisms

EXPERIMENTAL

The following viable test fungi are treated as described below:

Fusarium oxysporum
Fusarium roseum
Rhizopus nigricans
Rhizopus stolonifer
Aspergillus niger
Alternaria solani

One loopful of the above viable fungi cultures, spores and mycelia are transferred from agar slants to 80 ml. portions of the nutrient broth given below:

Component:	Percentage by wt.
Bacto-soytone	1.0
Bacto-dextrose	4.0
Deionized water	To volume

The 80 ml. portion of the fungi and broth are placed on a sterile trypsinizing flask (300 ml.) and placed on a rotary shaker for 72 hours at room temperature. At the end of this incubation time period, 20 ml. of the liquid is homogenized and placed into another sterile trypsinizing flask (300 ml.) containing 90 ml. of the above nutrient broth and 500 p.p.m. and 1000 p.p.m. respectively of the inhibitor being tested. The flasks are placed on a rotary shaker operating at 240 r.p.m. at room temperature for three days. After this second incubation time the flasks are taken off and examined for visible fungal growth. Untreated controls are used as the basis of comparison.

RESULTS

The following chemicals gave substantially complete inhibition of fungi growth at 500 p.p.m. to 1000 p.p.m.:

1,2-dimethylnaphthalene
1,2-diethylnaphthalene
1,8-dimethylnaphthalene
1,8-diethylnaphthalene
1,6-dimethylnaphthalene
1,6-diethylnaphthalene
6-methyl-2-hydroxymethylnaphthalene
6-propyl-2-ethylnaphthoate
1,8-dimethylnaphthoate
1,2-diethylnaphthoate
2,6-dihydroxymethylnaphthalene
1,6-dipropylnaphthoate

6-formyl-2-methylnaphthoate
6-formyl-2-hydroxymethylnaphthalene
8-formyl-1-hydroxymethylnaphthalene

EXAMPLE II

Evaluation of compositions as inhibitors of sludge formation in jet fuels

STANDARDS PREPARATION

A 100 ml. portion of fuel designated by the A.S.T.M. as J.P.-4 fuel is layered over 10 ml. of mineral salt medium in 250 ml. "Boston Round Bottles." Sufficient test compound is added (none is added for the control) to give concentrations of 500 and 1000 p.p.m. in the water phase.

EXPERIMENTAL

Each of the above two test standards (500 and 1000 p.p.m.) containing test chemical to be evaluated is inoculated with a sludge containing viable microorganisms such as bacteria, molds, and actinomycetes. The sludge-test chemical systems are incubated at room temperature (25° C.) for 2 weeks and then are inspected for growth. The results appear in the table which follows the "key" of evaluating control.

Key

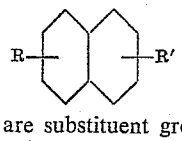
++++—luxuriant growth, no control
+++—substantial growth, no effective control
++—moderate growth, a little control
+—little growth, fairly good control
None—no growth, complete control

TABLE I

Chemical Tested	Concentration in p.p.m. and Control Obtained	
	500 p.p.m.	1,000 p.p.m.
1,2-dimethylnaphthalene	++	+
1,2-diethylnaphthalene	++	+
1,8-dimethylnaphthalene	++	+
1,8-diethylnaphthalene	++	++
1,6-dimethylnaphthalene	+++	++
1,6-diethylnaphthalene	+++	++
6-methyl-2-hydroxymethylnaphthalene	++	++
6-propyl-2-ethylnaphthoate	++	+
1,8-dimethylnaphthoate	+	+
1,2-diethylnaphthoate	++	+
2,6-dihydroxymethylnaphthalene	+	None.
1,6-dipropylnaphthoate	++	++
6-formyl-2-methylnaphthoate	+	None.
6-formyl-2-hydroxymethylnaphthalene	+	None.
8-formyl-2-hydroxymethylnaphthalene	+	+

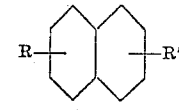
We claim:

1. A hydrocarbon distillate aviation jet fuel composition comprising a major amount of an essentially aromatic-free hydrocarbon distillate fuel to which has been added a minor amount of a disubstituted naphthalene of the structure



wherein R and R' are substituent groups having from 1 to 6 carbon atoms which substituents are selected from the group consisting of alkyl, hydroxyalkyl, formyl, and the alkyl esters of carboxy, said disubstituted naphthalene being present in sufficient concentration to inhibit the formation of microbiologically induced sludge, slime, and sedimentation.

2. A method of protecting airplane fuel tanks and fuel filter systems from clogging and corrosion caused by microbiological growth in said fuel tanks and said fuel filter systems which comprises contacting said fuel tanks and said fuel filter systems with a hydrocarbon distillate aviation jet fuel composition comprising a major portion of an essentially aromatic-free hydrocarbon distillate aviation jet fuel to which has been added a minor amount of a disubstituted naphthalene of the structure



wherein R and R' are substituent groups having from 1 to 6 carbon atoms which substituents are selected from the group consisting of alkyl, hydroxyalkyl, formyl, and the alkyl esters of carboxy, said disubstituted naphthalene being present in sufficient concentration to inhibit the formation of microbiologically induced sludge, slime, and sedimentation.

3. The composition of claim 1 wherein the di-substituted naphthalene is a mixture of 1,8-dialkyl, 1,2-dialkyl and 1,6-dialkylnaphthalenes.

4. The composition of claim 1 wherein the di-substituted naphthalene is 1,8-dimethylnaphthalene.

5. The composition of claim 1 wherein the di-substituted naphthalene is 1,2-dimethylnaphthalene.

6. The composition of claim 1 wherein the di-substituted naphthalene is 1,6-dimethylnaphthalene.

7. The composition of claim 1 wherein the di-substituted naphthalene is 6-hydroxyalkyl-2-alkylnaphthoate.

8. The composition of claim 1 wherein the disubstituted naphthalene is 1,8-dialkylnaphthoate.

9. The composition of claim 1 wherein the di-substituted naphthalene is 1,2-dialkylnaphthoate.

10. The composition of claim 1 wherein the di-substituted naphthalene is 1,6-dialkylnaphthoate.

11. The method of claim 2 wherein the disubstituted naphthalene is a mixture of 1,8-dialkyl, 1,2-dialkyl, and 1,6-dialkylnaphthalenes.

12. The method of claim 2 wherein the disubstituted naphthalene is 1,8-dimethylnaphthalene.

13. The method of claim 2 wherein the disubstituted naphthalene is 1,2-dimethylnaphthalene.

14. The method of claim 2 wherein the disubstituted naphthalene is 1,6-dimethylnaphthalene.

15. The method of claim 2 wherein the disubstituted naphthalene is 6-hydroxyalkyl-2-alkylnaphthoate.

16. The method of claim 2 wherein the disubstituted naphthalene is 1,8-dialkylnaphthoate.

17. The method of claim 2 wherein the disubstituted naphthalene is 1,2-dialkylnaphthoate.

18. The method of claim 2 wherein the disubstituted naphthalene is 1,6-dialkylnaphthoate.

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