

969.043



PATENT SPECIFICATION

NO DRAWINGS

969.043

Date of Application and filing Complete Specification: Oct. 13, 1961.

No. 36823/61.

Application made in United States of America (No. 64261) on Oct. 24, 1960.

Two Applications made in United States of America (Nos. 65268 and 65273) on Oct. 27, 1960.

Complete Specification Published: Sept. 9, 1964.

© Crown Copyright 1964.

Index at acceptance:—C5 G1A1

International Classification:—C 10 g

COMPLETE SPECIFICATION

Preservation of Kerosine During Storage

h,
K

We, THE STANDARD OIL COMPANY of Midland Building, Cleveland 15, Ohio, United States of America, a company incorporated under the laws of the State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preservation of kerosine-type hydrocarbons in storage.

It is well known that hydrocarbon fuels when kept in storage vessels such as at oil refineries, distribution terminals, and in the 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 of the storage vessel. This metabolism is responsible for the consumption of some amount of petroleum product, tank corrosion, and results in general product deterioration by forming rust, hydrogen sulphide, gums, peroxides, acids, coloured substances and filamentous material at the interface between the water and the hydrocarbon.

Bacteria seem especially to favour hydrocarbons having a long carbon chain length for a diet and hence bacterial action such as that above described is more prevalent and far more difficult to control in kerosine stocks 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 per cent. cooling above 400°F. seldom exceeds 10%. Gasoline has at least 40% of its components boiling below 250°F. As used herein the term "kerosine-type hydrocarbons" means those in which at least 30% boils above 400°F., or in which not more than 15% boils

below 250°F., or both. Kerosine-type hydrocarbons are almost invariably unleaded, i.e. do not contain a tetra-alkyl lead compound. This includes diesel fuel which is a fraction from crude oil boiling between 300 and 700°F., at least 90% boiling above 400°F. and aviation fuel for turbo-jet 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 100 and 600°F. and preferably between 150 and 550°F. The following data are presented to illustrate one particular product, namely JP-4, which is a relatively wide-cut petroleum fraction.

Distillation

20% evaporation	270°F.	
50% evaporation	370	
90% evaporation	470	65
Residue, % volume	1.5	
Loss %	1.5	
Sulphur, per cent. by weight		
max.	0.4	
Freezing point	-76°F.	70
Btu/lb.net, min.	18,400	
Flash point	10°F.	

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. $\pm 25^\circ\text{F.}$, no component boils below 250°F.

In addition, kerosine stocks more so than gasoline stocks seem to stabilise 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 kerosine phase and has the tendency to clog filters and strainers in the storage and transport facilities and in the filters of the engines in which kerosine is 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

[Price 4s. 6d.]

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 U.S.A. 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 inner-connecting cells with numerous low points where water may collect and in which bacterial action may be propagated. In many jet aircraft, particularly military types, these fuel cells are practically inaccessible for cleaning or flushing and microbiological action continues unabated.

In the past it has been proposed to control fungal and bacterial action in the storage of hydrocarbon fuels by treating the water phase of each storage vessel with an effective bactericidal agent. It will be obvious from the foregoing, however, that in the case of fuel tanks or fuel cells associated with engines the treatment in this manner is not always possible. Furthermore, such a method of control becomes impractical and uneconomical when it is desired to guard against the bacterial problem over an entire fuel distribution system due to the large number of tanks involved in such a system.

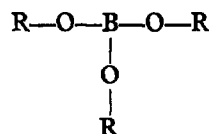
It is therefore the primary object of the present invention to provide a bactericidal agent which can be incorporated directly into kerosine-type hydrocarbons so that the bactericidal agent is carried along with the kerosine-type hydrocarbons as the kerosine-type hydrocarbons are transferred from one storage vessel to another, including their transfer through the fuel system of the engine in which it is eventually burned. In this manner effective control of bacterial action prior to the use of the fuel may be accomplished by merely adding the agent to the kerosine-type hydrocarbons prior to its storage. In order to fulfil this aim successfully the bactericidal agent must obviously satisfy a number of requirements. The agent must, of course, be soluble in the kerosine to the extent of permitting a lethal concentration to be incorporated into the fuel. Furthermore, the agent selected must function as a potent killer of bacteria. It has been found that some agents may initially control bacterial development but they are effective for only a limited length of time because the bacteria adapt to the agent and develop an immunity thereto. Obviously to control the problem outlined hereinbefore, adaptation must not occur and the bactericidal agent chosen must kill the bacteria.

Furthermore, the agent selected must not change the performance of the kerosine stock as a fuel. This is a particularly difficult requirement to satisfy where the fuel is intended

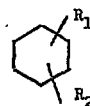
as a fuel for military jet aircraft due to the exacting specifications, particularly with respect to freedoms from deposits, which such a fuel must meet. Moreover, the bactericidal agent must be sufficiently surface-active in nature to penetrate below the hydrocarbon-water interface into the water phase in order to act on the bacteria where they actually live, but at the same time, must not exhibit such surface activity as to cause an undue amount of water-in-oil emulsification. A still further requirement is that the agent must have balanced extractability characteristics. This means that the agent must not be too readily water-extractable or else an undue amount of the agent will be lost to the water bottoms in the first tanks in the distribution system with the result that there will be inadequate amounts of the agent remaining in the kerosine to be potent against the bacteria present in the remaining tanks of the system or in the fuel tank of the engine itself. At the same time, however, it is important that some of the agent be extracted into the water bottoms of the tanks, serially contacted so that a lethal concentration builds up therein.

In accordance with the present invention, it has been found that the above object may be accomplished meeting the stated criteria in an optimum manner by adding to the kerosine prior to its storage a small amount of a more dipophilic than hydrophilic oxygenated organoboron compound as a protector.

Accordingly the present invention provides a process for protecting kerosine-type hydrocarbons stored over water bottoms against the degradation of said hydrocarbons caused by microbiological action at the hydrocarbon water interface, which comprises adding to said kerosine-type hydrocarbons (as hereinbefore defined) as a protector a borate compound of the general formula:



wherein (1) each R is the same or different and is an alkyl radical containing from 2 to 12 carbon atoms or is an aryl radical of the general formula:

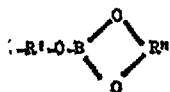


in which R_1 and R_2 are the same or different and are each a hydrogen atom or an alkyl group containing up to three carbon atoms and wherein one R can be a hydrogen atom, or (2) two R radicals are bonded together

and the third R radical is a hydrogen atom or the group



or the group



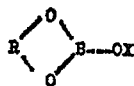
5

wherein R^{11} is an alkylene chain of 2 or 3 carbon atoms in length and wherein R^1 contains from 3 to 12 carbon atoms, in an amount equivalent to 0.0001 to 0.01% by weight of boron calculated on the total weight of the kerosine-type hydrocarbons and the protector.

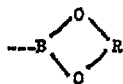
10

The protector may comprise at least one glycol borate compound of the general formula:

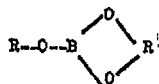
15



in which X is a hydrogen atom or the group



or the group

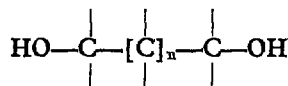


20

wherein R is an alpha or beta alkylene radical containing from 3 to 12 carbon atoms.

The glycol borate compounds used in the present invention may be readily prepared by reacting orthoboric acid in a molecular ratio of from 1:1 to 3:2 with the corresponding glycol having the general formula:

25



in which n equals 0 or 1 and the unattached valencies are linked to hydrogen or to straight chain or branched alkyl radicals to provide a total of from 3 to 12 carbon atoms.

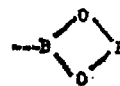
30

In forming the compounds of the foregoing formula where X is hydrogen, the glycol and boric acid are reacted together in equimolecular amounts. Two moles of water of reaction form for each mole of acid and glycol employed in the reaction. The water may or

35

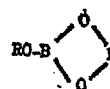
may not be removed, although usually it is desired to remove at least a part of this water. In forming the compounds where X is

40



the glycol and boric acid are reacted together in equimolecular amounts and for each mole of acid and glycol used in the reaction, $2\frac{1}{2}$ moles of water must be removed. In forming the compound where X is

45



boric acid is reacted with a glycol in a 2:3 ratio and 3 moles of water are removed for each mole of acid employed in the reaction.

50

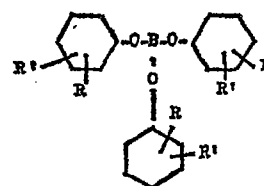
The water of reaction when removed is preferably separated overhead, such as by blowing with nitrogen at slightly elevated temperatures or by distillation. Due to the low boiling point of these compounds, removal of the desired amount of water by simple boiling causes a certain amount of loss of the product to volatilisation. For this reason, the water of reaction is preferably removed by azeotropic fractional distillation. Illustrative examples of solvent which can be used for this purpose are benzene, toluene and xylene.

55

60

In accordance with the present invention the protector may comprise at least one triaryl borate compound of the general formula

65

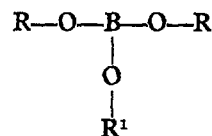


wherein R and R^1 are the same or different and are each a hydrogen atom or an alkyl group containing up to three carbon atoms. Examples are tri-phenyl borate, tri-tolyl borate, tri-xylol borate, tri-cumenyl borate, tri-ethylphenyl borate and tri-methylethylphenyl borate.

70

75

Following another aspect of the invention, the protector may comprise a boron alkyl compound of the general formula:



wherein R is an alkyl (straight or branched chain) group containing from 2 to 12 carbon atoms and R¹ is a hydrogen atom or R and wherein R may be the same or different for the various positions for R in the molecule.

5 The amount of the boron compound added to the fuel will vary depending upon several factors. In general it has been found that in order to gain complete bacterial control, 10 the water bottoms must build up a concentration of approximately 0.04% by weight of elemental boron. The amount of the glycol borate in the kerosine, which is preferably expressed in terms of boron, can be estimated 15 from this figure together with the ratio of kerosine-type-hydrocarbons to water and the determination of the distribution ratio of the boron compound between the hydrocarbon and water phases. The latter determination 20 can readily be made for any compound by merely adding the compound to a known mixture of the kerosine-type hydrocarbons and water, analysing for the amount of elemental boron in the hydrocarbon and water phases 25 separately and then dividing the larger number by the smaller one. In considering the amount of water, not only must the water in any one tank be estimated but the number of tanks in the distribution system that the kerosine-type hydrocarbons must be transferred across must be taken into account since normally each tank will represent a fresh body of water to sterilise. The choice of boron compound will determine how much of the 35 boron compound will be extracted into the water phase in the first tank and how much will remain in the kerosine-type hydrocarbons to distribute between the kerosine-type hydrocarbons and water in successive tanks in the distribution system. In the case of glycol 40 borate compounds in general, the longer the carbon chain length in the glycol portion of the boron compound the less water-soluble or water-extractable the boron compound will be. For example, butylene glycol borate is 45 more water-soluble than is hexylene glycol borate. In the case of tri-aryl borate compounds in general, the greater the number of carbon atoms in the R and R¹ substituents in the molecule of the foregoing general formula, the less water-extractable the boron compounds will be. In the case of boron alkyl 50 compounds in general, the greater the number of carbon atoms in the alkyl groups of the molecule, the less water-extractable the boron compound will be. For example, tri-butyl borate is more water-soluble than tri-octyl borate. So less of more water-soluble compound would be needed in kerosine in the 60 first tank containing water to give a concentration of 0.05% of boron in the water. However, since more of a more water-soluble boron compound would migrate to the first body of water with which the kerosine-type hydrocarbons contact, less boron compound would 65

remain in the kerosine-type hydrocarbons for remaining tanks in which water bottoms are to be contacted than a less water-soluble boron compound. It will be understood from this that the choice of boron compound for a system will depend at least in part upon how far through a tank distribution system treatment is required. As a further consideration it must be noted that each charge of kerosine need not contribute a fully lethal dose of boron to the water bottoms of each tank because succeeding charges of kerosine containing a boron compound will eventually build up the boron content of the water to the lethal level. Obviously, the particular agent or mixtures of agents to be used and the amounts thereof required in the kerosine-type hydrocarbons must be worked out for the particular distribution system under consideration utilising the general guides set forth hereinabove. However, as a workable starting point, an amount of compound to provide approximately 0.0001 to 0.0004% by weight of boron calculated on the kerosine-type hydrocarbons should be considered as the smallest amount that will offer any significant effect in the first contact. (Namely, 0.0001% of tri-aryl borate compound, or 0.0002% of glycol borate compound, or 0.0004% of boron-alkyl compound). Amounts of boron compound in the kerosine-type hydrocarbons to provide between 0.004% and 0.006% by weight of boron are usually preferred, particularly where there are two or more tanks to be treated. (Namely 0.0004—0.004% of tri-aryl borate, or 0.0005—0.006% glycol borate, or 0.001—0.006% of boron-alkyl compound). Use of amounts in excess of 0.01% are not required and usually cannot be justified economically.

A surprising aspect of the present invention resides in the fact that much less boron content is required in the water phase in the form of the more lipophilic than hydrophilic organo-boron compounds hereof to inhibit bacterial action than is needed in accordance with prior art treating methods whereby water-soluble boron compounds are added directly to the water bottoms of the storage tanks containing kerosine. Since the growth occurs at the interface, the transfer of the boron compound from the kerosine-type hydrocarbons to the water necessarily passes through this interface. This is not true when the boron compound is in the water phase initially, because then there is no transfer from the water phase to the kerosine phase.

The boron compound may be added directly to the kerosine stock in the amounts required. If desired, a concentrate of the boron compound can be formed by use of a mutual solvent and the concentrate then blended into the kerosine to provide the desired amount of boron.

A better understanding of the invention will

70

75

80

85

90

95

100

105

110

115

120

125

130

be gained from the ensuing detailed description of several examples of the invention. The following test on kerosine stocks can be used to simulate with actual storage tank conditions for such stocks over water bottoms and correlates therewith. This test involves the contact of one charge of kerosine containing boron compounds hereof with water in a ratio of 100:1. The test involves the use of a device including a large wheel having 16 spokes. To each spoke two bottles similar to one U.S.A. pint Mason jars are fastened mouth to mouth. Each of the bottle assemblies is filled with 400 cc. of the kerosine stock to be tested and 4 cc. of water. A polished steel bar was included in each bottle assembly so that the effect of bacteria on corrosion could be observed and the influence of rust formation on bacterial development would simulate that occurring in actual storage conditions. The water was taken from an artificial lake which contains bacteria similar to those found by investigation to exist in the water in tank bottoms. The wheel is then rotated at 3 rpm. for a time of 48 hours to study the growth of bacteria. Each bottle assembly is up-ended twice in each revolution of the wheel and hence the contents of the bottles slosh back and forth six times each minute during the test. This motion simulates what happens in a storage tank when large volumes of kerosine are introduced or removed, keeping the contents of the tank in a rolling motion.

At the end of the 48 hours, the bacterial populations were estimated by the conventional plate method wherein plates are inoculated with a given size sample taken from the water bottoms and with progressive decade dilutions thereof. To accomplish this, a 1 ml. sample is pipetted from the water layer of the kerosine water mixture and transferred to a sterile Petri dish. Then approximately 20 ml. of sterile nutrient agar solution at a temperature of 40°C. is poured into the dish and the contents swirled until the mixing is complete. The mixture on the plate is then allowed to cool to room temperature whereupon the agar congeals. The plate is then inverted and placed in an incubator maintained at 37°C. After incubation for 48 hours the colonies are counted using an illuminated crossed-hatched field. The counts reported as the result of the test are bacteria per millilitre of sample. Tables I, II and III below show the results for this test on kerosine treated and untreated with a bactericidal agent of the invention. The kerosine stock employed in these tests was a material meeting the JP-4 fuel specifications.

TABLE I

Run No.	Glycol borate Additive Concentration at 0.002% by weight Boron.	Count/ml.
1	none (base kerosine)	5,500,000
2	1,3-propane diol borate (1:1 compound)	40
3	50 mole % 1,3-propane diol borate (1:1 compound) + 50 mole % 2-methyl-2,4-pentane diol borate (1:1 compound)	120
4	1,3-butane diol borate (1:1 compound)	3,200
5	2-methyl-2,4-pentane diol borate (1:1 compound)	6,300

The above results clearly indicate that based on contacting just one body of water the 1,3-propane diol borate offers optimum results. It will be noted from the above reported results that the greater the number of carbon atoms in the glycol forming the boron compound the less effective the agent is in the first contacting. As a corollary of this it has been found that as the number of carbon atoms in glycol forming the boron compound is increased the amount of elemental boron transferred to the water phase decreases. Furthermore, as the number of carbon atoms in the glycol forming the boron compound is increased, the more is the amount of elemental boron remaining in the kerosine after the first contacting for treating the remaining tanks in a distribution system. For this reason, it is often desirable to use a glycol borate compound derived from a short chain glycol and a glycol borate compound derived from a longer chain glycol in admixture. This is particularly the case when the 1,3 propane diol borate compound is employed, since in itself it exhibits only limited solubility in kerosine stocks.

TABLE II

Run No.	Tri-aryl borate Additive Concentration at 0.001% by weight Boron	Count/ml.
1	none (base kerosine)	5,500,000
2	tri-phenyl borate	3
3	tri-tolyl borate	4
4	tri-xylyl borate	1,200

It will be noted from the above results that the compounds used in this invention have very effective bactericidal activity at very low concentrations. Since the tri-xylyl borate is the least water-extractable it is less effective in the first contacting. On the other hand, since more boron remains in the kerosine phase after the first contacting the tri-xylyl borate agent will carry through to a greater number of tanks in the distribution system.

TABLE III

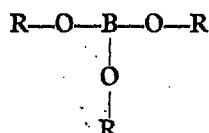
Run. No.	Boron alkyl Additive at 0.004% by weight Boron	Count/ml.
1	none (base kerosine)	5,500,000
2	tri-ethyl borate	4,000
3	tri-propyl borate	700
4	tri-butyl borate	100
5	tri-amyl borate	25
6	tri-hexyl borate	9
7	di-hexyl borate	5
8	tri-octyl borate	0
9	tri-decyl borate	11
10	tri-dodecyl borate	130

It will be noted from the above results that the compounds used in this invention have very effective bactericidal activity at very low concentrations. Based on contacting one body of water the boron compounds wherein the number of carbon atoms in the alkyl groups ranges between 6 to 10 carbon atoms, offer optimum results.

All the kerosine compositions reported in Tables I, II and III successfully passed the Erdco Coker Test run in accordance with ASTM—D1660. This test is used to evaluate a kerosine fuel for burning cleanliness and is currently regarded as the most reliable test for predicting the actual performance of fuels in turbo-jet and jet engines. Compositions other than 1 showed no significant difference from composition 1 with respect to the amount or nature of deposits produced, indicating that the bactericidal agents of the invention do not harmfully affect the base fuel with respect to deposit rating or in any other manner known to the inventors for use in a turbo-jet or jet engine.

WHAT WE CLAIM IS:—

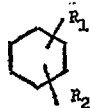
1. A process for protecting kerosine-type hydrocarbons (as hereinbefore defined) stored over water bottoms against the degradation of said hydrocarbons caused by microbiological action at the hydrocarbon water interface, which comprises adding to said kerosine-type hydrocarbons as a protector a borate compound of the general formula:



10

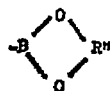
wherein (1) each R is the same or different and is an alkyl radical containing from 2 to 12 carbon atoms, or is an aryl radical of the general formula:

15



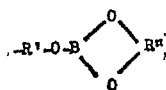
in which R₁ and R₂ are the same or different and are each a hydrogen atom or an alkyl group containing up to three carbon atoms, and wherein one R can be a hydrogen atom, or (2) two R radicals are bonded together and the third R radical is a hydrogen atom or the group

20



or the group

25

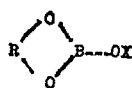


wherein R¹¹ is an alkylene chain of 2 or 3 carbon atoms in length and wherein R¹ contains from 3 to 12 carbon atoms, in an amount equivalent to 0.0001 to 0.01% by weight of boron calculated on the total weight of the kerosine-type hydrocarbons and the protector.

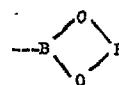
30

2. A process as claimed in claim 1 wherein the protector comprises at least one glycol borate compound of the general formula

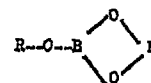
35



in which X is a hydrogen atom or the group



or the group



40

wherein R is an alpha or beta alkylene radical containing 3 to 12 carbon atoms, the amount of said compound in the kerosine-type hydrocarbons being equivalent to at least 0.0005% by weight of boron.

45

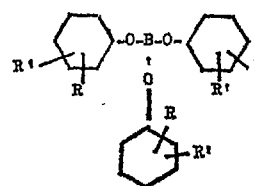
3. A process as claimed in claim 2 in which R is the radical derived from 1,3-propane diol.

4. A process as claimed in claim 2, wherein the protector comprises a mixture of glycol borate compounds and in one of which R is derived from a propane diol and in the other of which R is derived from a hexane diol.

50

5. A process as claimed in claim 2 wherein the protector comprises at least one tri-aryl borate compound of the general formula:

55



wherein R and R¹ are the same or different and are each a hydrogen atom or an alkyl group in an amount to provide at least 0.0001% by weight of boron calculated on the kerosine-type hydrocarbons.

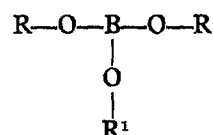
60

6. A process as claimed in claim 5 wherein the tri-aryl borate is tri-phenyl borate.

7. A process as claimed in claim 5 wherein the tri-aryl borate is tri-tolyl borate.

65

8. A process as claimed in claim 2 wherein the protector comprises at least one boron alkyl compound of the general formula:



70

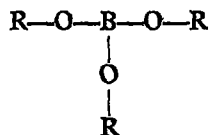
wherein R is an alkyl group containing from 2 to 12 carbon atoms and R¹ is a hydrogen atom or is R and wherein R may be the same or different for the various positions for R in the molecule, in an amount to provide at least 0.0004% by weight of boron,

75

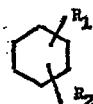


calculated on the kerosine-type hydrocarbons.

- 5 9. A kerosine-type hydrocarbon based mixture stored over water bottoms and more particularly a kerosine-based jet aircraft fuel comprising a borate compound of the general formula



- 10 wherein (1) each R is the same or different and is an alkyl radical containing from 2 to 12 carbon atoms, or is an aryl radical of the general formula:



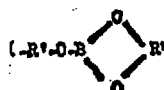
- 15 in which R₁ and R₂ are the same or different and are each a hydrogen atom or an alkyl group containing up to three carbon atoms and wherein one R can be a hydrogen atom, or (2) two R radicals are bonded together and

the third R radical is a hydrogen atom or the group



20

or the group



wherein R¹¹ is an alkylene chain of 2 or 3 carbon atoms in length and wherein R¹ contains from 3 to 12 carbon atoms protecting said kerosine-type hydrocarbons against degradation caused by microbiological action at the kerosine-water interface when produced by a process as claimed in any one of the preceding claims.

25

30

ELKINGTON & FIFE,
Chartered Patent Agents, *SC.*
High Holborn House,
52/54 High Holborn, W.C.1.
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

