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PREVENTION OF MICROBIAL GROWTH, CORROSION, AND THE LIKE

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This application is a continuation-in-part of my copending application Serial No. 191,333, filed April 30, 1962, now abandoned.

This invention relates to the storage, handling and transportation of organic materials, petroleum, petroleum derivatives, hydrocarbon derivatives, hydrocarbon fuels, and the like. In accordance with one aspect, this invention relates to a method for reducing the distribution or partition coefficient of hydrocarbon fuel additives so as to minimize partitioning and loss of additives from the hydrocarbon fuel to a water phase in contact therewith. In accordance with another aspect, this invention relates to the protection of organic materials, petroleum and petroleum products, and the like, against additive partitioning, microbial growth, corrosion, icing, and the like, when in contact with water.

The storage and transportation of hydrocarbon fuels, for example, is in many instances complicated due to the fact that certain additives present in the hydrocarbon fuels are lost to water, which is nearly always present in fuel storage and transportation facilities. Even though precautions are taken to prevent water from entering storage tanks and other fuel handling equipment, nevertheless water enters these systems and is, therefore, an ever present problem. For example, water enters floating roof storage tanks since many of the roofs drain water directly into the tank. After prolonged periods of storage, many fuels will have lost all of one or more water soluble additives to the water phase. Thus, when the hydrocarbon fuel is ultimately passed to a place of utilization, the additive lost to the water during storage and handling must be replaced. Replacement of lost additives is not only inconvenient but also expensive.

During the past few years a number of consumers of distillate products have indicated operational difficulties which they have attributed to microbiological activity in fuel storage systems. In the case of burner or diesel fuels, biological activity has been associated with fuel filter plugging, dirty injector nozzles, color instability and corrosion. In the case of aviation turbine fuels, fouling of filters and erratic operation of fuel-quantity indicating systems are reported. However, the facet of microbiological activity of most concern to the aircraft industry is corrosion damage to integral wing fuel tanks. The serious nature of this corrosion has been indicated by an aircraft where 30 percent of the entire wing was corroded within a 4-month period with corrosion pit depths of 0.010 inch in the wing skin and 0.030 inch in the stringers. Similar severe corrosion has been reported in service aircraft by USAF and airline operators.

Although all of the mechanisms of corrosion have not been completely defined, one which has been postulated involves, as a first step, the softening of fuel tank topcoatings by water itself. Iron rust particles enter the aircraft fuel tank by various means, such as through deteriorated filter separators, attract and hold the water, and thus provide an environment for the accelerated growth of bacteria in direct contact with the topcoating. Organic acids, produced by the metabolic activity of bacteria, may react with iron rust which, in turn, deteriorates and penetrates the water-softened topcoating. Once the coating

is perforated, the organic acid by-products attack the aluminum tank wall/wing skin. Other mechanisms such as electrolytic corrosion may also be operative, and it is not essential that iron rust particles be present for the undesirable effects of microbial growths to be experienced.

It is apparent from the foregoing discussion that such aircraft corrosion problems as may result from microbial action would be reduced if a material were present in all discrete water in the fuel system in a concentration sufficient to sterilize the water. If at the same time this added material also were to improve the condition of the topcoating, by increasing its resistance to softening by water, the possibility of aluminum corrosion would be reduced even further.

Accordingly, an object of this invention is to provide a method of reducing additive loss from hydrocarbon fuels during storage and transportation.

Another object of this invention is to provide materials that are soluble in water, but substantially insoluble in the hydrocarbon fuel, that will reduce the partitioning coefficient of hydrocarbon fuel additives, inhibit microbial growth in hydrocarbon fuels, metal corrosion, and the like.

A further object of this invention is to provide hydrocarbon jet fuels that have been stored in the presence of water without any appreciable loss of additive, microbial attack, and the like.

Other objects, aspects as well as the several advantages of the invention will be apparent to those skilled in the art upon a further consideration of the specification and the appended claims.

According to the invention set forth in said copending application, the loss of additives due to partitioning from liquid hydrocarbon fuels into water is minimized during storage and transportation by the step of adding to the fuel and/or water a depressant or retardant material compatible with the fuel that is soluble in water, but substantially insoluble in the hydrocarbon fuel, in an amount sufficient to substantially reduce the distribution or partitioning coefficient of one or more of the additives in the fuel, thereby minimizing partitioning of additive into the water phase. Actually, the depressant added functions to prevent additive from entering the water phase as well as displace additive already present in the water phase.

More specifically, it has been found according to said copending application that the addition of from about 10 to about 300 volume percent of a polyhydroxy compound base on the amount of water present in a given system in contact with the fuel to a liquid hydrocarbon fuel and water phase substantially reduces the tendency of additives present in the hydrocarbon fuel to partition into the water phase when in contact with water. The amount of retardant added based on the amount of fuel will ordinarily range from 0.01 to 5 volume percent, preferably from 0.1 to 2 volume percent.

Thus, according to the invention of said copending application, there is provided, in a preferred embodiment, a distribution or partitioning coefficient retardant or depressant material suitable for use in a liquid hydrocarbon fuel and/or water, comprising a polyhydroxy alcohol containing from 2 to about 22 carbon atoms and from 2 to 5 OH groups wherein each OH is attached to different carbon atoms.

Representative examples of polyhydroxy alcohols that can be used according to the invention of said copending application include the polyethylene glycols having molecular weights preferably ranging from 200–700 and having the formula $HOCH_2(CH_2OCH_2)_xCH_2OH$ wherein x ranges from 1–10 such as: diethylene glycol; triethylene glycol; tetraethylene glycol; pentaethylene glycol; deca-

ethylene glycol; dipropylene glycol, and the like. Other polyhydroxy alcohols that can be used include

ethylene glycol;
1,2-dihydroxypropane;
1,3-dihydroxypropane;
glycerol;
1,2,3-trihydroxybutane;
1,2,4-trihydroxybutane;
2-(hydroxymethyl)-1,3-dihydroxypropane;
erythritol;
pentaerythritol;
1,2,3,4-tetrahydroxypentane;
1,2,3,5-tetrahydroxypentane;
1,2,4,5-tetrahydroxypentane;
2-(hydroxymethyl)-1,3,4-trihydroxybutane;
1,2,3,4,5-pentahydroxypentane,

and the like.

It is also within the scope of the invention of said copending application to utilize other retardant materials to treat the fuel or water phase to prevent partitioning of an additive from a hydrocarbon phase to a water phase when the two phases are in contact with each other. Other retardants that can be used include one or more of the glycol ethers as defined hereinbelow with regard to the anti-icing additives preferred. Also, it is within the scope of the invention to "spike" the hydrocarbon fuel with extra additive or glycol ether in order to compensate for additive or glycol ether lost to the water phase coming in contact with the fuel.

The amount of partitioning coefficient depressant or retardant added according to the invention of said copending application will vary appreciably but will ordinarily be preferably at least 10 volume percent of the water present or in contact with the hydrocarbon fuel containing additives which one does not want to lose to the water phase. However, ordinarily the amount of depresant or retardant added will range from about 50 to about 300 volume percent base on the amount of water in a given system and in contact with the fuel.

In actual operation, the polyhydroxy alcohol partitioning coefficient retardant material employed, according to the invention, is added directly to a storage tank or other facility containing a water phase and a hydrocarbon fuel having water soluble additives. If a water phase is present in the storage tank prior to the addition of the fuel, the retardant can be conveniently added directly to the water phase to concentrate the additive therein. When the fuel is removed from the storage tank and replaced with another batch of fuel, in some instances it may not be necessary to add more retardant unless more untreated water enters the system or storage tank since the retardant will remain in the water phase. As indicated above, the retardant can also be added to low places in pipelines or other fuel handling facilities containing water so as to prevent additive loss from the hydrocarbon fuel into the water phase. The particular procedure and place of addition is well within the skill of the art and can be readily determined depending upon the particular problem and facilities at hand.

It has now been found, according to the invention, that microbial growth and metals corrosion, in particular, can be inhibited, or even eliminated, in hydrocarbon fuels systems containing moisture or water by the addition either to the fuel or to the water associated wih the fuel a least one additive selected from the polyhydroxy alcohols and glycol ethers such as ethylene glycol, methyl Carbitol (diethylene glycol monomethyl ether), methyl Cellosolve (ethylene glycol monomethyl ether), and combinations of these such as methyl Cellosolve and glycerol, ethylene glycol and methyl Cellosolve, and the like. These materials can be added directly to the water phase to kill the microorganisms or can be added to the hydrocarbon fuel. When added to the hydrocarbon phase, a partition coefficient is set up between the hydrocarbon and the water so that the added material goes into the water phase in a concentration high enough to cause sterilization of the water phase and metals contacted by the added material, yet remaining in the hydrocarbon phase in sufficient quantity to protect the hydrocarbon fuel against icing during use in internal combustion engines, for example, which encounter subfreezing conditions.

Briefly described, the present invention involves the maintenance of a water layer in contact with petroleum, petroleum products, organic compounds, hydrocarbon derivatives, and like substances in storage tanks and other facilities in a condition capable of inhibiting microbial action over a sustained period of time, the condition being such that neither the stored substance nor the material of which the tanks are constructed is affected thereby. More specifically, the invention involves the maintenance of at least 7.5 volume percent of an antimicrobial agent defined herein in the water phase so as to inhibit the growth of micro-organisms and microbial action in the water and consequently prevent any undesirable effect on the stored material or the tank structure.

Thus, according to the invention, there is provided a microbial growth inhibitor, corrosion inhibitor, and the like, suitable for use in systems containing liquid hydrocarbon fuels in intimate contact with a minor proportion of an aqueous phase wherein the aqueous phase contains at least about 7.5 volume percent, preferably at least 10 volume percent of at least one compound selected from the group consisting of (*a*) polyhydroxy alcohols containing from 2 to about 22 carbon atoms, and from 2 to 5 OH groups wherein each OH is attached to a different carbon atom, and (*b*) glycol ether having the formula

$$R(OCH_2CH_2)_xOH$$

wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, phenyl and tolyl groups, when R is hydrogen, x is an integer of from 2 to 4 and when R is other than hydrogen, x is an integer of from 1 to 4.

Preferably, according to the invention, there is provided antimicrobial agents, corrosion inhibitor compositions, and anti-icing additives comprising a blend of (*a*) polyhydroxy alcohols containing from 2 to about 22 carbon atoms, and from 2 to 5 OH groups wherein each OH is attached to a different carbon atom, and (*b*) glycol ethers having the formula $R(OCH_2CH_2)_xOH$ wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, phenyl and tolyl groups, when R is hydrogen, x is an integer of from 2 to 4 and when R is other than hydrogen, x is an integer of from 1 to 4.

Further, according to the invention there is provided a liquid hydrocarbon fuel having an anti-icing additive incorporated therein in an amount ranging up to 1 volume percent or more of the fuel sufficient to set up a partition coefficient between the fuel and a water phase in contact therewith so that at least a portion of the additive goes into the water phase in a concentration high enough to inhibit microbial growth and inhibit corrosion of metals contacted by the water phase. The anti-icing additive most preferred comprises a synergistic blend of (1) a saturated acrylic polyhydroxy alcohol containing from 3 to 5 carbon atoms, from 2 to 5 OH groups each attached to different carbon atoms and wherein the ratio of OH groups to carbon atoms is in the range of 0.66:1 to 1:1, and (2) a glycol ether having the formula

$$R(OCH_2CH_2)_xOH$$

wherein: R is selected from the group consisting of a hydrogen atom, methyl, ethyl, propyl, butyl, phenyl, and tolyl groups; when R is hydrogen, x is an integer of from 2 to 4; and when R is other than hydrogen, x is an integer of from 1 to 4; however, the glycol ethers defined can be used alone effectively both as an anti-icing additive and as an anti-microbial agent.

Representative examples of compound (a) include the specific polyhydroxy alcohols set forth above with regard to the partitioning retardant. Representative examples of compound (b) and (2) include methyl ether of ethylene glycol (methyl Cellosolve); ethyl ether of ethylene glycol (ethyl Cellosolve); butyl ether of ethylene glycol (butyl Cellosolve); methyl ether of diethylene glycol (methyl Carbitol); ethyl ether of diethylene glycol (ethyl Carbitol); butyl ether of diethylene glycol (butyl Carbitol); methyl ether of triethylene glycol; ethyl ether of triethylene glycol; phenyl ether of ethylene glycol; tolyl ether of ethylene glycol; phenyl ether of diethylene glycol; tolyl ether of diethylene glycol; phenyl ether of triethylene glycol; tolyl ether of triethylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol, and the like.

Representative examples of compounds (1) include 1,2-dihydroxypropane; 1,3-dihydroxypropane; glycerol; 1,2,3-trihydroxybutane; 1,2,4-trihydroxybutane; 2-(hydroxymethyl)-1,3-dihydroxypropane; erythritol; pentaerythritol; 1,2,3,4-tetrahydroxypentane; 1,2,3,5-tetrahydroxypentane; 1,2,4,5 - tetrahydroxypentane; 2-(hydroxymethyl)-1,3,4-trihydroxybutane; and 1,2,3,4,5-pentahydroxypentane.

A presently preferred group of compounds effective as anti-microbial agents, corrosion inhibitors, and the like, according to the invention include ethylene glycol, methyl ether of diethylene glycol (methyl Carbitol), methyl ether of ethylene glycol (methyl Cellosolve), ethylene glycol-methyl Cellosolve mixture, ethylene glycol-methyl Carbitol mixture, and methyl Cellosolve-glycerol mixture.

As indicated above, microorganisms are a serious problem in the storage and handling of hydrocarbon fuels such as jet fuels and fuel oils because of growth in the fuel and in any water associated with the fuel and especially growth at the hydrocarbon-water interface. By their growth the organisms cause the fuel to become unacceptable for its intended use due to the formation of materials which plug filters, cause corrosion, produce off-color fuel, etc. According to the invention, the microbial growth encountered in the handling and storage of hydrocarbon fuels can be stopped and eliminated by the addition of one or more of the above-defined compounds to the system. The exact identity of these microorganisms is often difficult to ascertain, and, therefore, the invention is not limited to any specific scientific class of microorganism. In what manner the hydrocarbon fuels become infected has not been definitely established because of the many possible sources of contamination, such as, for example, contact with residual water in stationary storage tanks or storage tanks of marine transports, engine fuel systems, decaying vegetation, or merely air.

As indicated above, it has been found that the problem of microbial growth in hydrocarbon fuels can be alleviated by treatment thereof with the anti-microbial agents of the invention. Anti-microbial agents that are suitable for the purposes of this invention are those that are capable of destroying or killing hydrocarbon fuel gel-forming microorganisms.

The anti-microbial agents of this invention should be used in concentrations effective to destroy the microorganisms, i.e., in microbial proportions. The optimum concentration of the anti-microbial agents of this invention may, of course, vary with the nature of the individual agents themselves and possibly in some instances according to the degree of infection of the fuel by the microorganisms. Generally speaking, highly effective results will be obtained by addition to the hydrocarbon fuel, or to aqueous phase material in contact therewith, of anti-microbial agents of the kind disclosed herein in amounts such that the aqueous phase contains at least about 7.5 volume percent, preferably at least about 10 volume percent of the anti-microbial agents. From a practical standpoint and for other important reasons, the preferred upper limit of anti-microbial agent is at least 50 percent and, more preferably, 100 percent higher than the lower limit which gives biocidity. Thus, in the case of ethylene glycol monomethyl ether (methyl Cellosolve) or 98/2 mixture of methyl Cellosolve and glycerol, for example, assuming 15 volume percent in the water phase is biocidal, the upper preferred limit would be 30 volume percent. It has been found that as the concentration of glycol ethers, for example, in water is increased, there is a positive and significant increase in the degradation of materials which come into contact with such solutions. One such example is Buna-N-topcoating in aircraft fuel tanks. Other examples includes sealants and gasket materials at connections, joints, pumps and elsewhere. Thus, the upper limit of anti-microbial agent added ordinarily will be determined from a practical standpoint in view of the above problems. However, in no instance should the concentration of the agent be so great as to materially impair the ignition or combustibility of the fuel treated. Moreover, it has been found that the presence of glycerol, for example, in the anti-microbial agent tends to harden topcoatings such as Buna-N, and, therefore, higher concentrations can be employed when such agent is present. Thus, it is often preferred to utilize glycerol, or other polyhydroxy alcohols, with the glycol ethers as anti-microbial agents. In the case where microbial contamination is present at the bottom of a fuel tank which has perhaps been drained of free water, but where the organisms persist, and which is subsequently loaded with fuel which does not contain any significant amount of free water, concentrations of glycerol will build up, in proximity to the cultures, which will be biocidal.

The anti-microbial agents disclosed herein can be used to treat the hydrocarbon fuels that are subject to microbial attack in any suitable manner. For example, the anti-microbial agents of the invention can be added as such, either directly to the fuel or to an aqueous phase in contact therewith at the refinery. The agents of the invention can be added to the base of storage tanks that may or may not contain a water layer, either before fuel addition to the tank or after fuel addition.

The amount of anti-icing additive referred to above incorporated in the liquid hydrocarbon fuel ranges from 0.01:1, preferably 0.01:0.5, more preferably from 0.05 to 0.2 volume percent of the hydrocarbon fuel. The amount of 0.1 volume percent gives excellent results. The proportions of alcohol and ether in the anti-icing additive are usually from 0.5 to 50 volume percent of the alcohol and from 99.5 to 50 volume percent of the ether. A more preferred range is from 1 to 40 volume percent of alcohol and from 99 to 60 volume percent of ether. A still more preferred range is from 1 to 10 volume percent of alcohol and 99 to 90 volume percent of ether.

A better understanding of the invention will be obtained upon reference to the following illustrative examples which are not intended, however, to be unduly limitative of the invention.

EXAMPLE I

A jet engine hydrocarbon fuel (JP–4) containing a 90/10 blend of ethylene glycol monomethyl ether and glycerine as an anti-icing agent blend is stored in an 80,000 barrel tank which contains 300 barrels of water. Prior to introduction of the additive-containing fuel into the tank, the fuel contains 0.117 volume percent of the ether (93.6 barrels in the hydrocarbon fuel). After storage of the fuel in the tank with the 300 barrels of water, the ether concentration in the fuel dropped to 0.067 volume percent. Thus, the fuel contains 53.5 barrels of ether and the water phase contains 41 barrels.

Glycerine is added to the 80,000 barrel tank in varying amounts to minimize the partitioning of ether into the water phase. The improvement obtained by the addition of 150 barrels, 200 barrels and 300 barrels of glycerine to the tank is set forth below in Table I.

Table I

Run	Initial	1 Tank Containing 300 bbls. H_2O	2 Add 150 bbls. Glycerine to (1)	3 Add 200 bbls. Glycerin to (1)	4 Add 300 bbls. Glycerine to (1)
Ether Conc. in fuel, Vol. percent	0.117	0.067	0.080	0.083	0.10
Barrels ether in fuel	93.6	53.5	64	66.5	80
Barrels ether in H_2O	0	41.0	29	26.5	15
Barrels Glycerine in H_2O	0	0	150	200	300

From the above table, it can be seen that the additive of glycerine to the water phase displaced ether from the water phase as well as preventing additional ether from partitioning into the water phase.

EXAMPLE II

The distribution or partition coefficient for the system comprised of ethylene glycol monomethyl ether, hydrocarbon fuel and water is defined by

$$m=\frac{X_{AZ}}{X_{AY}}$$

where:
X_{AZ}=volume fraction ether in water phase
X_{AY}=volume fraction ether in fuel phase

and the subscripts are:

Y=fuel phase
Z=water phase
A=ethylene glycol monomethyl ether

Table II below presents the distribution coefficients for a fuel where the amount of glycol ether present in the fuel was varied from 0.09 to 0.24 volume percent.

Table II

Glycol ether original in fuel, vol. percent:	Glycol ether distribution coefficient
0.09	212
0.11	216
0.13	190
0.15	180
0.17	165
0.20	140
0.24	105

The addition of glycerol to the water phase materially changes the distribution coefficient of the water soluble glycol ether. As the concentration of glycerol in the water phase builds up, the distribution coefficient of the glycol ether decreases. This is illustrated in Table III where the water phase already contains 25 volume percent of glycol ether.

Table III

Glycerol in water phase, vol. percent:	Glycol ether distribution coefficient
0	180
8	154
16	130
24	105

Thus, from the above, it can be seen that the present invention provides a practical method of minimizing the loss of fuel additives by partitioning from a fuel to a water phase.

EXAMPLE III

A test was set up using jet fuel containing various concentrations of a deicing agent comprising methyl Cellosolve and glycerol using microorganisms contained in an aviation gasoline tank bottom. The organisms were added (equal conc.) to Bushnell-Haas media overlayed with the hydrocarbon. After a period sufficient for microbial growth and action to take place, the number of microorganisms remaining viable were counted on two media (plate count agar and Bushnell-Haas media with kerosene). The results show that:

INOCULUM FROM AVIATION GAS STORAGE TANK

	Number of Surviving Organisms per, ml. in Bushnell-Haas	
	Plate Count Agar	Kerosene Agar
Percent Additive Glycerol+Methyl Cellosolve (1:1):		
0	240, 000, 000	229, 000, 000
5	155, 000, 000	168, 000, 000
10	135, 000, 000	127, 000, 000
15	186	4, 900
20	147	300
25	36	33

Normally, bacteriologists would regard counts such as shown above for 15, 20 and 25 percent as being so low as to be "uncountable" and essentially zero. Also, these drops indicate a log kill generally following a logarithimic drop off which bacteriologists are familiar with and recognize as a normal kill pattern.

Another series of tests showing these biocidal effects was made in a similar manner using only 10 and 20 percent additives and components:

NUMBER OF SURVIVING ORGANISMS PER ML. IN PRESENCE OF—

Mixed Inoculum	Inoculum from Gasoline Tank
Methyl Cellosolve:	Methyl Cellosolve:
10% 1, 060, 000	10% 9, 000
20% 100	20% 1
Methyl Cellosolve and Glycerol:	Methyl Cellosolve and Glycerol:
10% 53, 000, 000	10% 1, 530, 000
20% 174, 000	20% 0

The visual appearance of the samples in all cases showed that the absence of the bacteria caused the hydrocarbon to remain clear as well as the water phase. In those tests with high bacteria counts, the interface was ragged showing high microbial attack of the fuel and the water phase was turbid. This killing of the microorganism will also stop bacterial corrosion of tanks and equipment.

EXAMPLE IV

The biocidal aspects of ethylene glycol monomethyl ether (EGME) were checked using twelve composited cultures, three combinations of EGME and glycerol, and six concentrations of these combinations. These cultures included nine combinations of twenty-eight cultures received from an aircraft company and three combinations from five refinery tanks. Among the additive combinations evaluated were:

100 percent EGME
75/25 volume percent EGME and glycerol
50/50 volume percent EGME and glycerol

Each of the above additives was tested at concentrations of 0, 5, 10, 12.5, 15, 20 and 25 volume percent

against each of the twelve cultures, making a total of two hundred and fifty-two sample bottles. Each sample was inspected for bacterial activity at frequent intervals up to thirty-nine days storage. The criterion for bacterial growth was the appearance of the kerosene-Bushnell-Haas media and the interface between the two phases. Bacterial activity was judged positive if growth was present at the interface of if the interface and media layer were cloudy. Bacterial activity was judged negative if the interface and media were clear. Judgment made by the visual inspection of the samples was confirmed in doubtful cases by microbial plate counts.

The results of the inspection at the end of the test period are recorded in Table IV as the effective concentration of ethylene glycol monomethyl ether in Bushnell-Haas media necessary to prevent microbial growth for each of the composite cultures. It will be noticed that microbial activity was prevented on all cultures when the Bushnell-Haas media contained from 7.5 to 15 volume percent EGME.

Table IV

BIOCIDAL CONCENTRATIONS OF ETHYLENE GLYCOL MONOMETHYL ETHER IN BUSHNELL-HAAS MEDIUM UNDER TURBINE FUEL FOR VARIOUS CULTURES (39 DAY TEST)

No.	Culture	EGME	75/25% EGME/ Glycerol	50/50% EGME/ Glycerol
1	Aircraft company	10	11.3	10
2	do	12.5	15	12.5
3	do	10	11.3	10
4	do	10	9.4	10
5	do	10	9.4	10
6	do	10	11.3	10
7	do	10	11.3	12.5
8	do	12.5	11.3	10
9	do	12.5	15	12.5
10	Mixed Culture from Airport Tank including four Nocardia species, one mold and four Pseuedomonas species.	12.5	11.3	10
11	50/50 Mixture of Cultures from Refinery Heavy and Regular Diesel Fuel Tank Bottoms.	12.5	11.3	7.5
12	50/50 Mixture of Cultures from 0.4% and 1% Sulfur Diesel Fuel Tank Bottoms.	12.5	11.3	10

NOTE: The biocidal concentration of glycerol itself is 45 volume percent.

Table V

COMPOSITION OF BUSHNELL-HAAS MEDIUM

$MgSO_4$	gm.	0.2
$CaCl_2$	gm.	0.02
KH_2PO_4	gm.	1.0
K_2HPO_4	gm.	1.0
NH_4NO_3	gm.	1.0
$FeCl_3$ (conc. sol.)	ml./liters	0.1
Deionized water	ml.	1000

EXAMPLE V

Two airline cultures were used to determine the length of time required to bring a culture count to zero under optimum growth conditions with various combinations and concentrations of EGME-glycerol. The test procedure was similar to that described earlier with 50 ml. Bushnell-Haas/additive media covered with 25 ml. kerosene. Since one approach to sterilization might be to flood either an aircraft or a storage tank bottom with EGME-glycerol, using a suitable device, a test was made, at various concentrations, to see how rapidly sterilization might be obtained. Each sample bottle was shaken vigorously before sampling to obtain representative counts on TGE agar. These data are presented in Table VI.

Table VI

BACTERIAL COUNT ON AIRLINE CULTURES 1 AND 2

Airline Culture No. 1				Airline Culture No. 2			
Times, Days	Number of Organisms Per Ml. in Presence of— EGME-Glycerol			Times, Days	Number of Organisms Per Ml. in Presence of— EGME-Glycerol		
	0%	10%	15%		0%	10%	15%
0	24, 500			0	17, 700		
1	30, 000, 000	1, 000	300	1	149, 000	1, 000	300
2	15, 300, 000	300	199	2	740, 000	300	147
3	19, 500, 000	400	300	3	14, 500, 000	400	281
4	22, 400, 000	363	53	4	15, 400, 000	153	13
7	26, 800, 000	2	0	7	14, 400, 000	400	0

It will be noted that within 4 to 7 days complete sterilization of these cultures is obtained with between 10 and 15 percent of EGME-glycerol.

Any suitable type of hydrocarbon fuel can be employed in the practice of the invention. Said fuels which can be so employed include the conventional jet engine fuels which comprise a blend of hydrocarbons boiling in the range from about 100 to about 700° F., such as gas oils, kerosene, and gasolines, including aviation gasoline. Fuels of the paraffin and naphthenic type having relatively low aromatic content, i.e., not more than about 20 liquid volume percent aromatics, as well as fuels of the aromatic type having high aromatic contents ranging from about 20 up to about 88 percent or higher liquid volume percent aromatics, can be used in operating continuous combustion turbo type aircraft engines according to the practice of the invention. Hydrocarbon fuels having wide boiling ranges, such as JP–3, JP–4, or fuels of the kerosene type, such as JP–5, can be employed, the boiling range of these fuels generally being in the range of about 200 to about 600° F.

EXAMPLE VI

A series of tests was carried out to demonstrate that ethylene glycol will function as a biocide in the presence of methyl Cellosolve or methyl Carbitol. The ethylene glycol was used as representative of other glycols. The test procedure consisted of storing 4 ounce vented bottles containing 50 cc. of Bushnell-Haas media with various concentrations of the additive overlayed with 20 cc. of kerosene. The inoculum consisted of a mixed culture from 40 different tank bottoms in order to get as broad a spectrum as possible for challenging. The concentration of the additive is in the water phase. Two cc. of inoculum was used to each sample.

The test compounds were:

(1) Ethylene glycol (free of ethers).
(2) Methyl Carbitol (diethylene glycol monomethyl ether).
(3) Methyl Cellosolve (ethylene glycol monomethyl ether).

(4) 50–50 mix of ethylene glycol and methyl Carbitol.
(5) 50–50 mix of ethylene glycol and methyl Cellosolve.
(6) 50–50 mix of glycerol and methyl Carbitol.
(7) 50–50 mix of glycerol and methyl Cellosolve.
(8) Glycerol.

Table VII

Test Compound	Additive							
	1	2	3	4	5	6	7	8
0	+	+	+	+	+	+	+	+
5%	+	+	+	+	+	+	+	+
7.5%	+	+	+	+	+	+	+	+
10%	+	+	+	+	+	+	+	+
12.5%	+	−	−	+	+	+	+	+
15%	+	−	−	−	−	+	+	+
20%	−	−	−	−	−	−	−	+
25%	−	−	−	−	−	−	−	+
30%	−	−	−					+
35%								−
40%								−
45%								−

From the above data it can be seen that additives Nos. 4 and 5 (a 50–50 mixture of ethylene glycol and glycol ether) are effective at 15 percent in the water phase. Additive No. 7 is a 50–50 mixture of glycerol and methyl Cellosolve but 20 percent of this mixture was required to kill the bacteria. The additive treatment of fuel required to achieve the biocidal additive concentrations in the water phase as shown by the above table, must be considered in terms of the partition coefficient for each compound between hydrocarbon and adjacent water layer. The partition coefficients of these compounds are as follows:

Compound:	Partition coefficient
Methyl Cellosolve	220
Methyl Carbitol	350
Ethylene glycol	12,000

Since ethylene glycol has a higher partition coefficient than the other compounds, an effective biocidal concentration can be achieved in a small water phase with a lower quantity of a bactericide consisting of ethylene glycol and an ether in the fuel phase than treatment with either glycol or ether alone. As an illustration, the water phase of fuel storage tanks at service stations has been found to contain 14 to 16 percent methyl Carbitol and 23 to 26 percent ethylene glycol, giving a total of 37–42 percent of biocidal agents, after filling with fuel treated with .042 percent of anti-icing blend of 95 percent methyl Carbitol and 5 percent ethylene glycol. Assuming this to have been the glycol ether, either alone or with glycerol, containing no ethylene glycol (or a very much lower value), the partitioned total amount of additive components to water would be less.

The following table compares the partitioning effect of ethylene glycol with glycol ether from a fuel phase to a water phase in contact therewith.

[Fuel/water ratio=1000:1]

Vol. Percent Additive in Hydrocarbon Fuel	Vol. Percent Additive Components in Aqueous Phase					
	98/2 Ether/Glycerol Exposure Cycles			88/10/2 Ether/Et. Glycol/ Glyc. Exposure Cycles		
	1	2	3	1	2	3
.02	3.5	4.2	4.4	5.0	7.3	9.0
.03	5.3	6.3	6.4	7.5	11.0	13.5
.04	7.3	8.3	8.6	10.0	14.6	18.0
.05	8.8	10.4	10.7	12.6	18.0	22.0

Referring to the above table, it will be noted that with glycol ether/glycerol the low limit of 10 volume percent in the water phase is not reached until two exposures at 0.05 volume percent in the fuel are experienced. However, with added ethylene glycol the 10 percent level is reached in only three cycles at about 0.025 percent in the fuel, and at two cycles using slightly less than 0.03 percent in the fuel. This clearly shows the advantage of ethylene glycol inclusion in nonaviation usage, in that it allows use of lower additive concentrations in the fuel to reach biocidity.

The combinations of ethylene glycol and glycol ethers are presently preferred to glycol ether-glycerol mixtures as bactericides because the ethylene glycol is a more effective bactericide than glycerol. The concentration range for ethylene glycol in blends with glycol ethers is limited by the solubility of ethylene glycol in hydrocarbon fuels.

Thus, while the invention has been described herein with particular reference to hydrocarbon fuels, more specifically JP–4 jet engine fuel, the invention is not limited thereto. The invention can be used with all grades of engine fuels, as well as other materials subject to microbial attack when in contact with water or other microbe-containing materials. The antimicrobial additives of the invention can also be used with advantage in gasolines for reciprocating engines, in diesel fuels for compression-ignition engines, as well as other petroleum products, both liquid and solid, such as distillate fuels, fuel oil, turbine fuel, LPG, naphthas, gas oils, lubricating oils and stocks, waxes, asphalts, petrolatum, mineral oils, and the like.

The compositions containing anti-microbial additives treated according to the invention can also contain commonly used other additives such as anti-corrosion agents, oxidation inhibitors, and the like, when desired.

As will be evident to those skilled in the art, many variations and modifications of this invention can be practiced in view of the foregoing disclosure. Such variations and modifications are clearly believed to come within the spirit and scope of the invention.

I claim:

1. A method for inhibiting microbial attack of liquid hydrocarbon fuels when said fuels contact a water phase, which method comprises: injecting directly into said water phase, from a source other than said fuel, a microbial growth inhibiting amount of at least one additive selected from the group consisting of (a) polyhydroxy alcohols containing from 2 to about 22 carbon atoms and from 2 to 5 OH groups per molecule wherein each OH is attached to a different carbon atom, and (b) glycol ethers having the formula $R(OCH_2CH_2)_xOH$ wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, phenyl and tolyl groups, when R is hydrogen, x is an integer of from 2 to 4, and when R is other than hydrogen, x is an integer of from 1 to 4; and contacting said fuel and the resulting water phase containing said additive.

2. A method according to claim 1 wherein said additive is ethylene glycol monomethyl ether.

3. A method according to claim 1 wherein said additive is diethylene glycol monomethyl ether.

4. A method according to claim 1 wherein said additive is a mixture of glycerol and ethylene glycol monomethyl ether.

5. A method according to claim 1 wherein said additive is a mixture of glycerol and diethylene glycol monomethyl ether.

6. A method according to claim 1 wherein said additive is a mixture of ethylene glycol and ethylene glycol monomethyl ether.

7. A method according to claim 1 wherein said additive is present in said water phase in an amount of at least 7.5 volume percent, based on said water phase.

8. A method for inhibiting the corrosion, in the presence of moisture, of a tank of metal construction which holds a liquid hydrocarbon fuel which method comprises the step of: placing directly in the bottom of the tank, from a source other than said fuel, a corrosion inhibiting

amount of at least one compound capable of inhibiting said corrosion and selected from the group consisting of (a) polyhydroxy alcohols containing from 2 to 22 carbon atoms and from 2 to 5 OH groups per molecule wherein each OH group is attached to a different carbon atom, and (b) glycol ethers having the formula $R(OCH_2CH_2)_xOH$ wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, phenyl and tolyl groups, when R is hydrogen, x is an integer of from 2 to 4, and when R is other than hydrogen, x is an integer of from 1 to 4.

9. In a process for the storage and handling of a liquid hydrocarbon fuel wherein said fuel contacts a water phase at an interface therebetween and is subject to attack by microorganisms at said interface and wherein metals employed during said storage and handling are subject to corrosion as a consequence of said microbial attack, the method of substantially preventing microbial growth, and corrosion of said metals during said storage and handling, which method comprises: injecting directly into said water phase, from a source other than said fuel, a microbial growth inhibiting amount of at least one additive selected from the group consisting of (a) polyhydroxy alcohols containing from 2 to 22 carbon atoms and from 2 to 5 OH groups per molecule wherein each OH is attached to a different carbon atom, and (b) glycol ethers having the formula $R(OCH_2CH_2)_xOH$ wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, phenyl and tolyl groups, when R is hydrogen, x is an integer of from 2 to 4, and when R is other than hydrogen, x is an integer of from 1 to 4; and contacting said fuel with the resulting water phase containing said additive so as to inhibit said microbial growth and said corrosion.

10. In a process for the storage and handling of a liquid hydrocarbon fuel wherein said fuel is brought into contact with a water phase at an interface therebetween, said fuel is subject to attack by microorganisms at said interface, and wherein metals employed during said storage and handling are subject to corrosion as a consequence of said microbial attack, the method of substantially preventing microbial growth and corrosion during storage and handling, which method comprises: injecting directly into said water phase, prior to said contacting of fuel and water, a microbial growth inhibiting concentration in the amount of at least 7.5 volume percent, based on said water phase, of an additive comprising (a) from about 0.5 to 50 volume percent of glycerol and (b) from about 99.5 to 50 volume percent of ethylene glycol monomethyl ether; and then effecting said contact of said fuel with the resulting water phase containing said additive.

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