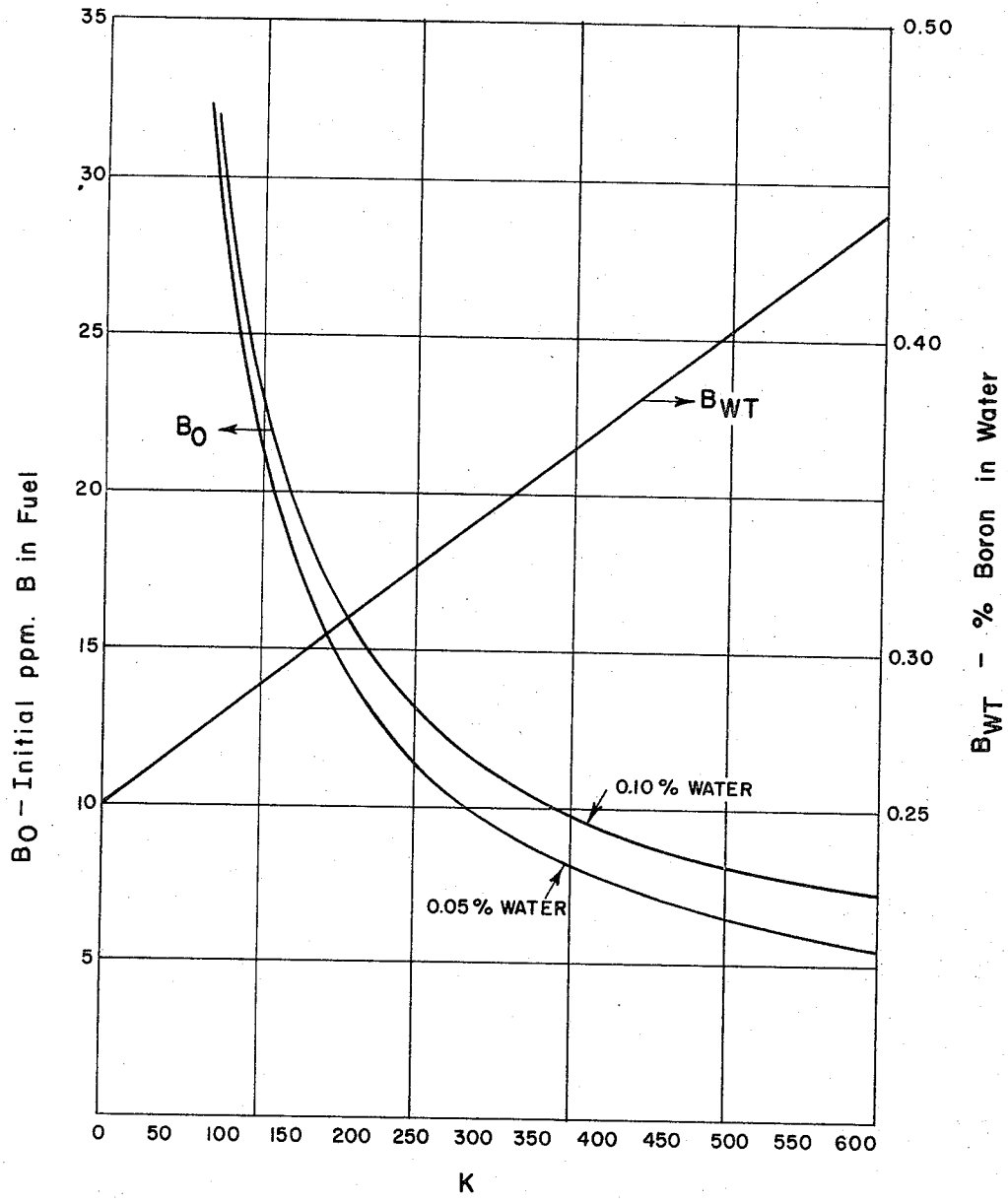
Oct. 17, 1967 R. J. DE GRAY ETAL 3,347,646

PRESERVATION OF KEROSINE DURING DISTRIBUTION AND STORAGE

Filed Jan. 16, 1967 3 Sheets-Sheet 1

FIG. 1

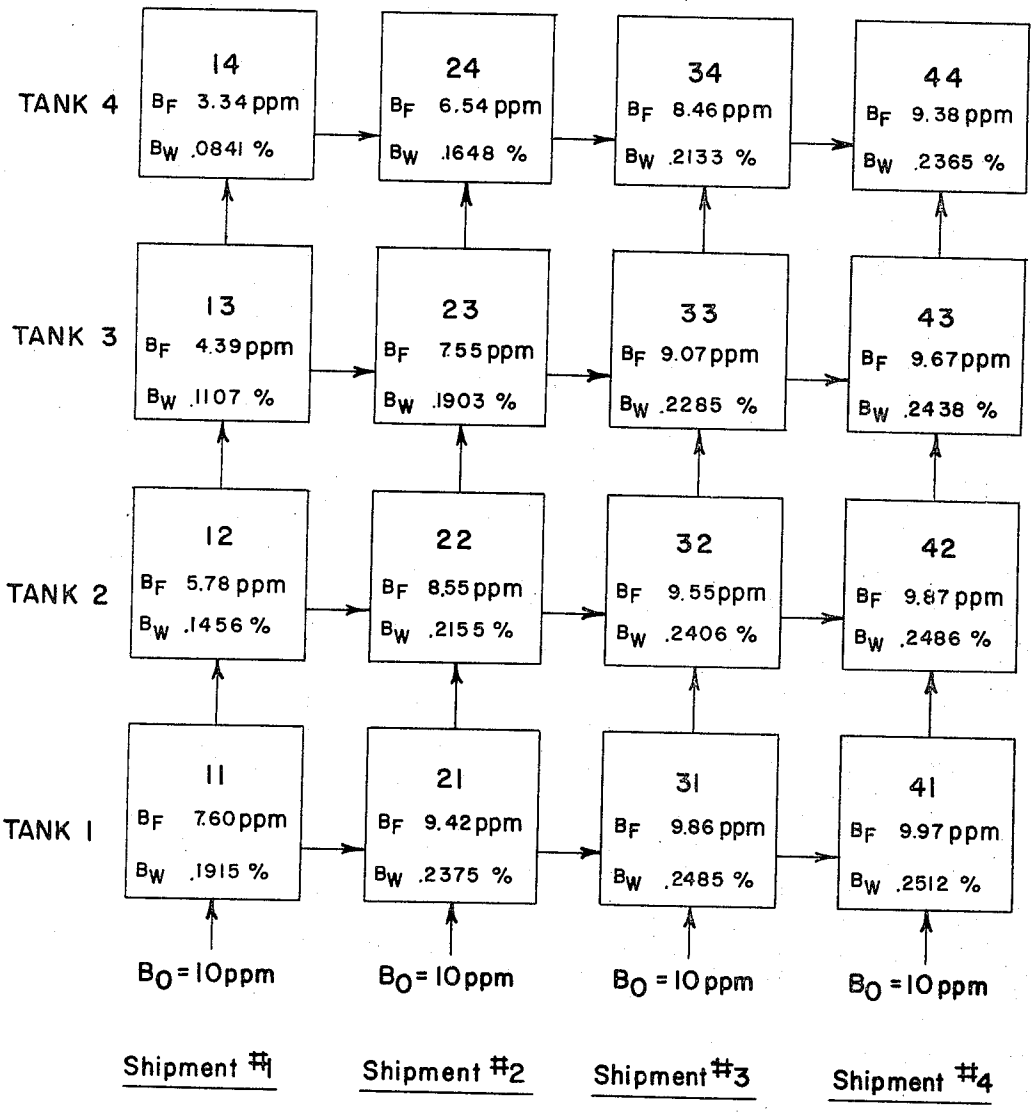


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PRESERVATION OF KEROSINE DURING DISTRIBUTION AND STORAGE

Filed Jan. 16, 1967 3 Sheets-Sheet 2

FIG. 2

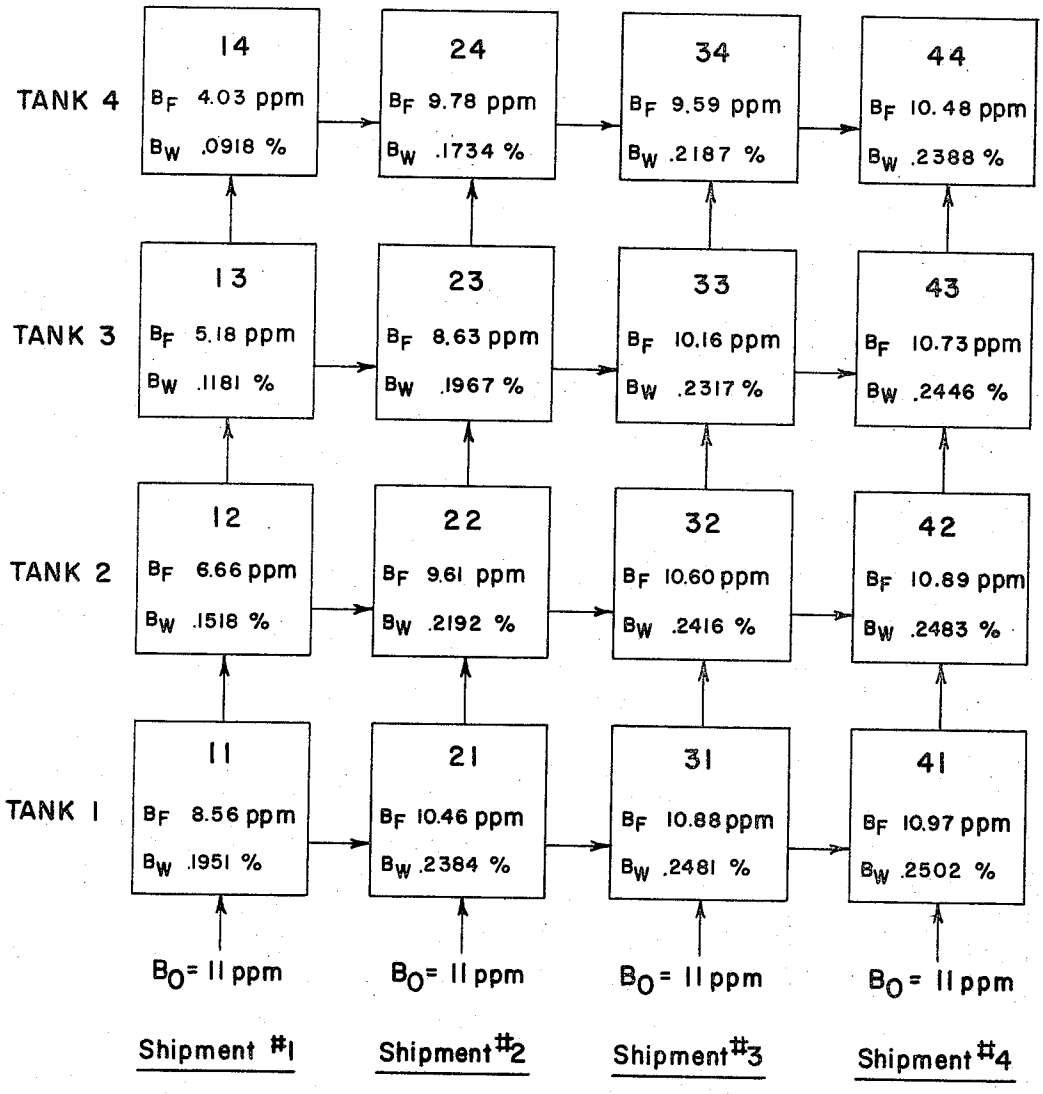


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Filed Jan. 16, 1967 3 Sheets-Sheet 3

FIG. 3



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PRESERVATION OF KEROSINE DURING DISTRIBUTION AND STORAGE

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Filed Jan. 16, 1967, Ser. No. 619,111
18 Claims. (Cl. 44—76)

This application is a continuation-in-part of copending applications Serial No. 64,261, filed October 24, 1960, Serial No. 498,783, filed October 20, 1965, and Serial No. 554,908, filed June 2, 1966, now all abandoned.

This invention relates to the preservation of kerosine-type hydrocarbons during storage and distribution. More particularly, this invention relates to an improved process for the control of growth in hydrocarbons boiling in the kerosine range of lyophilic hydrocarbon-ingesting microbes indigenous to water and present in water brought into contact with such hydrocarbons during storage and distribution thereof.

It is well known that storage vessels such as oil refinery tanks, distribution terminal tanks, and engine fuel tanks almost invariably contain small amounts of water at the bottom thereof. Some species of bacteria and fungi normally found in soil and ground water have been found also to exist in the water bottoms of such storage vessels, deriving their nutrition from the hydrocarbon phase as well as from trace elements found in the water phase. Their metabolism is responsible for the consumption of some amount of the hydrocarbons and tank corrosion, and results in product deterioration by forming rust, hydrogen sulfide, gums, peroxides, acids, colored substances, and filamentous material at the interface between the water and the hydrocarbon.

Microbes seem to prefer hydrocarbons having a C_{10} to C_{20} carbon chain for a diet, and hence such microbial action is more prevalent and far more difficult to control in kerosine hydrocarbons than in gasoline stocks stored over corresponding water bottoms. Gasoline generally has an end point below 450° F. and often below 400° F. Even when the end point is 450° F., the percent boiling above 400° F. seldom exceeds 10%. Gasoline has at least 40% of its components boiling below 250° F. Kerosine hydrocarbons are higher boiling. As used herein, the term "kerosine hydrocarbons" includes kerosines of which at least 30% boils above 400° F., or not more than 15% boils below 250° F., or both, including diesel fuel, which is a fraction from crude oil boiling between about 300 and 700° F., at least 90% boiling above 400° F., and aviation fuel for turbojet and jet aircraft. These latter fuels are blends of petroleum fractions made to meet a variety of specifications and may have a boiling range between about 100 and 600° F. and preferably between about 150 and 550° F. Kerosine hydrocarbons are almost invariably unleaded; i.e., they do not contain a tetra-alkyl lead compound. The following data are presented to illustrate one particular product; namely, JP–4, which is a relatively wide-cut kerosine fraction.

Distillation:	
20% evaporation	270° F.
50% evaporation	370° F.
90% evaporation	470° F.
Residue, percent volume	1.5
Loss, percent	1.5
Sulfur, percent wt. max.	0.4
Freezing point	−76° F.
B.t.u./lb. net, min.	18,400

Thus, about 35% boils above 400° F. In JP–5, 80 to 90%

boils above 400° F. In a close-cut kerosine boiling at 300° F.±25° F., no component boils below 250° F.

In addition, kerosine hydrocarbons (more so than gasoline stocks) seem to stabilize the water-in-fuel emulsions resulting from the slimes and filamentous material produced by microbiological action, and hence much of this contamination remains suspended in the hydrocarbon phase and has a tendency to clog filters and strainers in the storage and transport facilities and in the engines in which kerosine hydrocarbons are used as a fuel.

Filter clogging is a particularly serious problem in jet aircraft operated on kerosine-based fuel, because of the consequences of operational failure. Moreover, the tendency toward filter clogging in jet engines is aggravated due to the design of these engines and the nature of their operation. The volume of fuel consumed by a jet aircraft engine is very large, and may range as high as 1000 gallons per hour or more. In volumes of such magnitude, a very low concentration of contaminants can quickly become a troublesome amount of residue in the filter system of the engine. Furthermore, instead of a single fuel tank, a jet aircraft usually has a maze of interconnecting cells with numerous low points where water may collect and in which microbial action may be propagated. In many jet aircraft these fuel cells are practically inaccessible for cleaning or flushing, and microbiological action continues unabated.

The problem has received considerable attention and study, and there are many reports of investigations of the problem in the literature. Allen, J. Inst. Petroleum 31, 9 (1945), stated that bacterial action on gasoline results in the precipitation of tetraethyl lead and in the formation of peroxides and gums. Bushnell and Haas, Bacteriol. 41, 653 (1941) reported the presence of bacteria in the water bottoms of tanks containing gasoline and kerosine. Harris and Strawinski, U.S. Patent No. 2,680,058, dated June 1, 1954, stated that bacterial action results not only in loss through consumption of the fuel by the bacteria, but also in the formation of hydrogen sulfide, gums, peroxides, acids and colored substances. Bakanauskas, Bacterial Activity in JP–4 Fuel, WADC Technical Report No. 58–32, March 1958, demonstrated that bacterial slime developing at the water-JP–4 interface caused operational difficulties in KC–97 and B–47 jet aircraft by clogging the fuel filters.

Various proposals have been made to counteract this microbial action. Harris et al. suggested that if the water layer were brought above pH 8.5, and borax added thereto, preferably as a saturated solution, the bacteria might be controlled. However, Alton E. Prince, Developments in Industrial Microbiology, volume 2, Proceedings of the 17th General Meeting of the Society for Industrial Microbiology held at Stillwater, Oklahoma, August 28 to September 1, 1960, pages 197 to 203, reported that sodium tetraborate was really ineffective. Prince stored jet fuel over water containing a concentrated 6% solution of sodium tetraborate for thirty days, and then ran a jet engine on this fuel for one hundred hours. The engine ran, but when a field trial was carried out adding 2% by weight commercial grade sodium tetraborate to the water bottom of large storage tanks, it was found to be difficult to maintain the required concentrations. Although the bacterial population was kept down in some cases, in others the bacteria multiplied very fast, and it was not possible to reach a lethal concentration. Consequently, Prince recommended that the tanks be kept as free of water as possible, and clean. This, however, is hardly a satisfactory answer, since that is exactly what cannot be done, most of the time, which is why there is the problem.

In any event, the addition of a microbicide to the water bottom of tanks is hardly as effective an answer as the addition of the microbicide to the jet fuel. The latter addi-

tion can readily be carried out by the fuel manufacturer, and eliminates any concern or special additions on the part of fuel personnel. It furthermore saves a transportation problem to remote areas, where fuel may happen to be stored, particularly in case of war. However, addition of a microbicide to the fuel presents a special problem.

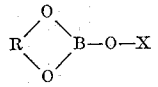
Any given body of fuel can be expected to encounter not one but several water bottoms before use, since fuel customarily is stored not only at the plant of the manufacturer but also at the point of use, and it may be stored in storage tanks of a warehouser or intermediary before reaching the ultimate consumption point. Each of the storage tanks has water bottoms, and thus it is essential that a sufficient amount of the microbicide be added to the jet fuel to retain adequate lethal action through the last tank. This means that the microbicide must be sufficiently soluble in the fuel, so that a massive concentration can be initially added, which will partition with the water bottoms in the course of the several contacts thereafter in a sufficient amount to impart a lethal concentration to each of the water bottoms it contacts, without exhausting the reserve supply of microbicide in the fuel.

In fact, no microbicide has been known that is capable of this. Most microbicides are either soluble in the fuel or soluble in water, but not both, and very few are sufficiently soluble in both of these media to partition between them in the desired amounts to provide in the water a concentration lethal to the microbes in each of a series of water contacts.

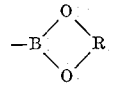
The problem is especially difficult because of the very large variety of microbes that can be encountered. Bacteria, spores, fungi, molds and yeasts are plentiful in the air, in the soil, and in ground water, and many species of these microbes are apparently capable of feeding on hydrocarbons. Thus, any microbicide to be useful at all must be completely effective against a wide spectrum of microbes.

In accordance with the invention, a process is provided for controlling the growth in hydrocarbons boiling in the kerosine range of lyophilic hydrocarbon-ingesting microbes indigenous to water and present in water brought into contact with such hydrocarbons. This process comprises dissolving in the kerosine hydrocarbon a hydrocarbon-soluble, partially water-soluble, water- and hydrocarbon-partitionable, alkylene glycol borate that is resistant to hydrolysis by water and lethal to lyophilic microbes. The alkylene glycol borates in accordance with the invention are partitionable between the hydrocarbon and water by virtue of their having a distribution ratio water:hydrocarbon within the range from about 180 to about 260, and this property is important to their effectiveness in the process of the invention.

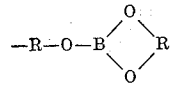
Alkylene glycol borates effective in the invention and having such distribution ratios are defined by the formula:



in which X is selected from the group consisting of hydrogen,



and



and R is selected from the group consisting of alpha- and beta-alkylene radicals having from three to about twelve carbon atoms.

Not all alkylene glycol borates falling within this formula have a distribution ratio within the stated range. When they do not, however, it is possible to employ them in admixture, such mixtures including at least one alkylene glycol borate having a distribution ratio above the range, and at least one alkylene glycol borate having a distribution ratio below the range, in amounts which, weighted by the proportion of the alkylene glycol borates present, give a distribution ratio average for the mixture within the stated range.

An important property of alkylene glycol borates falling within the above formula is their resistance to hydrolysis by water. If they are readily hydrolyzed by water, they generate the alkylene glycol and boric acid. Boric acid is ineffective as a microbicide, and furthermore, is normally insoluble in the hydrocarbon, and only sparingly soluble in water. Consequently, hydrolysis destroys the effectiveness of the alkylene glycol borate, which must accordingly be sufficiently resistant to hydrolysis to survive unhydrolyzed in the hydrocarbon until use, even if it is brought into contact with several water bottoms in so doing.

In the process of the invention, it is further contemplated that the hydrocarbon containing the alkylene glycol borate dissolved therein be brought into interfacial contact with several bodies of water containing lyophilic hydrocarbon-ingesting microbes, permitting the alkylene glycol borate to partition itself between the kerosine hydrocarbon and the water to provide a cumulative lethal concentration of alkylene glycol borate in the water and kill any microbes present therein, and any microbes that enter the water bottoms thereafter. The hydrocarbons containing the alkylene glycol borate can be brought into interfacial contact with as many bodies of water as may be necessary before use. In each case, upon such interfacial contact, the alkylene glycol borate partitions itself between the hydrocarbon and the water, to provide a lethal concentration of alkylene glycol borate in the water to kill any microbes present, and those that seek to enter thereafter, thereby during storage of the hydrocarbons preventing growth of such microbes in the water and in the hydrocarbons, and preventing the build-up of slime and sludge therein due to microbial action, maintaining the hydrocarbon sufficiently clean until use, so that it can be used in a jet engine without clogging.

The amount of alkylene glycol borate in the fuel will be selected according to the amount of water in the tank bottoms and the number of water bottoms expected to be encountered, the extent of microbial contamination, the distribution ratio of the alkylene glycol borate, and the speed with which it is desired to effect a complete kill. In general, amounts providing 5 to 100 p.p.m. boron in the fuel are useful, with a preferred range being 10 to 40 p.p.m. The alkylene glycol borate can be added directly to the fuel in the amount required. Alternatively, a concentrate of the alkylene glycol borate can be formed in a mutual solvent, and the concentrate then blended into the fuel.

A better understanding of the invention will be had from the following detailed description, taken in conjunction with the attached drawings, of which:

FIGURE 1 is a graph showing the relationship between the distribution ratio (K) of an alkylene glycol borate and the initial concentration of alkylene glycol borate in the fuel required to effect a complete kill;

FIGURE 2 is a diagrammatic representation of typical results of treating a four-tank fuel distribution system under specified conditions with an alkylene glycol borate having a distribution ratio of 252; and

FIGURE 3 is a diagrammatic representation of typical results of treating a four-tank fuel distribution system under specified conditions with an alkylene glycol borate having a distribution ratio of 228.

The partitioning of an alkylene glycol borate between a kerosine fuel and water is conveniently expressed as a

distribution ratio or partition coefficient which for purposes of this disclosure is defined as:

$$\frac{\text{Percent boron}^1 \text{ in the water phase}}{\text{Percent boron in the fuel phase}} = K$$

[1] Unless otherwise indicated, all percent boron notations are percent by weight of the solvent in which the alkylene glycol borate or other boron compound is dissolved.

where K is the distribution ratio or partition coefficient.

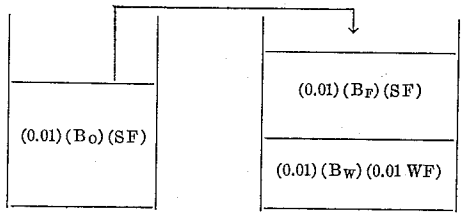
The value of K for any alkylene glycol borate can be determined experimentally in the following manner.

To a volume of fuel F, whose specific gravity is S (and therefore whose weight is SF), is added an alkylene glycol borate in an amount to provide a percent boron concentration B_o.

The treated fuel is transferred into a container contaminated with W volume percent of water, based on the volume of fuel introduced. Assuming a specific gravity of 1.0 for water at ambient temperatures, the weight of water will be (0.01)(W)(F).

Upon partitioning of the alkylene glycol borate between the fuel and the water, the percent boron in the fuel decreases from B_o to a new level B_F, and the percent boron in the water increases from zero to a new level B_W.

It follows that at equilibrium the weight of boron in the fuel is (0.01)(B_F)(SF), and the weight of boron in the water is (0.01)(B_W)(0.01 WF). This can be represented graphically as follows:



A material balance gives:

$$(0.01)(B_F)(SF)+(0.01)(B_W)(0.01\ WF)=(0.01)(B_o)(SF).$$

From the definition of distribution ratio: $K=B_W/B_F$, or $B_W=KB_F$.

Combining Equations 1 and 2:

$$B_F=\frac{B_oS}{S+(0.01)(W)(K)}$$

The distribution ratio for any alkylene glycol borate falling within the invention can be determined by experiment. The following procedure is illustrative.

A stock solution of a hexylene glycol orthoborate (2-methyl pentane diol-2,4 orthoborate) in kerosine (specific gravity of 0.7958 at 75° F. was prepared, to give a final concentration of 0.426 gram of orthoborate per 100 ml. of kerosine solution.

The orthoborate compound has a theoretical boron content of 7.51% so that the target B_o for the stock solution was

$$\frac{(0.0426)(0.751)}{79.58}=0.0040\%$$

Quantitative analysis of the stock solution for boron by electrometric titration of the increased acidity caused by the addition of mannitol established B_o as 0.00398%.

Four hundred ml. of stock solution were transferred to a pint bottle containing 4.00 ml. water (W=1%). The bottle was sealed and placed in a shaking apparatus overnight, whereafter the bottle was allowed to stand until the separation of the two phases was complete.

A 100 ml. sample of fuel was analyzed for boron, with the result that B_F was found to be 0.00227%.

The water puddle was then removed from the bottle and placed in a small separatory funnel. Clear water was drawn off and analyzed for boron, with the result that B_W was found to be 0.138%.

Equation 1 permits a check of the material balance:

$$(0.01)(0.000227)(0.7958)(400)+(0.01)(0.138)(0.01)(1.0)(400)=0.012746$$
$$(0.01)(0.00398)(0.7958)(400)=0.012669$$

It thus appears that 100.61% was recovered, which is in very satisfactory agreement with the theoretical recovery.

The distribution ratio was then determined by using Equation 2:

$$(0.00227)=\frac{(0.00398)(0.7958)}{(0.7958)+(0.01)(1.0(K)}$$

$$K=59.94\cong 60$$

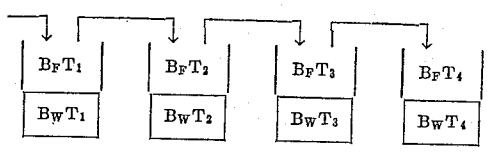
In this same same manner the distribution ratio of other alkylene glycol borate in a jet fuel-water system was determined, with the following results:

Alkylene glycol borate:	Distribution ratio
Trimethylene glycol orthoborate	1000
Trimethylene glycol pyroborate	1000
Butylene glycol-1,3 orthoborate	400
Tributylene glycol-1,3 biborate	300
Neopentyl glycol orthoborate	220
Tri(2-methyl-pentanediol-2,4) biborate	60
2-Ethyl-2-butyl-propanediol-1,3 orthoborate	15

It is apparent that as the molecular weight increases and water solubility of the borates decreases, the distribution ratio decreases. Since the efficacy of the invention depends on the partitioning of the alkylene glycol borates between the fuel and water, it will also be understood that the above enumerated compounds are not equivalent in their usefulness for purposes of the invention. For instance, a compound as water-soluble as trimethylene glycol orthoborate is partitioned in such a high ratio to the first water bottom contacted that an insufficient amount remains in the fuel phase for transfer to water in subsequent water contacts. Conversely, a compound as water-insoluble as 2-ethyl-2-butyl-propanediol-1,3 orthoborate, is partitioned to the water in such a small ratio that it would take an unreasonably high initial concentration in the fuel to build up a lethal dosage of the borate in the water.

This can be illustrated by showing the partitioning of alkylene glycol boron between a quantity of treated fuel and each of four successive 0.1% water bottoms. For comparative purposes, separate quantities of fuel were treated, respectively, with a K=60, a K=300 and a K=1000 alkylene glycol borate. The amount of alkylene glycol borate initially added to the fuel (B_o) was that amount (to the closest p.p.m. B) which would provide at least 0.25% B in the first water bottom. This level was chosen because 0.25% B has been determined experimentally to be a lethal dosage for all types of microorganisms found in a kerosine fuel-water system. B_o was determined by first solving Equation 2 above for B_F and then solving Equation 3 for B_o. An amount in excess of 0.25% B is excessive, and such amounts are referred to as overkill, whose magnitude is measured by the excess above 0.25% B.

The partitioning of the alkylene glycol borate and the equilibrium boron concentrations through the four successive water contacts can be illustrated as follows:



By solving Equations 2 and 3 for the various B_W's, the following data are obtained:

Water Bottom	Boron Concentration		
	K=60	K=300	K=1000
B_wT_1, percent	0.251	0.261	0.311
B_wT_2, percent	0.233	0.190	0.138
B_wT_3, percent	0.217	0.138	0.061
B_o (p.p.m.)	45	12	7

It is apparent from these data that the $K=1000$ alkylene glycol borate, being overly water-soluble, gave the worst distribution; the second water bottom received only slightly better than half of the target lethal dosage of 0.25% B. The $K=300$ alkylene glycol borate was not much better. The $K=60$ alkylene glycol borate distributed itself quite well in each of the water bottoms, but did not meet the required minimum target dosage of 0.25% B. Also, it required a relatively high initial boron concentration in the fuel ($B_o=45$ p.p.m.) even to accomplish what is shown.

If these alkylene glycol borates were to be used in fuels brought into contact with water bottoms containing alkylene glycol borate from a previous shipment, they can raise the boron concentration to the target dosage of 0.25% B. The presence of some alkylene glycol borate in the water bottoms prior to the introduction of the new shipments will cause less alkylene glycol borate to be extracted from the fuel in the partitioning to a new equilibrium in, say, tanks **1** and **2** and, consequently, leave more alkylene glycol borate in the fuel for extraction into the water bottoms of tanks **3** and **4**.

This effect is shown by the data in the table below, which shows the total boron concentration in the water bottoms of the four tanks **1**, **2**, **3** and **4** after this renewed contact with alkylene glycol borate-containing fuel.

Water Bottom	Boron Concentration		
	K=60	K=300	K=1000
Tank 1, percent	0.269	0.358	0.633
Tank 2, percent	0.269	0.354	0.515
Tank 3, percent	0.269	0.341	0.383
Tank 4, percent	0.269	0.326	0.266
B_o (p.p.m.) each shipment	45	12	7

These data show that in this special case the $K=60$ alkylene glycol borate, can now provide lethal concentrations of boron in each water bottom with very little overkill; i.e., the boron concentration in each water bottom closely approximates the target value of 0.25% B. The only drawback of the $K=60$ compound is that it needs the residual percent B of 45 p.p.m. of four previous contacts, plus the high concentration of boron in each shipment to achieve the desideratum.

The $K=1000$ boron compound was used at an economic rate of 7 p.p.m. boron per shipment, but wastefully left behind gross overdoses of boron in the water bottoms of the first three tanks.

The $K=300$ boron compound rather evenly distributes itself among the water bottoms, but at a concentration some 30 to 40% in excess of the target lethal dosage.

Of course, for commercial purposes none of compounds $K=60$, $K=300$ and $K=1000$ is acceptable, since at a commercially acceptable concentration of boron it is not possible to rely on contact only with a water bottom already containing enough boron to bolster the inadequate contribution of a fuel containing these alkylene glycol borates.

From these and other data generated in the same fashion, it is possible to plot a curve showing the effect of K on the initial concentration of boron in the fuel (B_o) required to provide 0.25% B in the water bottoms of a system of tanks. FIGURE 1 shows such a curve where the water bottoms are 0.10% and a companion curve for 0.05% water bottoms. Field experience shows that these are practical limits for kerosine fuel, particularly jet fuel distribution systems.

Superimposed on these two curves is a plot of boron concentration in the water for some terminal tank (B_{WT}) versus K, and it will be seen that B_{WT} increases in direct proportion with K.

To achieve exactly the target B_{WT} of 0.25% B theoretically requires a compound of $K=0$, but at $K=0$, B_o (initial concentration of boron in the fuel) is infinity. Therefore, as a practical matter, some overkill must be tolerated.

The slope of the B_{WT} versus K curve shows that the increase of overkill per 10 K numbers is constant at 0.003% B, so that the controlling factor is the rate of change of B_o with K, and it will be seen that the rate of change for 0.10% water bottoms practically parallels the rate of change for 0.05% water. Considering both curves together, it is apparent that as K increases over the range of 155 to 165, the required B_o drops about 2 p.p.m., but the B_o is in a fairly high concentration range. As K increases over the range of 310 to 320, the required B_o drops only about ½ p.p.m., but the B_o is in a reasonably low concentration range. It follows that boron compounds having a K within the approximate range of 220±40 will completely sterilize water bottoms of about 0.05 to 0.10% while striking a reasonable balance between initial boron concentration (B_o) and overkill.

The table of distribution ratios shows that neopentyl alkylene glycol borate is the only one having a K value within the preferred range. However, this compound is costly, and is not available in large quantities.

Surprisingly, it has been found that in lieu of an alkylene glycol borate having a distribution ratio within the stated range, a mixture of alkylene glycol borates having higher and lower distribution ratios but not too far removed from the limits of the range can be employed. It would normally be expected that such mixtures would be wholly inoperative, inasmuch as the compounds themselves are outside the range, but in practice, the mixture of alkylene glycol borates is quite effective, provided the alkylene glycol borates do not have a ratio below about 10 or above about 1000. Thus, for example, tributylene glycol biborate at $K=300$ and hexylene glycol pyroborate at $K=60$, commercially available and while individually their distribution ratios fall outside the range of 220±40, mixtures of these compounds, within certain proportions, provide distribution ratios within the preferred range. The distribution ratio value for a given mixture corresponds to the sum of the values obtained by multiplying the K of a compound by the proportional concentration of that compound in the mixture. For instance, a mixture consisting of 20% hexylene glycol pyroborate ($K=60$) and 80% tributylene glycol borate ($K=300$) will have a distribution ratio of:

$$K_{mixture}=(60)(.2)+(300)(.8)=252$$

As another example, a mixture of 30% hexylene glycol pyroborate and 70% tributylene glycol biborate will provide a K for the mixture of 228, and further calculation will show that mixtures consisting of 15 to 50% hexylene glycol pyroborate and 85 to 50% tributylene glycol biborate will have distribution ratios within the approximate range of 220±40.

The following examples are illustrative of and represent the best embodiments of the invention, in the opinion of the inventors.

Example I

In twenty gallons of turbine fuel A–2 (specific gravity 0.7985) was dissolved 7.90 grams of a mixture of 80% hexylene glycol pyroborate and 20% tributylene glycol biborate ($K_{mixture}=252$). The fuel contained 10 p.p.m. elemental boron (i.e., $B_o=10$).

Four portions of this fuel were used sequentially to treat 0.1% water bottoms in a series of four tanks (five-gallon glass carboys). The path of the treated fuel can best be understood by reference to FIGURE 2, which shows four vertical columns of four boxes each.

The box in the lower left-hand corner represents the first shipment of fuel to the first tank; reading up the left-hand column shows the transfer of the first shipment of fuel from tank **1** to tanks **2**, **3** and **4**.

Reading from left to right along the bottom row of boxes depicts the first, second, third and fourth shipments of fuel to tank **1**; the next row of four boxes shows the first, second, third and fourth shipments of fuel to tank **2**, and so forth.

Each box carries a two-digit number; the first digit represents the fuel shipment to the tank and the second, the tank number. Thus, box **11** shows the first shipment to tank **1**, box **32** shows the third shipment to tank **2** and box **24** shows the second shipment to tank **4**.

To begin the experiment, 18 liters of fuel and 18 ml. of an aqueous phase were added to a carboy to establish a system containing a 0.1% water bottom. The aqueous phase consisted of Bushnell-Haas medium [1] having the following composition:

	Gm./l.
$MgSO_4 \cdot 7H_2O$	0.2
$CaCl_2 \cdot 2H_2O$	0.2
KH_2PO_4	1.0
K_2HPO_4	1.0
$FeCl_3 \cdot 6H_2O$	0.05
NH_4NO_3	1.0

This medium supplies the nutritional requirements of microbes except for carbon. The microbe that cannot utilize hydrocarbons or atmospheric CO_2 will starve.

This medium was then inoculated with a mixed culture of microorganisms indigenous to kerosine hydrocarbons and representative in stamina and resistance to kill of the over eight species of organisms found in such fuels: *Achromobacter, Bacillus sp., B. globigii, Candida lipolytica, Cladosporium resinae* (synonym of *Hormodendrum*), *Corynebacteria, Cylinodrogloea bacterigena, Flavobacterium, Micrococcus sp., Nocardia.* The contents of the carboy were stirred with a magnetic stirrer overnight, to ensure equilibrium partitioning of the alkylene glycol borates between the hydrocarbon and aqueous phases.

A separation of the phases was then effected; the hydrocarbon phase was then contacted with a second 0.1% water bottom (first shipment to tank **2**) and the aqueous phase was contacted with a 99.9% fresh charge of the fuel (second shipment to tank **1**). After overnight stirring and phase separation, the first shipment of fuel to tank **2** was transferred into contact with a 0.1% water bottom in tank **3**, the second shipment of fuel to tank **1** was transferred to tank **2**, and a fresh charge of fuel was introduced into tank **1** as the third shipment to that tank. This procedure was continued until the fourth shipment of fuel reached the fourth tank.

Due to the fact that small quantities of fuel and water were lost in the course of phase separations, the net volumes of fuel and water phases decreased and adjustments were made as required to maintain a 99.9:0.1 ratio of fuel to water.

FIGURE 2 shows typical distribution values for boron between the hydrocarbon and aqueous phases in the system just described. Of particular interest are the boron concentrations developed in each of the four tanks following the fourth shipment of fuel; these values will be found in the boxes in the right-hand vertical column, and with the exception of tank **4**, for reasons which will be explained presently, the boron concentration in the water bottoms of tanks **1**, **2** and **3** closely approximated the target value of 0.25% B. Microbial assays of these four

[1] J. Bacteriology, vol. 41, p. 653 (1941).

water bottoms using conventional dilution pour-plate techniques were as follows:

Tank Number	Shipment No.	Box No.	Count (organisms/ml.)
1	1	11	4
	2	21	0
	3	31	0
	4	41	0
2	1	12	1,400,000
	2	22	(1)
	3	32	0
	4	42	0
3	1	13	2,900,000
	2	23	20
	3	33	0
	4	43	0
4	1	14	84,000,000
	2	24	300,000
	3	34	<2
	4	44	2
Control [2]			6,000,000

[1] Approx. 4.
[2] The same hydrocarbon-aqueous system as above but without boron.

This confirms the lethal effect on all of the microorganisms present of a boron concentration as alkylene glycol borate in the water bottoms approaching 0.25%.

It is evident that if the alkylene glycol borate is stable to hydrolysis by water, the concentration can be built up to a lethal concentration, the distribution ratio and water solubility of the compound permitting, within four contacts with four different batches of fuel.

A concentration of 0.25% boron acid, on the other hand, is completely ineffective.

The value of the boron concentration in tank 4, fourth shipment (Box No. 44) shows that the average distribution ratio calculated for this mixture is in fact obtained in practice, confirming that the mixture behaves differently from the individual compounds, taken separately.

The reason the tank **4** water bottom fell short of the target 0.25% B concentration will be found in FIGURE 1. Recalling that an initial boron concentration (B_o) of 10 p.p.m. in the fuel was employed in a system containing 0.1% water, it will be seen that a mixture of compounds having a distribution ratio of 252 actually requires a B_o of about 13 p.p.m. to achieve the target boron concentration of 0.25% in the water bottoms. Accordingly, had 13 p.p.m. instead of 10 p.p.m. been used in the experiment, the water bottoms in all tanks would have contained 0.25% B.

Example II

The procedure of Example I was repeated on turbine fuel A–2 in contact with water containing the same microorganisms noted in Example I, using a mixture of 70% hexylene glycol pyroborate and 30% tributylene glycol biborate (K=228) at an initial concentration (B_o) of 11 p.p.m.

FIGURE 3 shows typical distribution values for boron between hydrocarbon and aqueous phases in this system. The right-hand vertical column of boxes shows the boron levels in the two phases following the fourth shipment of fuel to each tank. Again, because the B_o of 11 p.p.m. actually used is slightly below the 14 p.p.m. required to achieve 0.25% B in the water bottoms (see FIGURE 1), the buildup of boron in the water bottoms of tank **4** fell a little short of the mark.

Microbial assays of the four water bottoms using conventional dilution pour-plate techniques were as follows:

Tank Number:	Count (organisms/ml.)
1	0
2	0
3	0
4	5
Control [1]	12,000,000

[1] The same hydrocarbon-aqueous system as above but without boron.

This confirms the lethal effect on all of the microorganisms present of a boron concentration in the water bottoms approaching 0.25%.

Example III

The following experiments were carried out in order to demonstrate how the alkylene glycol borates kill microbes.

Erlenmeyer shake flasks (125 ml.) were used, each containing a final volume of 50 ml. of aqueous phase and 25 ml. of commercial turbine fuel A–2 containing the requisite concentration of organoborate, the dosage being calculated on the basis of elemental boron which would be contributed by the fuel to the 50 ml. of aqueous phase. This was subsequently confirmed by direct boron analysis of the aqueous phase. The aqueous phase consisted of 20 ml. of mineral salts solution and 30 ml. of inoculum. The mineral salts solution was essentially Bushnell-Haas medium, the final pH being adjusted to 6.8.

For the inoculum, a mixed culture was used. This was obtained from water bottoms of three storage tanks used in a commercial turbine fuel distribution system. The samples drawn from these three tanks included some of the associated fuel; the two-phase samples were stored at 40° C. To prepare the inoculum, the three tank-bottom samples were pooled, and 0.5 ml. added to 50 ml. of mineral salts solution. An overlay of 25 ml. of straight turbine fuel (no organoborate) was added, and the whole incubated in a 125 ml. Erlenmeyer shake flask for 40 hours at 25° C., with constant agitation. At this time there would be over 10^8 organisms per ml. of aqueous phase. The pH was adjusted to 6.8, and 30 ml. of this inoculum was added to the test flask containing 20 ml. of mineral salt solution and 25 ml. of turbine fuel containing the desired additive.

The test flasks were placed on a gyrorotatory shaker at 25° C. and were sampled daily for up to 18 days. The samples were assayed for viable organisms by the conventional dilution-pour plate technique, using nutrient agar. The plates were incubated for 96 hours at 30° C., and counted on a Quebec Colony Counter.

The boron compounds used in this work were boric acid and three organoborates. The organoborates were the four-carbon, the six-carbon, and the nine-carbon compounds. The boric acid was added to the aqueous phase while the organoborates were added to the hydrocarbon. Single organoborates were used, rather than mixtures, even though their distribution ratios were outside of the invention, firstly, because the use of mixtures would have complicated interpretation of the results, and secondly, because the distribution ratio was not a factor under the conditions of the experiments. The organoborates used were known to be toxic under the test conditions.

Boric acid gave no appreciable kill even after eighteen days. The C_4 compound showed a reduction in population, but no complete kill. The C_6 compound showed complete kill at 14 days, while the C_9 compound required only three days. All of these results were at a concentration of boron of 0.20% in the aqueous phase.

Light field and phase contrast microscopy showed no gross morphological changes with either the boric acid, which did not kill at the concentrations used, or with the organoborates, which did kill.

As a measure of the relative effectiveness of these organoborates, the number of days required for the number of survivors to approach zero is taken. Thus, the C_9 compound is rated at 2.6 days, the C_6 compound at 14, the C_4 compound at +18, and the boric acid at ∞. The higher the molecular weight (the greater the lipophilicity), the greater the relative effectiveness.

Further work was carried out on the hexylene glycol borate in an endeavor to elucidate the mechanism of action of the borate. The procedure described was repeated, but with the addition of mannitol to the aqueous phase in 1:1, 2:1 and 4:1 concentrations (moles added per mole of boron). The 4:1 ratio is used in the standard analytical method for the estimation of boron in aqueous media, and is accepted as the ratio required completely to complex boron. Such a complexing would render the borate innocuous as a biocide, if it is effective as the borate. For purposes of comparison, a similar experiment was carried out using boric acid, which would be expected to be fully complexed using 4:1 ratio of mannitol. The results were as follows:

Concentration:	Change-days
1:1 [1]	0
2:1 [1]	+2
4:1 [1]	∞

[1] Moles additive per mole boron.

It is evident from the data that 4:1 ratio of mannitol completely reverses the biocidal activity of the alkylene glycol borates. Thus, at this ratio when the organoborate is complexed, there is no kill.

The work was then repeated, except that the daily samples were plated on nutrient agar and nutrient agar containing 2% mannitol. The ratio of mannitol to boron in a 2% mannitol agar is better than 8:1 molar ratio. In this work, the counts were the same as those obtained previously in the absence of mannitol.

Thus, it is apparent that if the microbe is placed in contact with an organoborate complexed with 4:1 mannitol, there is no kill, but if the microbe is placed in contact with the organoborate followed by even an 8:1 mannitol in the recovery medium, no recovery ensues. This means that the organoborate has penetrated within the cell and killed the bacteria, or has proceeded so far in this direction that it can no longer be complexed, and is therefore not inactivated by the aqueous mannitol. Thus, it can be assumed that the organoborates are themselves toxic to the microbe because of diffusion through a protective membrane. Mannitol diffuses through a cell wall slowly, if at all, so that an organoborate which has been in contact with a microbe for a day or more, and has travelled into the cell wall, can no longer be complexed by mannitol. Boric acid is inferior as a microbicide to the organoborates, because it is lipophobic and unable to pass through a cell wall. This demonstrates that the organoborates in accordance with the invention do not function as boric acids, but instead function as organoborates.

This hypothesis was checked by studying the effect of 0.2% boron acid in the presence of 0.1% sodium lauryl sulfate. The detergent reduced the time to kill from infinity to fourteen days. The sodium lauryl sulfate can be expected to assist in the transport of the boric acid across the cell walls and thereby increase the microbicidal effectiveness of the boric acid.

Example IV

A number of alkylene glycol borates were subjected to a test procedure designed to duplicate actual use conditions of contact of plural water bottoms, in order to establish effective distribution ratio limits.

In this test procedure, 1800 ml. of Turbine Fuel A–2 (API gravity 45.4, specific gravity 0.799) was used. In it was dissolved enough of the alkylene glycol borate or mixture of alkylene glycol borates to be tested to supply 15 p.p.m. elemental boron or 0.0015%. The resulting solution was then divided into four parts, and each part was used as a shipment, over a series of 0.1% water bottoms in 5 gallon glass carboys, each serving as a tank. The first tank was used with each of the separated portions of the solution, in sequence. The path of the treated fuel was as shown in FIGURE 2 which shows four vertical columns of four boxes each.

The box in the lower left-hand corner represents the first shipment of fuel to the first tank; reading up the

left-hand column shows the transfer of the first shipment of fuel from tank 1 to tanks 2, 3 and 4.

Reading from left to right along the bottom row of boxes depicts the first, second, third and fourth shipments of fuel to tank 1; the next row of four boxes shows the first, second, third and fourth shipments of fuel to tank 2, and so forth.

Each box carries a two-digit number; the first digit represents the fuel shipment to the tank and the second, the tank number. Thus, box 11 shows the first shipment to tank 1, box 32 shows the third shipment to tank 2 and box 24 shows the second shipment to tank 4.

To begin the experiment, 18 liters of fuel and 18 ml. of an aqueous phase were added to a carboy to establish a system containing a 0.1% water bottom. The contents of the carboy were stirred with a magnetic stirrer overnight, to ensure equilibrium partitioning of the alkylene glycol borates between the hydrocarbon and aqueous phases.

A separation of the phases was then effected; the hydrocarbon phase was then contacted with a second 0.1% water bottom (first shipment to tank 2) and the aqueous phase was contacted with a 99.9% fresh charge of the fuel (second shipment to tank 1). After overnight stirring and phase separation, the first shipment of fuel to tank 2 was transferred into contact with a 0.1% water bottom in tank 3, the second shipment of fuel to tank 1 was transferred to tank 2, and a fresh charge of fuel was introduced into tank 1 as the third shipment to that tank. This procedure was continued until the fourth shipment of fuel reached the fourth tank.

Due to the fact that small quantities of fuel and water were lost in the course of phase separations, the net volumes of fuel and water phases decreased and adjustments were made as required to maintain a 99.9:0.1 ratio of fuel to water.

After contact with the four shipments, the amount of boron in the water in the last tank was analyzed. In order to provide an effective lethal concentration in the water, a minimum of 0.25% boron was taken as the target, and the water analysis after the fourth shipment was compared to the target, and indicated whether this compound could ever achieve this target concentration in contact with a plurality of portions of fuel. If the alkylene glycol borate or mixture thereof passed this test, it was apparent that it would be effective in use.

Because the volume of the water in each tank was so small, the water layers were not analyzed for boron until after the last, in most cases, the third or fourth, shipment had been put in contact with the water. However, a value for boron content after each shipment can be approximated by a material balance calculated from the boron content of the fuel. These calculated values are shown in parentheses in the data which follows, and which was obtained in the course of this series of experiments.

The data given is for bi(hexylene glycol) boric anhydride 2:2 alone, tri(hexylene glycol) biborate 3:2 alone, tri(butylene glycol) biborate 3:2 alone, and mixtures of bi(hexylene glycol) boric anhydride 2:2 and tri(butylene glycol) biborate 3:2, and of propylene glycol boric anhydride 2:2.

The K values are also given for each alkylene glycol borate or mixture tested. The data show that the alkylene glycol borates or mixtures having a K value of less than about 180 are not capable of imparting a boron concentration of 0.25% in the last tank after four shipments, and that those in excess of about 260 are too water-soluble to impart a boron concentration of 0.25% in a sufficient number of tanks to be practically useful.

(I) *Bihexylene glycol boric anhydride 2:2 K=60.*—The boron content of the original solution analyzed 15.12 p.p.m.

Shipment	Tank	Boron in Fuel, p.p.m.	Boron in Water
First	First	13.96	(0.085%)
Second	do	14.90	(0.090%)
Third	do	15.00	(0.090%)
Fourth	do	15.02	0.091%

Since with this material an asymptotic value had been reached at this stage, it was clear that the boron content of the water would never go above 0.090%, so the experiment was stopped.

(II) *Trihexylene glycol biborate 3:2 K=50.*—The boron content of the original solution analyzed 14.95 p.p.m.

Shipment	Tank	Boron in Fuel, p.p.m.	Boron in Water
First	First	14.05	(0.082%)
Second	do	14.75	(0.089%)
Third	do	15.01	(0.089%)
Fourth	do	14.89	0.089%

Again, there was no hope of ever reaching 0.25% boron, so the experiment was abandoned, at this stage.

(III) *70% bihexylene glycol boric anhydride 2:2, 30% tributylene glycol biborate 3:2 K=132.*

Shipment	Tank	Boron in Fuel, p.p.m.	Boron in Water
First	First	12.88	(0.170%)
Second	do	14.72	(0.195%)
Third	do	15.00	0.197%
First	Second	11.00	(0.147%)
Second	do	14.30	(0.181%)
Third	do	14.90	0.194%
First	Third	9.47	(0.125%)
Second	do	13.60	(0.177%)
Third	do	14.60	0.193%
First	Fourth	8.10	(0.107%)
Second	do	12.80	(0.165%)
Third	do	14.40	0.190%

Thus, this mixture ($K=132$) is not capable of imparting the lethal dose of 0.25% of boron in the water starting with 15 p.p.m. in the fuel.

(IV) *50% bihexylene glycol boric anhydride 2:2, 50% trihexylene glycol biborate 3:2 K=180.*—The boron content of the starting solution analyzed 15.00 p.p.m.

Shipment	Tank	Boron in Fuel, p.p.m.	Boron in Water
First	First	12.20	(0.220%)
Second	do	14.50	(0.260%)
Third	do	14.90	0.269%
First	Second	10.00	(0.180%)
Second	do	13.60	(0.247%)
Third	do	14.70	0.263%
First	Third	8.00	(0.147%)
Second	do	12.70	(0.228%)
Third	do	14.30	0.259%
First	Fourth	6.65	(0.120%)
Second	do	11.60	(0.208%)
Third	do	13.80	0.248%

Thus, this mixture is capable of imparting the lethal boron concentration ($K=180$) of 0.25% or better in the first, second, third and fourth tanks, by the third shipment. Its K value is within the range stated.

(V) *15% propylene glycol borate, 85% bihexylene glycol boric anhydride K=201.*—The boron content of the solution analyzed 14.50 p.p.m.

Shipment	Tank	Boron in Fuel, p.p.m.	Boron in Water
First	First	12.00	(0.241%)
Second	do	14.50	0.289%

The test was halted after only two shipments because the fuel already prepared for the third shipment showed

evidence of separation of the propylene glycol borate constituent. This would have happened on the first and second shipments if they had stood an equal length of time without water. Thus, this mixture, while it imparts the target boron concentration, is excluded because it becomes insoluble in the fuel.

(VI) *30% bihexylene glycol boric anhydride 2:2, 70% tributylene glycol biborate K=228.*—The boron content of the original solution analyzed 15.00 p.p.m.

Shipment	Tank	Boron in Fuel, p.p.m.	Boron in Water
First	First	11.60	(0.267%)
Second	do	14.30	0.325%
Third	do	14.80	(0.338%)
First	Second	9.10	(0.205%)
Second	do	13.10	(0.300%)
Third	do	14.70	0.336%
First	Third	7.00	(0.161%)
Second	do	11.80	(0.268%)
Third	do	14.00	0.324%
First	Fourth	5.50	(0.125%)
Second	do	10.49	(0.237%)
Third	do	13.30	0.302%

This composition was completely satisfactory.

(VII) *Tributylene glycol biborate 3:2 K=300.*—The content of the original solution analyzed 14.80 p.p.m.

Shipment	Tank	Boron in Fuel, p.p.m.	Boron in Water
First	First	10.90	(0.327%)
Second	do	13.90	(0.416%)
Third	do	14.70	(0.441%)
First	Second	7.90	(0.238%)
Second	do	12.30	(0.367%)
Third	do	14.00	0.420%
First	Third	5.80	(0.172%)
Second	do	10.50	(0.314%)
Third	do	13.10	0.390%
First	Fourth	4.20	(0.126%)
Second	do	8.80	(0.262%)
Third	do	11.90	0.357%

This compound is far too soluble in water. The large overdoses of boron in the water are evident, and as the first shipment's boron concentration decrease shows, from the first to the fourth tank, lead to virtual exhaustion of the reserve supply of boron compound in the fuel, so that protection can be prematurely lost after the contact with the fifth or sixth water bottom. Thus, this compound is excluded.

The data for Example I confirm the lethal effect on all of the microorganisms present of a boron concentration as alkylene glycol borate in the water bottoms approaching 0.25%.

It is evident that if the alkylene glycol borate is stable to hydrolysis by water, the concentration can be built up to a lethal concentration, the distribution ratio and water solubility of the compound permitting, within four contacts with four different batches of fuel.

These data also show the significance of the distribution ratio. The data show that unless the distribution ratio is within the range from about 180 to about 260, the compound even though it may be biocidal is not effective in a sequence of contacts with water bottoms, and consequently, is not employed in the invention which is the subject of the above-identified application.

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. A composition for controlling the growth in hydrocarbons boiling in the kerosine range of lyophilic hydrocarbon-ingesting microbes indigenous to water and present in water comprising in combination a mixture of alkylene glycol borates, one of which has a partition coefficient below about 1000, and the other of which has a partition coefficient above about 50, in amounts to give a weighted average partition coefficient within the range from about 180 to about 260.

2. A composition in accordance with claim **1**, in which said alkylene glycol borate mixture has a weighted average partition coefficient of about 252.

3. A composition in accordance with claim **1**, in which said alkylene glycol borate mixture has a weighted average partition coefficient of about 228.

4. A composition in accordance with claim **1**, in which the alkylene glycol borate mixture comprises a mixture of 15 to 50 volume percent hexylene glycol pyroborate and 85 to 50 volume percent tributylene glycol biborate.

5. A composition in accordance with claim **1**, in which the alkylene glycol borate mixture is a mixture of 70% hexylene glycol pyroborate and 30% tributylene glycol biborate.

6. A fuel composition consisting essentially of hydrocarbons boiling in the kerosine range and selected from the group consisting of nongasoline hydrocarbon mixtures of which at least 30% boils above 400° F. and of which not more than 15% boils below 250° F., and both, and a composition in accordance with claim **1** in a sufficient amount to supply a boron concentration in the hydrocarbons within the range from about 5 to about 100 p.p.m. boron, to impart to each of successive bodies of water brought into interfacial contact therewith a lethal concentration of alkylene glycol borate, to kill lyophilic hydrocarbon-ingesting microbes present in such water.

7. The composition in accordance with claim **6**, in which the alkylene glycol borate mixture has a weighted average partition coefficient of about 252.

8. The composition in accordance with claim **6**, in which the alkylene glycol borate mixture has a weighted average partition coefficient of about 228.

9. A composition in accordance with claim **6**, in which the alkylene glycol borate mixture comprises a mixture of 15 to 50 volume percent hexylene glycol pyroborate and 85 to 50 volume percent tributylene glycol biborate.

10. The composition in accordance with claim **6**, in which the alkylene glycol borate mixture is a mixture of 70% hexylene glycol pyroborate and 30% tributyl glycol biborate.

11. A process for controlling the growth in hydrocarbons boiling in the kerosine range, selected from the group consisting of nongasoline hydrocarbon mixtures of which at least 30% boils above 400° F. and mixtures of which not more than 15% boils below 250° F. and both, of lyophilic hydrocarbon-ingesting microbes indigenous to water and present in water brought into contact with such hydrocarbons during storage and distribution thereof, which comprises dissolving in such kerosine hydrocarbons a composition in accordance with claim **10**, in an amount to supply a boron concentration in the hydrocarbon within the range from about 5 to about 100 p.p.m. boron, the boron concentration and the partition coefficient being sufficient to impart to each of successive bodies of water brought into interfacial contact therewith a cumulative concentration of alkylene glycol borate, lethal to any hydrocarbon-ingesting lyophilic microbes present in the water; bringing the said kerosine hydrocarbons and alkylene glycol borates dissolved therein into interfacial contact with water containing lyophilic microbes therein, and permitting the alkylene glycol borates to partition themselves between the kerosine hydrocarbons and the water to provide such lethal concentration in the water to kill any microbes present; and if necessary bringing the kerosine hydrocarbons and the remaining alkylene glycol borates dissolved therein into interfacial contact with further bodies of water containing lyophilic microbes, permitting the alkylene glycol borates to partition themselves between the kerosine hydrocarbons and such further bodies of water to provide cumulative concentrations therein of alkylene glycol borates lethal to any microbes therein, thereby during storage of the kerosine hydrocarbons preventing the growth of such microbes in the water and in the kerosine hydrocarbons, and pre-

venting the build-up slime and sludge therein due to microbial action, maintaining the kerosine hydrocarbons sufficiently clean until use, so that they can be used in a jet engine without clogging.

12. The process of claim 11, in which the alkylene glycol borate mixture has a weighted average partition coefficient of about 252.

13. The process of claim 11, in which the alkylene glycol borate mixture has a weighted average partition coefficient of about 228.

14. A process in accordance with claim 11, in which the alkylene glycol borate mixture comprises a mixture of 15 to 50 volume percent hexylene glycol pyroborate and 85 to 50 volume percent tributylene glycol biborate.

15. A process in accordance with claim 11, in which the body of water amounts to from about 0.05 to about 0.1 volume percent of the kerosine hydrocarbons.

16. A process in accordance with claim 15, in which the alkylene glycol borate mixture comprises a mixture of from 15 to 50 volume percent hexylene glycol pyroborate and 85 to 50 volume percent tributylene glycol biborate.

17. A process in accordance with claim 15, in which the alkylene glycol borate mixture has a weighted average coefficient of about 252.

18. A process in accordance with claim 15, in which the alkylene glycol borate mixture is a mixture of 70% hexylene glycol pyroborate and 30% tributylene glycol biborate.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,347,646 October 17, 1967

Richard J. De Gray et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 32, for "hydrocarbons" read -- hydrocarbon --; column 6, line 6, for "(0.000227)" read -- (0.00227) --; lines 15 and 16, the equation should appear as shown below instead of as in the patent:-

$$(0.00227) = \frac{(0.00398)(0.7958)}{(0.7958)+(0.01)(1.0)(K)}$$

column 8, line 46, after "K=60," insert -- are --; column 10, line 30, after "boron" insert -- as boric --; column 15, in the first table, third column, line 11 thereof, for "10.49" read -- 10.40 --; same table, fourth column, line 2 thereof, for "0.325%" read -- (0.325%) --; same table, fourth column, line 3 thereof, for "(0.338%)" read -- 0.338% --; column 17, line 1, after "build-up" insert -- of --; column 18, line 5, after "age" insert -- partition --.

Signed and sealed this 17th day of December 1968.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,347,646 October 17, 1967

Richard J. De Gray et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 16, line 57, "borate" should read -- borates --.

Signed and sealed this 12th day of August 1969.

(SEAL)
Attest:

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WILLIAM E. SCHUYLER, JR.
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