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(54) Method of reducing microbial growth in storage systems containing hydrocarbon liquids.

(57) A method for reducing or eliminating the growth of micro-organisms in a storage system (10) containing hydrocarbon liquids is disclosed which comprises adding water (18) containing a biocide into the lower portion (14) of said system in an amount sufficient to cover at least a portion of the floor thereof, contacting the biocide in the water with the microbial growth for a period of time sufficient to kill a substantial portion of said microbial growth, and then removing the water containing said biocide (20) from said system.

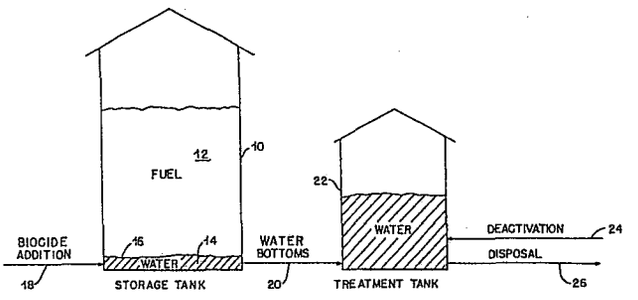


FIG. 1

EP 0 296 882 A1

Description

METHOD OF REDUCING MICROBIAL GROWTH IN STORAGE SYSTEMS CONTAINING HYDROCARBON LIQUIDS.

1. Field of the Invention

The present invention relates to a method for using biocide treated water to reduce microbial growth in storage systems containing hydrocarbon liquids.

2. Description of Related Art

Hydrocarbon liquids such as kerosene, jet fuel, gas oils and lubricating oils are often stored in systems such as storage tanks, aircraft fuel tanks and holds of tankers. When so stored, water invariably accumulates in the bottom of the system due to condensation of water from warm air onto the walls of the system, separation of free-water entering the system with the hydrocarbon liquid or leaks in the system. Frequently, micro-organisms such as bacteria, fungus, yeast and mold are present in the air and water entering the storage system. These contaminants will multiply rapidly because the hydrocarbon liquid at the water/hydrocarbon interface serves as a nutrient for their growth. If not corrected, the result of this microbial growth is (1) corrosion of the metal substrate of the system; (2) plugging of equipment such as filters, engine fuel pipes, nozzles, separators, etc.; and (3) contamination of the hydrocarbon liquid with water due to malfunction of equipment such as a filter/ separator. Items (2) and (3) are particularly critical when the hydrocarbon liquid is a jet fuel since free-water, which forms ice crystals at high altitude, or particulates in the fuel could lead to filter plugging onboard the aircraft.

Various methods have been suggested to combat the problems associated with microbial growth in storage systems. For example, although individual cells may remain viable in the hydrocarbon liquid, micro-organisms can only grow and reproduce within an aqueous environment. Accordingly, the most effective way to prevent microbial growth is to eliminate all water from the system. However, the liquid storage system may not be operated properly or be free-draining such that microbial growth develops in the accumulated water. Currently, the only remedy in such cases is to drain the storage system and clean the microbial growth from the system manually. This procedure is costly due to both cleaning costs and system down-time.

The use of biocides has also been suggested to control microbial growth. However, for the biocide to be effective, it must be present in the water phase, either through direct addition or through partition from the hydrocarbon liquid. If added directly to the water phase in the system and allowed to remain for an extended period of time; i.e. typically a week or more (as illustrated in British Patent 1,372,560 and U.S. Patent 3,251,662, the disclosures of which are incorporated herein by reference), the biocide can diffuse from the water into the hydrocarbon liquid, making it unacceptable for use. This is particularly true for jet fuel which must meet stringent specifications, such as ASTM test D-1655 in the United States which does not allow biocide addition. In addition, disposal of the water phase is complicated since it now contains a biocide.

If the biocide is added to the hydrocarbon liquid (as for example in U.S. Patents 3,628,926 and 4,086,066, the disclosures of which are incorporated herein by reference), the biocide will diffuse into the water phase so as to control microbial growth. However, this approach has the same deficiencies as the addition of biocide to the water phase in that the biocide will be present in the hydrocarbon liquid, which may not meet required specifications, and thus, is unacceptable for use.

In view of the deficiencies associated with remedies suggested in the prior art, it would be desirable to have available a simple yet effective method for controlling microbial growth in storage systems containing hydrocarbon liquids, particularly jet fuels, which minimizes biocide contamination of said liquids without having to first remove them from the system.

SUMMARY OF THE INVENTION

Now according to the present invention, a convenient yet effective method for controlling microbial growth in a storage system while minimizing any adverse affects on the quality of the hydrocarbon liquid contained therein has been discovered. More specifically, in its broadest embodiment, this method comprises:

1. adding water containing a biocide having an active anti-microbial ingredient to a storage system containing a hydrocarbon liquid in which a microbial growth is located on at least a portion of the floor of said system,

2. contacting said microbial growth with the active ingredient in said biocide treated water for a period

of time sufficient to kill at least a portion of said growth, and

3. removing at least a portion of said biocide treated water from said system, said system being maintained in a quiescent state during steps 1-3 so as to minimize transfer of said active ingredient to said hydrocarbon liquid.

The active ingredient in the discharged water may then be neutralized to a non-toxic form to facilitate disposal of the water. The hydrocarbon liquid should also be tested to confirm that it meets appropriate specifications. Further treatment of the hydrocarbon liquid (e.g. by clay filtration) may be performed to ensure removal of any residual active ingredient.

The method described herein provides a simple technique for utilizing biocide treated water to effectively reduce or eliminate microbial growth in a storage system containing hydrocarbon liquid without adversely affecting the quality of the liquid remaining in the system during biocide treatment. This method, which may conveniently be applied to essentially any type of storage or fuel handling system, also provides for environmentally acceptable water treatment and disposal.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a preferred embodiment of the biocide treatment process of the present invention.

Figures 2-5 show the percent of bacteria and fungus killed during laboratory tests using two commercially available biocides at several concentrations.

DETAILED DESCRIPTION OF THE INVENTION

Having thus described the invention in general terms, reference is now made to Figure 1 which is shown only for the purpose of illustration. Such details are included as are necessary for a clear understanding of how the present invention may be applied. No intention is made to limit the scope of the present invention to the particular configuration shown as other configurations are contemplated. Various items such as instrumentation and other process equipment and control means peripheral to the present invention have been omitted for the sake of simplicity. Variations obvious to those having ordinary skill in the art of controlling microbial growth are included within the broad scope of the present invention.

Referring now to Figure 1, there is shown a storage system 10 which is partially filled with an upper layer of hydrocarbon liquid 12. The source of the hydrocarbon liquid is not critical and may vary broadly. Typically, the liquid will be a petroleum hydrocarbon liquid, such as kerosene, gasoline, jet fuel, diesel fuel, gas oils and the like. Storage system 10 also contains a lower layer of water 14 in contact with the bottom or floor of system 10, said water having one or more micro-organism therein and being separated from the hydrocarbon liquid 12 by a hydrocarbon liquid/water interface 16.

As a first step in the present invention, water containing a biocide having an active anti-microbial ingredient is introduced into the lower portion of system 10 through line 18, preferably at a point below the level of hydrocarbon liquid/water interface 16 (e.g., a drain line). The amount or volume of water added is not critical. However, since the micro-organisms will tend to proliferate on the floor of system 10, the amount of water added should be sufficient to cover at least a portion, preferably a major portion of the floor of system 10. Best results will be obtained if the amount of water added will be sufficient to cover essentially the entire floor of system 10. The water may be derived from any suitable source including distilled water, city water or industrial water.

The particular biocide used is not critical and may be chosen from a wide variety of compounds available in the marketplace, depending upon the particular micro-organism or organisms contaminating the system. Typically, the biocide will contain an active anti-microbial ingredient to react with the microbial growth as well as other materials which could be inerts, carrying solvents and the like. Suitable biocides include those sold under the tradenames DBNPA 7287 (Dow), Omadine TBAO (Olin) and Kathon FP (Rohm and Haas).

Similarly, the concentration of the biocide in the water is not critical and can vary broadly depending upon the concentration of the active ingredient in the particular biocide chosen as well as the period of time said active ingredient is in contact with the microbial growth. In general, the concentration of active ingredient in the water need only be that sufficient to kill or reduce at least a portion of the microbial growth contacted. If the concentration of active ingredient is too low, very little reduction in microbial growth will be obtained or extended contact time (i.e. in excess of 7 days) will be required to achieve significant reduction in microbial growth. However, very high concentration of active ingredient will promote transfer of the biocide components (including the active ingredient) into the hydrocarbon liquid. Accordingly, it is preferred that the concentration of active ingredient in the water be sufficient to eliminate a major portion, more preferably at least 99% and most preferably essentially all (i.e. at least 99.9%) of the microbial growth contacted within a period of time of five days or less, more preferably within about three days or less. Typically, the concentration of active ingredient in the water will be at least about 10 wppm, preferably at least 20 wppm, and will range from about 10 to about 200 wppm or more, preferably from about 20 to about 100 wppm for contact times of 120 hours or

less, preferably 100 hours or less and more preferably 75 hours or less.

The minimum contact time will vary depending upon the concentration of active ingredient in the water and the desired reduction in microbial growth. Accordingly, the minimum contact time need only be that sufficient to kill at least a portion of the microbial growth contacted. In practice, however, the contact time will be at least 24 hours. As such, the contact time of active ingredient with microbial growth will typically vary from about 24 hours to about 120 hours, preferably from about 24 hours to about 100 hours and more preferably from about 24 to about 75 hours.

Following contact of the biocide treated water with the microbial growth, at least a portion, preferably essentially all, of the spent biocide treated water is removed from system 10 through line 20 located in the lower portion thereof. This will also minimize transfer of the biocide components into said hydrocarbon liquid 12.

During the above procedure, particularly the contacting step, it is preferred that hydrocarbon liquid 12 and biocide treated water 14 be maintained in a quiescent state to further minimize transfer of the biocide components into liquid 12.

Following its removal, the spent biocide treated water may be stored for further use, used to treat microbial growth in other storage systems (with additional biocide being added as make-up) or disposed of in an environmentally acceptable manner. Possible disposal techniques include sending the biocide treated water to a waste treatment plant provided the concentration of active ingredient is sufficiently low (i.e. typically 1 wppm or less) or chemically deactivating the active ingredient. As an example of the latter method, Figure 1 shows that spent biocide treated water is passed through line 20 to a treatment tank 22 in which said water is contacted with a chemical introduced into tank 22 through line 24. If Kathon FP were used, the active ingredient (isothiazoline) has been found to be effectively neutralized by sodium bisulfite, with from about 18 to about 36 parts of bisulfite being required for each part of isothiazoline. Once the active ingredient is degraded, the water can then be disposed of in a conventional manner through line 26.

Although the contact time between hydrocarbon liquid 12 and biocide treated water 14 should be minimized and system 10 should be kept quiescent, it is preferred that samples of liquid 12 be taken following removal of said water and analyzed for contamination by the active ingredient. Typically, hydrocarbon liquid 12 will be essentially free of active ingredient; i.e., the concentration of active ingredient in hydrocarbon liquid 12 will be 0.5 wppm or less. However, as an additional safeguard, liquid 12 could undergo further treatment (e.g., clay treatment) to remove any residual active ingredient.

The temperature and pressure at which the above described biocide treatment process is carried out is not critical and could vary broadly. However, ambient conditions are preferred.

The present invention will be further understood by reference to the following examples which are not intended to restrict the scope of the claims appended hereto.

Example 1

A series of experiments were performed in a five gallon can using two commercially available biocides at several different concentrations. Fifteen liters of aviation fuel having a specific gravity of about 0.8 and 150 ml of Bushnell-Haas media having a specific gravity of about 1 were added to the can such that. the fuel to water ratio was 100. Actively growing populations of bacteria (Pseudomonas aeruginosa) and fungus (Cladosporium resinae) were then added to the water layer in the can using a long needle syringe. The mixed microbial populations were allowed to grow for seven days, thereby creating mats on the bottom of the can. The contaminated water was then contacted (or treated) with water containing from 20 to 160 wppm Kathon FP (i.e. from 2.4 to 19.2 wppm isothiazoline) and the percent bacteria and fungus killed at each concentration determined by measuring the level of viable organisms in water samples withdrawn immediately prior to biocide addition and at 8 hours, 1 day, 2 days and 3 days thereafter. Microbial levels were determined using the Viable Plate Count Method in which a sample of the water phase is diluted in sterile dilution broth (isotonic saline) and a 1 ml. portion thereof is placed on a Petri dish containing nutrient agar. Each microbial cell will form a colony on the dish in 2-3 days and by counting the number of colonies and taking into account the dilution factor, the original count can be determined (see Stanier, R. Y. et al., The Microbial World, pp. 301-302, Prentice-Hall, New York (1970) for further information on the Viable Plate Count Method).

The percent bacteria and fungus killed using Kathon FP are shown in Figures 2 and 3. Figure 2 shows that about 99.99% reduction in bacteria can be achieved with about 10 wppm of isothiazoline in a 24 hour period. Greater reductions (i.e. 99.999% or more) require about 20 wppm isothiazoline and a 72 hour contact time. Similarly, Figure 3 shows that at least about 10 wppm of isothiazoline was required to achieve about 99% reduction of fungus in about 48 hours, while about 20 wppm isothiazoline gave 99.9% reduction in the same period.

Similar tests were performed using from 200 to 1600 wppm of DBNPA 7287 (i.e. from 40 to 320 wppm di-bromo-nitrilo-propionamide). The results of these tests are presented in Figures 4 and 5. Figure 4 shows that at 40 wppm DBNPA, 99.9999% reduction in bacteria can be obtained in 24 hours, while 99.999999% reduction can be obtained in 72 hours. Figure 5 shows that 40 wppm DBNPA will eliminate more than 99% of the fungus in 24 hours, with about 99.999% being eliminated in 72 hours.

Figures 2-5 also show that contact time of the microbial growth with the active anti-microbial ingredient can be reduced by using higher concentrations of active ingredient.

Example 2

The present invention was field tested in a 40,000 barrel storage tank containing 20,000 barrels of aviation fuel. Two 5,000 gallon batches of clean water, each containing 24 wppm of isothiazoline, were pumped into the tank through a discharge line below the level of the fuel. Two hundred gallons of water bottoms from other storage tanks having bacteria and fungus populations were then pumped into the tank through the discharge line to ensure a measurable biological population is present initially. The water phase in the tank was sampled immediately after addition of the contaminated water and at 16, 40 and 64 hours thereafter. Bacteria and fungal viable counts were determined using the Viable Plate Count Method described in Example 1 and the results summarized in Table 1 below:

TABLE 1

Sample Hr.	Bacteria Cells/ml	Fungus CFU/ml
0	1×10^7	4×10^2
16	2×10^5	1×10^2
40	<1	<1
64	<1	1

The water phase was then drained from the storage tank into a tank truck and contacted with 1000 wppm of sodium bisulfite, which provided 99.9% neutralization of the isothiazoline. Samples of the fuel remaining in the storage tank were analyzed for isothiazoline contamination using high performance liquid chromatography (HPLC). The results of these tests are shown in Table 2 below:

TABLE 2

Tank Sample Height, Ft.	Isothiazoline wppm
1	0
5	0
10	0

Although isothiazoline contamination of the fuel was undetectable following neutralization, the fuel underwent further treatment with attapulgus clay to ensure complete absence of the active ingredient.

Example 3

A sample of aviation fuel containing 100 wppm Kathon FP was passed through a clay sidestream sensor capsule loaded with 30/60 L-V-M attapulgus clay at 100 ml/min. Samples were taken before and after the clay at selected intervals and analyzed by HPLC. The results of the HPLC analysis are shown in Table 3 below.

TABLE 3

Sample, Min.	651 Conc., wppm		573 Conc., wppm	
	In	Out	In	Out
15	17.2	0	2.7	0
45	16.9	0	2.7	0
60	16.8	0	2.5	0

Table 3 shows that attapulgus clay can effectively remove essentially all of the more fuel soluble fraction of Kathon FP (the 651 component) as well as the less fuel soluble fraction (the 573 component) from aviation fuel.

Notes
1 foot (ft) = 30.48 cm.
1 (U.S.) gallon = 3.785 liter.
1 Barrel = 158.97 liter.

Claims

1. A method for eliminating at least 99% of a microbial growth present on the bottom of a storage system containing a hydrocarbon liquid, said method comprising the following steps:

(a) adding water containing at least about 10 wppm of an active anti-microbial ingredient to said system at a point below said hydrocarbon liquid and in an amount sufficient to cover essentially all of the bottom of said system;

(b) contacting said active ingredient with the microbial growth covered by said water for 120 hours or less; and

(c) removing essentially all of said water from said system so as to leave a hydrocarbon liquid in said system that is essentially free of active ingredient, said system being maintained quiescent during steps (a) to (c).

2. The method of claim 1 wherein at least 20 wppm of said active ingredient is present in said water.

3. The method of claim 1 or claim 2 wherein the contact time in step (b) is in the range of from about 24 to about 120 hours.

4. The method of any one of claims 1 to 3 wherein the contact time in step (b) is in the range of from about 24 to about 100 hours.

5. The method of any one of claims 1 to 4 wherein said hydrocarbon liquid is selected from kerosene, gasoline, jet fuel, diesel fuel, gas oils and mixtures thereof.

6. The method of any one of claims 1 to 5 wherein said active ingredient is isothiazoline.

7. The method of any one of claims 1 to 6 wherein the hydrocarbon liquid from step (c) is contacted with clay to remove residual active ingredient from said liquid.

8. The method of any one of claims 1 to 7 wherein said microbial growth is selected from bacteria, fungus, yeast, mould and mixtures thereof.

9. The method of any one of claims 1 to 8 which comprises the further steps of:

(d) neutralizing the active ingredient in the water removed in step (c); and

(e) disposing of the water formed in step (d).

10. The method of claim wherein said active ingredient is neutralized with sodium bisulfite.

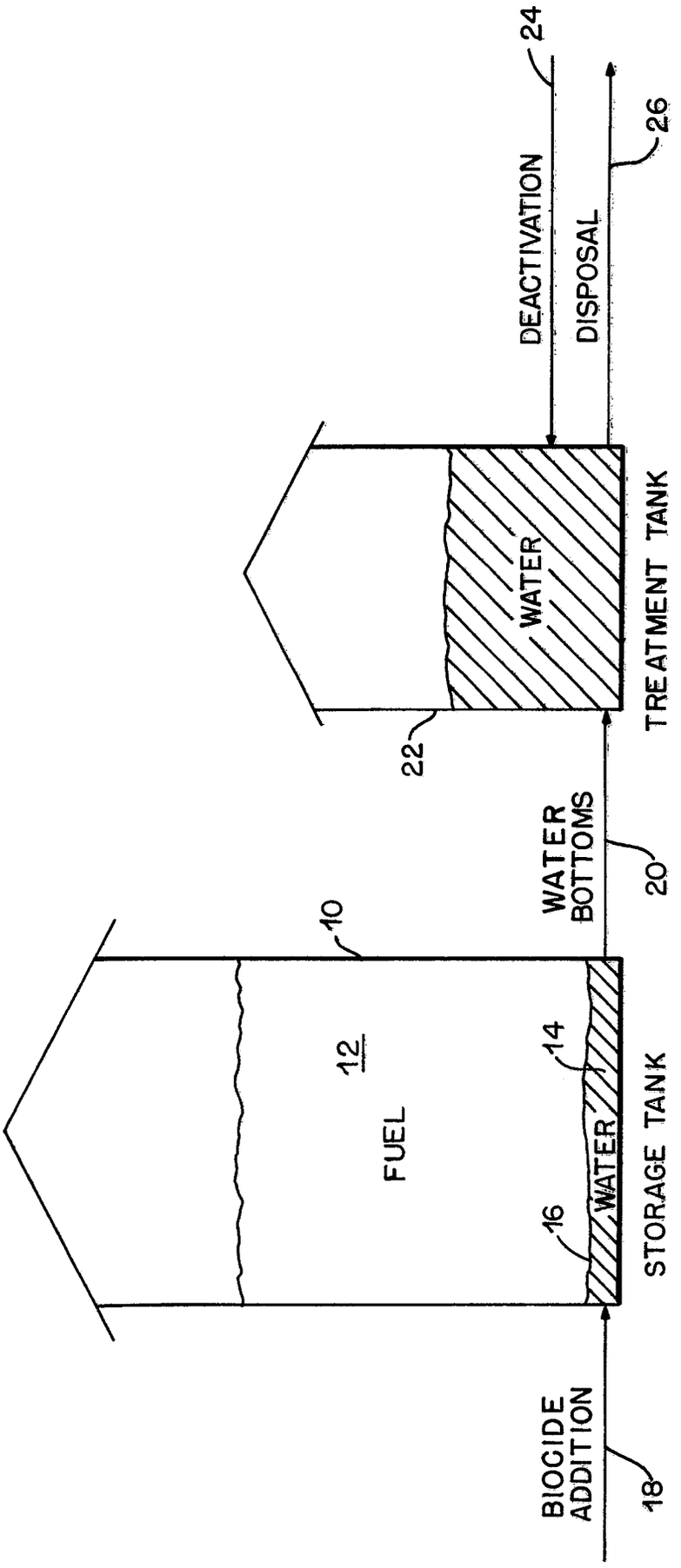

BIOCIDE ADDITION
18
STORAGE TANK
16
WATER
14
12
FUEL
10
WATER BOTTOMS
20
TREATMENT TANK
22
WATER
DISPOSAL
26
DEACTIVATION
24

FIG. 1

FIG. 2

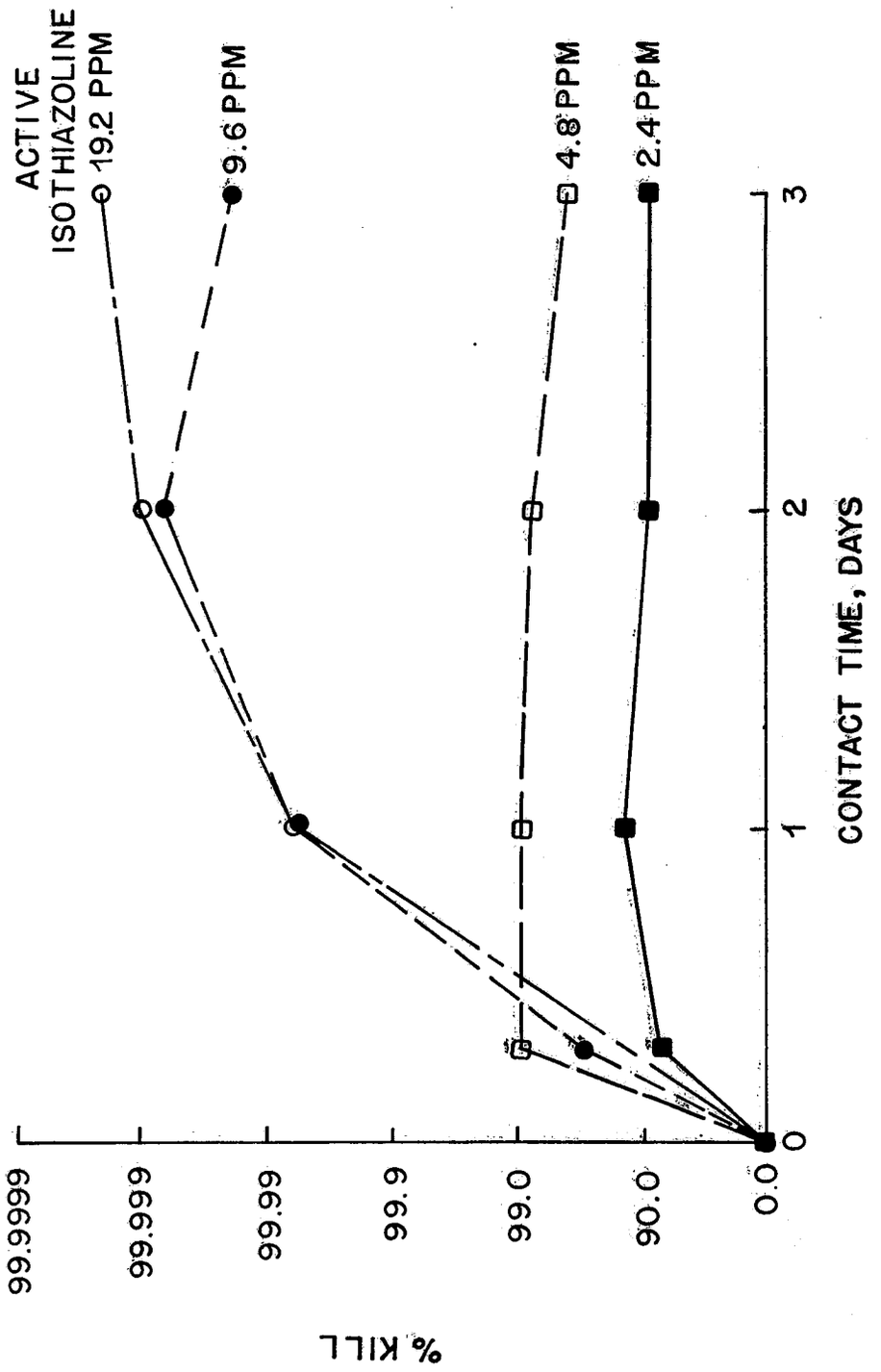
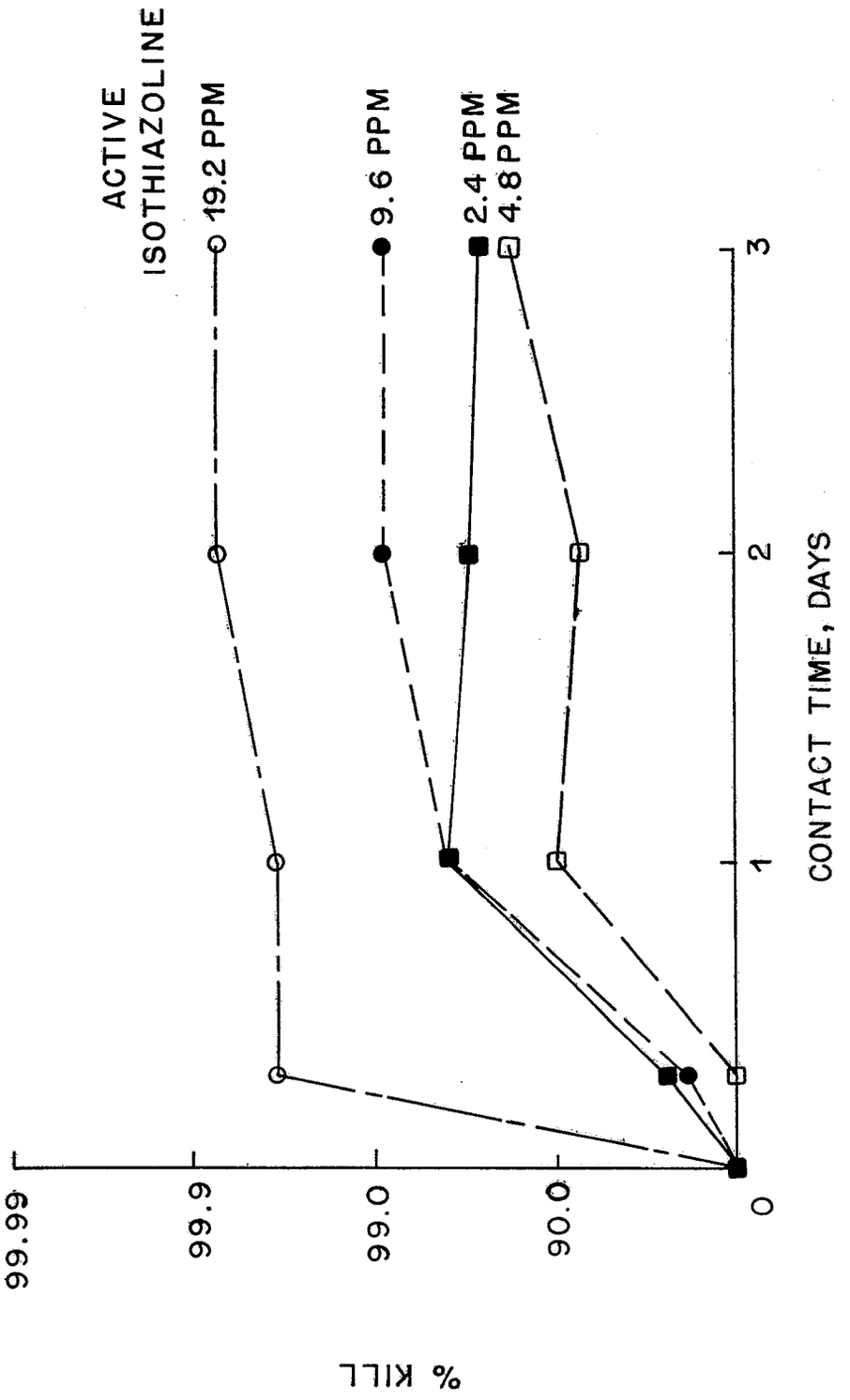

ACTIVE ISOTHIAZOLINE
19.2 PPM
9.6 PPM
4.8 PPM
2.4 PPM
% KILL
99.9999
99.999
99.99
99.9
99.0
90.0
0.0
0
1
2
3
CONTACT TIME, DAYS

FIG. 3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9.6 PPM
2.4 PPM
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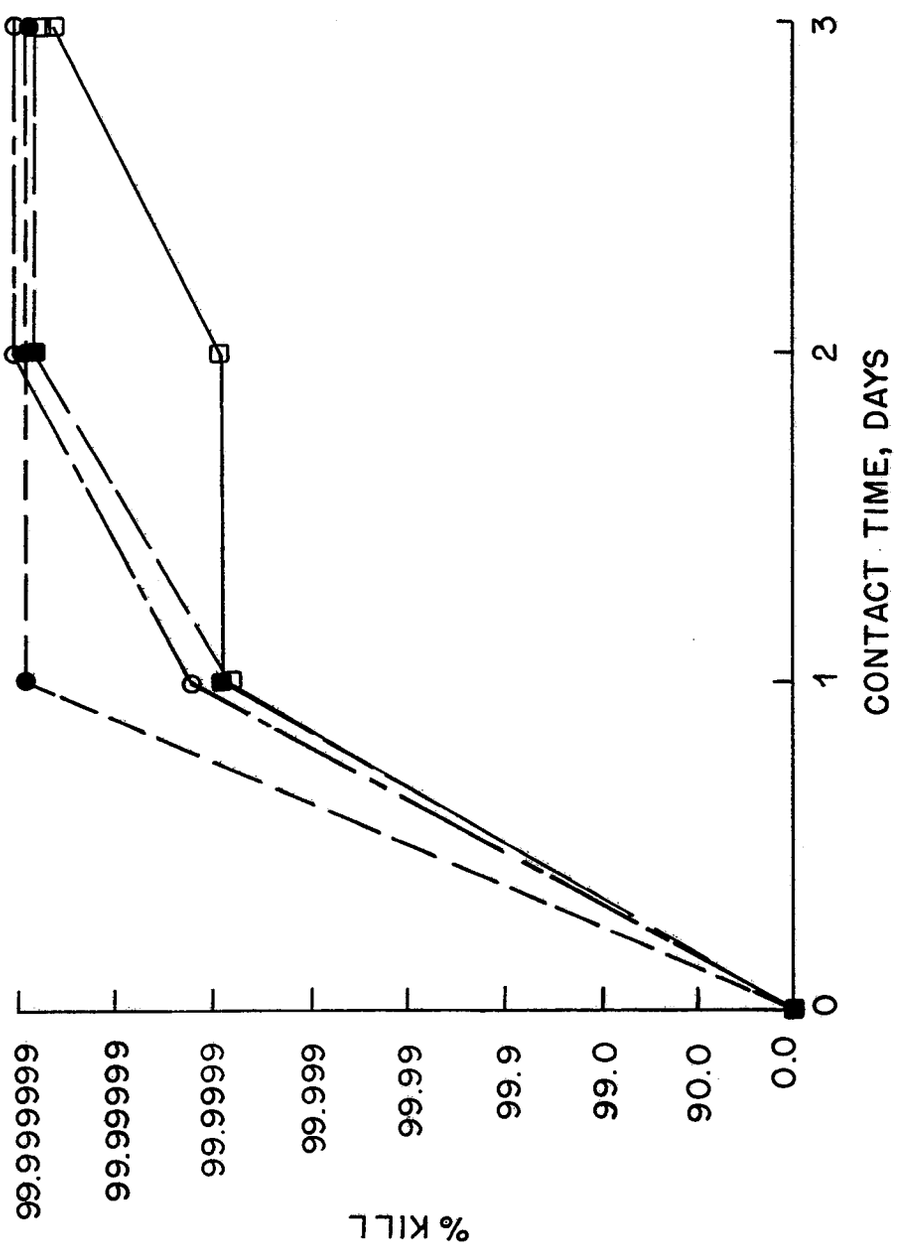
1
2
3
CONTACT TIME, DAYS

FIG. 4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80 PPM
160 PPM
320 PPM
% KILL
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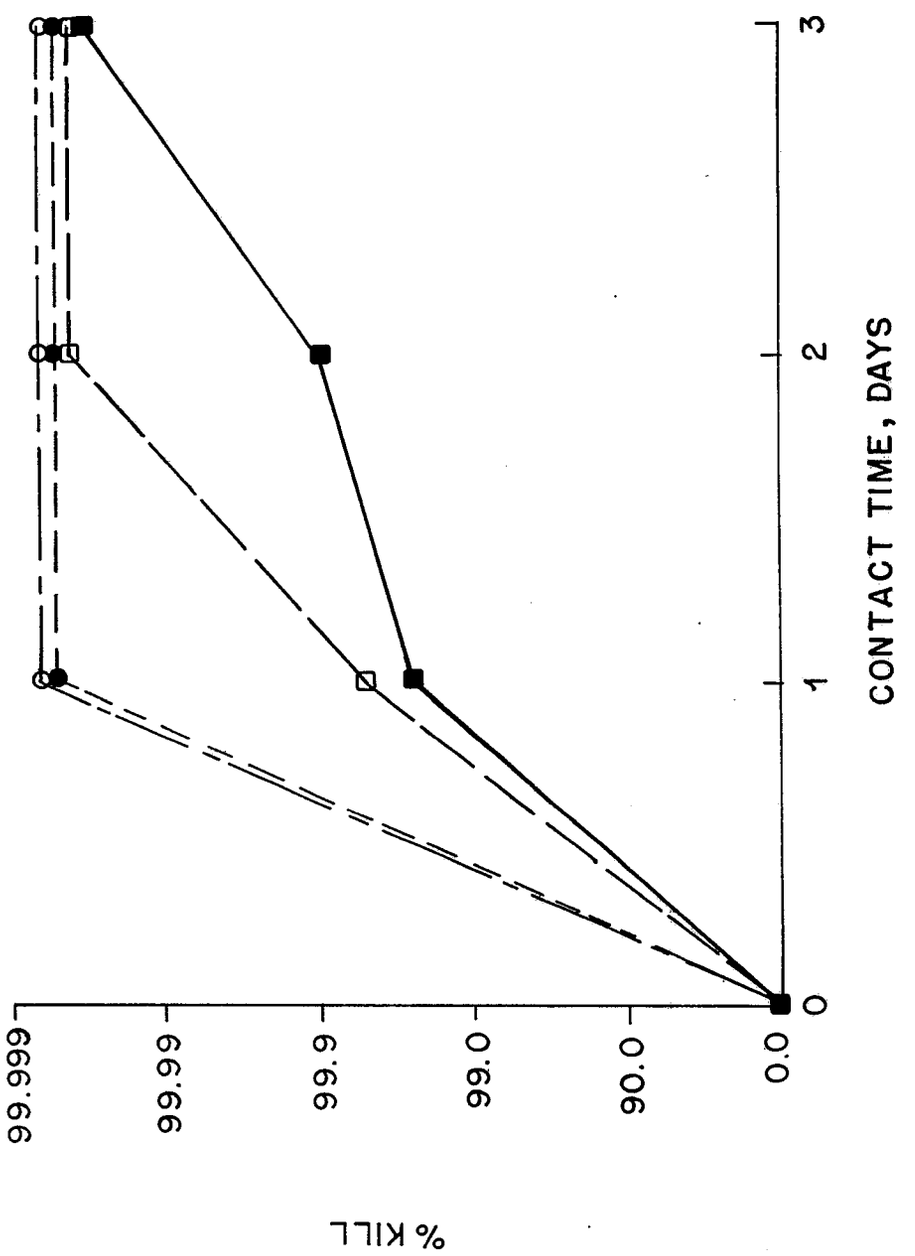
99.0
90.0
0.0
0
1
2
3
CONTACT TIME, DAYS

FIG. 5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99.0
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0
1
2
3
CONTACT TIME, DAYS

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 5791

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	GB-A-1 372 560 (NIPPON) * Claims 1,3 *	1,2,5	C 10 G 31/08

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 10 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-10-1988	DE HERDT O.C.E.

CATEGORY OF CITED DOCUMENTS

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