ORGANISATION AFRICAINE DE LA PROPRIETE INTELLECTUELLE (O.A.P.I.)

(19) OAPI

(11) N° 010069

(51) Inter. Cl. 5

A 01 N 31/04, 43/16
A 01 N 43/78, 45/00, 59/26
A 61 K 31/07, 31/51, 31/59

(12) BREVET D'INVENTION

(21) Numéro de dépôt : 60538

(22) Date de dépôt : 15.07.1994

(30) Priorité(s) : AUSTRALIA
n° PL 0426/92 du 15.01.1992

(24) Délivré le : 14.10.1996

(45) Publié le : 14.10.1996

(73) Titulaire(s) :

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION
Limestone Avenue, Campbell,
Australian Capital Territory, 2601
(Australia)

(72) Inventeur(s) :

1) Henry Jonathan BANKS
10 Beltana Road, Pialligo,
Australian Capital Territory,
2609 (Australia)

(suite au verso)

(74) Mandataire : Cabinet J. EKEME
B.P. 6370
YAOUNDE (Cameroun)

(54) Titre : CARBONYL SULPHIDE FUMIGANT AND METHOD OF FUMIGATION.

(57) Abrégé :

The gaseous chemical compound, carbonyl sulphide, has hitherto been unknown as a fumigant for the control of insects and mites. Experiments have shown conclusively that carbonyl sulphide can be used as such a fumigant, with fumigation properties comparable to those of phosphine and methyl bromide. The effectiveness of carbonyl sulphide against insects (both adult and immature stages), mites, termites and moulds is demonstrated. In addition, its low absorbtion by grain, lower flammability than phosphine, lack of influence on seed germination, and apparent environmental safety make carbonyl sulphide particularly beneficial as a fumigant of stored grain. It may also be used to fumigate other stored produce (including perishable foodstuff), soil, timber and spaces (such as buildings) and any material likely to be infested by insects or mites, or act as a source of such infestation.

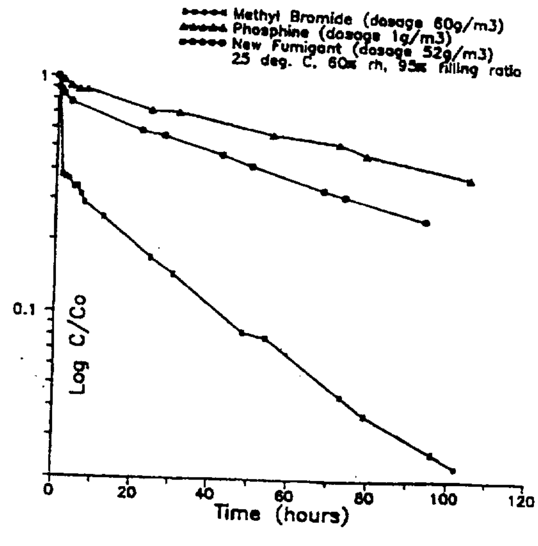

FIG. 1

TITLE: "CARBONYL SULPHIDE FUMIGANT AND METHOD OF FUMIGATION"

Technical Field

This invention concerns gaseous fumigants. More particularly, it concerns the gas carbonyl sulphide (COS), which has also been termed carbon oxysulphide, as a fumigant.

Background to the Invention

Fumigants are widely used for the disinfestation, and protection against infestation, that is usually required to protect particulate materials (such as grain) and other stored produce (including durable and perishable foodstuff), porous bulk materials (for example, soil or timber) and spaces (typically, empty buildings). An ideal fumigant should be toxic to insects, mites, nematodes, bacteria, fungi and moulds. It should be effective in low concentrations. It should have a low absorbtion by materials in the fumigated region. It should have a low mammalian toxicity and leave either no residue or an inert residue. In addition, the ideal fumigant should present no difficulties as far as safe handling is concerned, and it should not adversely affect the commodity or space that is being fumigated.

No fumigant meets all of these "ideal" criteria. The two fumigants most commonly used in the fumigation of grain, other particulate materials, fruit and timber are phosphine and methyl bromide. Phosphine is the preferred fumigant for grain stores and the like because it is effective against grain pests and leaves little residue (which is essentially a harmless phosphate). However, phosphine is spontaneously combustible when its concentration exceeds a relatively low value.

Methyl bromide is more toxic to grain pests than phosphine when used for short periods of fumigation, but phosphine is more toxic to grain pests when long term fumigation is effected. Methyl bromide has a lower flammability than phosphine, but recent work has shown that methyl bromide depletes the ozone layer. Thus approval of methyl bromide as a fumigant is currently under review, following the Montreal protocol.

Other fumigants that have been used against grain pests include acrylonitrile, carbon disulphide, carbon tetrachloride, chloropicrin, ethylene dibromide, ethylene dichloride, ethylene oxide, hydrogen cyanide and sulphuryl fluoride. It will be noted that a halogen is present in the majority of these "conventional" fumigants, none of which has the "ideal" fumigant properties.

For many years, there has been a constant seeking of new fumigants and there is no doubt that the quest for improved fumigants will continue.

Disclosure of the Present Invention

The prime object of the present invention is the provision of a new fumigant that has properties which make it a viable alternative to the conventional fumigants, particularly in the control of insects, mites and moulds.

This objective is achieved by the use of carbonyl sulphide as a fumigant.

Carbonyl sulphide is a well-known compound. It is a gas at STP (Standard Temperature and Pressure), with a boiling point of -50.2°C. It is colourless, flammable (but not as flammable as phosphine), and soluble in water. Its solubility in water is 1.4 grams per litre at 25°C, compared with the aqueous solubilities of 13.4 grams per litre and 2.2 grams per litre for, respectively, methyl bromide and carbon disulphide (phosphine has been reported to be "sparingly soluble" in water). When in aqueous solution, it slowly decomposes. Commercially, carbonyl sulphide is normally supplied in liquefied form in cylinders at about 160 p.s.i.g. However, it occurs naturally, being the major sulphur species in the atmosphere (where it occurs uniformly in the troposphere and lower troposphere at a concentration of 1.3 micrograms per cubic metre) and part of the natural sulphur flux in soils and marshes. Carbonyl sulphide is also formed from the anaerobic degradation of manure and compost and is present in most pyrolysis products and in oil refineries.

As a consequence of its role in the sulphur cycle, its presence in pyrolysis products and its use as a chemical feedstock, carbonyl sulphide has been widely studied, and its properties and uses are well known. However, an extensive review of the technical literature, and a Dialog computer-based evaluation search (conducted in the files of <u>CAB Abstracts</u> 1972-1991, <u>Biosis Previews</u> 1969-1991, <u>Life Sciences Collection</u> 1978 to 1991, <u>Agricola</u> 1970 to 1991, Agris International 1974 to 1991, European Directory of Agrochemical Products and Oceanic Abstracts 1964 to 1991), has revealed no use or contemplated use of carbonyl sulphide as a fumigant, and no reference to the insect toxicity of carbonyl sulphide. A separate manual search of Chemical Abstracts extended back to the year 1900, but found no reference to carbonyl sulphide as a fumigant.

It is known that carbonyl sulphide is a mammalian toxic gas. In the article by Robert J Ferm entitled "The Chemistry of Carbonyl Sulfide", which was published in Chemical Review, volume 57, 1957, pages 621 to 637, three references are given in support of the statement at page 627 that:

> "Cold blooded animals show more resistance to carbonyl sulfide than do warm-blooded animals. Mice and rabbits die quickly when they are exposed to air containing more than 0.3 per cent carbonyl sulfide."

And in the current Matheson Gas Products Catalogue, in the section entitled "Carbonyl sulfide" (pages 115 to 117), it is stated that (page 115):

> "Carbonyl sulphide acts principally upon the central nervous system, with death resulting mainly from respiratory paralysis. Rabbits showed some ill effects after exposure of one half hour to 1300 ppm. With mice, death occurred in ½ minute when they were exposed to 8900 ppm, in 1½ minutes on exposure to 2900 ppm, and in 35 minutes on exposure to 1200 ppm. Sixteen minutes

exposure to 900 ppm caused no perceptible effects."

However, it is known that gaseous compounds which are lethal to humans and smaller mammals, and also to cold-blooded vertebrates, may not be toxic to insects, moulds, mites and the like. One example of such a mammalian toxic gas is carbon monoxide. Thus, simply because carbonyl sulphide has a measured toxicity to mammals, it would be incorrect to conclude that carbonyl sulphide will also kill insects, moulds, mites and the like.

The present inventors, therefore, were surprised to find that carbonyl sulphide is useful as a fumigant. However, the present inventors have now established that when carbonyl sulphide is used as a fumigant, it may be applied undiluted, in a manner which allows it to mix with the atmosphere within the system under treatment, or it may be applied in a mixture with an inert diluent gas. The diluent gas will be used when a more dilute form of the fumigant is to be dispensed, or as an inhibitor to reduce flammability of the carbonyl sulphide. The diluent gas will normally be air, although other suitable carrier gases may be used.

The present invention also encompasses a method of fumigation of particulate materials, commodities, timber, spaces and soils which comprises applying gaseous carbonyl sulphide thereto.

Further details will now be provided, by way of example only, in the following discussion of the properties of carbonyl sulphide as a fumigant, including examples which demonstrate such properties.

Discussion of the Invention

The effectiveness of a fumigant is usually expressed as a "CT product", which is the concentration x time product for a specified effectiveness (usually for LC_{95} or LC_{99}, which are the lethal concentrations - doses - for 95 per cent and 99 per cent, respectively, of the population against which the fumigant is directed), expressed in milligram hours per litre. Normally, the temperature at which the fumigant is used is also given, for, in general, the higher the temperature of treatment with a fumigant, the lower the dose or concentration that is necessary to achieve a required effectiveness.

The concentration x time products, expressed in the usually adopted terms of LD_{90}, LD_{95} or LD_{99} (although strictly speaking these figures are $L(CxT)_{90}$, $L(CxT)_{95}$ and $L(CxT)_{99}$ values), for eleven previously known fumigants that are still in use against grain pests, are shown in Table 1. The data in Table 1, relating to eight species of grain pests, has all been obtained from prior art publications.

The present inventors have conducted numerous experiments to demonstrate the efficacy of carbonyl sulphide as a fumigant. A number of these experiments are detailed in the following Examples. In each case when carbonyl sulphide was used, the gas was produced by the reaction of potassium thiocyanate with sulphuric acid, as described by A Stock and E Kuss in their paper in Chemische Berichte der deutchen Gesellschaft, Volume 50, 1917, page 159. This method of production is recommended by R J Ferm in his aforementioned paper in Chemical Review, volume 57, 1957. The carbonyl sulphide thus produced was washed with a solution of lead acetate in water, to remove hydrogen sulphide. The purity of the carbonyl sulphide was measured using a GOW-MAC (Model 40-001) gas density detector; it typically had a purity between 80 per cent and 90 per cent V/V, with the major impurity being carbon dioxide. No hydrogen sulphide or sulphur dioxide was detected.

The fumigant concentrations in the experiments were analysed using a Shimadzu GC6 gas chromatograph, with a flame ionisation detector. Column conditions were 20 per cent OV 101 on Gas Chrom Q at 42°C column temperature, and injection temperature of 105°C.

The following species were subjected to tests of the efficacy of carbonyl sulphide as a fumigant: *Tribolium castaneum* (Herbst), (Coleoptera, tenebrionidae), strain CTC4; *T.confusum* (Jacq du Val) (Coleoptera, Curculionidae), strain CLS2; *Rhyzopertha dominica* (F) (Coleoptera, Bostrichidae), strain CRD2; *Oryzaephilus surinamensis* (L) (Coleoptera, Silvanidae), strain NOS4; *Ephestia cautella* (Walker) (Noctuidae, Pyralidae), strain CEC2; *Bactrocera tyroni* (Froggat), formerly *Dacus tyroni* (Diptera Tephrididae), collected Wollongong 1989; *Liposcelis bastrychophilus*; *Lepidoglyphus destructor* (Schrank); *Coptotermes acinaciformis* (Froggat) (Isoptera, Rhinotermitidae); and Cryptotermes domesticus (Haviland, Isoptera, Kalotermitidae)

Example 1 - Tests of the efficacy of carbonyl sulphide to control external stages of stored-product insects.

To test the effectiveness of carbonyl sulphide against the external stages of these stored product insects, glass serum vials (bottles) having a capacity of approximately 120 mL were used. These vials had a crimp top and were closed with a cap which permitted gas injection using a syringe (a "Mininert" valve). The bottles were left open in an atmosphere of 55 per cent relative humidity at the temperature at which the bioassay was to be performed (usually 25°C or 30°C).

To test the effectiveness of carbonyl sulphide against live insects, between 25 and 35 insects were added to each vial, which was then closed by its cap. A quantity of air, equal to the volume of gas to be injected, was then withdrawn from each bottle and the same volume of gas was injected into it. The bottle was kept at a constant temperature for the duration of the bioassay, which was usually 6 hours or 24 hours. At the end of this period, the insects in each bottle or vial were transferred to respective 60 mL glass jars, which contained 20 grams of wheat. The insects remained in the glass jars with the wheat for 14 days before the mortality assessment was made. All assays were replicated three or four times, and were accompanied by a control assay, in which no carbonyl sulphide was injected into the bottles containing the insects.

In the mortality assessment, the adult insects were classified as dead if they failed to respond to any stimuli. The control assay mortality was always assessed.

The assays of the effectiveness of carbonyl sulphide against the pupae of insects were conducted in a manner similar to the adult insect assays, except that, after treatment in the bottle, the pupae were transferred to glass jars containing 10 grams of flour. The mortality of the pupae was assessed as an inability of the pupae to become adults. The bioassays with pupae were all replicated three or four times, with control assays.

Corresponding assays of the effectiveness of carbonyl sulphide against insect larvae were conducted in the same manner as the bioassays with pupae, except that the mortality of the larvae was assessed, like that of adult insects, as an inability to respond to any stimuli. Larvae which successfully pupated after treatment were assessed as survivors.

Tests of the effectiveness of carbonyl sulphide against the eggs of insects were performed with the eggs on strips of filter paper. These strips were each approximately 1 cm x 5 cm, cut from S & S Rundfilter Nr 593, 90 mm diameter, filter papers, marketed by Schleicher and Schuell. The eggs of most species were oviposited directly onto the filter paper, after the adult insects had been added to a thin layer of wheat, brewers yeast and filter paper. In the case of <u>Tribolium castaneum</u> (Herbst), the eggs were oviposited on superfine flour and were recovered by sieving. The eggs were then transferred with a single hair brush, dipped into a 30 per cent sucrose solution, to strips of filter paper which were covered with double-sided adhesive paper - "Double Stick Tape", sold as "Scotch brand" (Trade Mark), marketed by 3M Consumer Products Group.

The adult insects were removed after 16 hours on the medium. Some eggs were dosed with carbonyl sulphide within 24 hours of the start of oviposition, these eggs being classified as "0-1 day old eggs". Other eggs were kept for a further four days, to generate "4-5 days old eggs", before being dosed with carbonyl sulphide.

Typically, 20 to 30 eggs were deposited on each strip of filter paper. The strips of filter paper, with the deposited eggs, were placed in respective glass vials (bottles) of the same type as those that were used to test the effect of carbonyl sulphide on adult insects, and were dosed with carbonyl sulphide in the same manner as the adult insects. After the exposure to carbonyl sulphide, the eggs were placed in a covered Petrie dish and stored at 30°C for seven days. At the end of this storage period, the numbers of hatched and unhatched eggs were counted, using a Nikon stereo microscope, equipped with a cold light source. The eggs that had failed to hatch were classified as dead. All assays using eggs were performed in triplicate, with a corresponding control (untreated by carbonyl sulphide) bioassay.

The results obtained with the bioassays for external stages are summarised in Table 2, which records the species, the stage of the insect (adult, pupae, larvae or eggs), the period of exposure to carbonyl sulphide, the temperature at which the bioassay was performed, the LC_{99} values (expressed in milligrams hours per litre - $mg.h.L^{-1}$), and the minimum effective tested dose. The minimum effective tested dose is the minimum tested dose that killed all insects in assays involving at least 100 insects. Entomologists will find that a comparison of the results in Table 2 with the prior art data collated in Table 1 demonstrates that the effectiveness of carbonyl sulphide against the external stages of insects is comparable to that of other, known fumigants.

The data presented in Table 2 clearly demonstrates the effectiveness of carbonyl sulphide against all external stages of the insects listed in Table 2.

<u>Example 2 - The effectiveness of carbonyl sulphide against internal stages of stored-product insects</u>.

In a series of experiments, adults of the grain pest <u>Rhyzopertha dominica</u> were allowed to oviposit for 4 to 5 weeks on 1,000 grams of wheat, maintained at 30°C and having a moisture content of 12 per cent. In each experiment, the adults were removed from the wheat, which was then divided into three portions; two for dosing with carbonyl sulphide and one for use as a control. Each portion of wheat was then placed in a glass jar having a capacity of 1.1 litre, and the jar was sealed with a screw cap which had been fitted with a septum. A dose of carbonyl sulphide in the range of from 8 mg per litre to 45 mg per litre was injected through the septum. After the assay period (for example, 24 hours), the screw cap was replaced with filter paper, to enable the fumigant to be aired. The wheat was then stored at either 25°C or 30°C. The emerging adults were counted at weekly intervals over a period of from four to five weeks. Replication of each experiment was performed by repeating the entire procedure.

The results of this series of experiments are given in Table 3. It will be noted that an exposure for 24 hours to a dose of 8 mg per litre of carbonyl sulphide gave, on average, 93.4 per cent control of all immature stages of R. dominica. The most tolerant stage was probably pre-pupae (that is, those insects which emerged in 7 to 14 days after dosing).

A second series of experiments, performed in the same manner but with exposure of the wheat to carbonyl sulphide for periods of 6 hours, 24 hours and 48 hours, produced the results recorded in Table 4. It will be noted, from these results, that extending the exposure time to a single dose of carbonyl sulphide increased the mortality of the internal stages, indicating that the toxic effect of carbonyl sulphide on insects in whole grain was not rapidly destroyed by sorption of the carbonyl sulphide.

A third series of experiments was performed to investigate the efficacy of carbonyl sulphide in the control of the internal stages of the grain pest Sitophilus oryzae. The same procedure was adopted, with carbonyl sulphide doses in the range of from 15 mg per litre to 91 mg per litre, and with exposures to a single dose ranging from 6 hours to 72 hours. The results of these experiments are given in Tables 5, 6 and 7.

A fourth series of experiments was performed, using the procedure of this Example, to investigate the relative efficacies of carbonyl sulphide, carbon disulphide and ethyl formate against the internal immature stages of S. oryzae and R. dominica in whole grain. The outcome of this series of experiments is shown in Table 8. The superiority of carbonyl sulphide as a controller of the internal stages of these grain pests is clearly evident.

Example 3 - The effectiveness of carbonyl sulphide in the control of stored-product mites and psocids.

A series of assays was conducted to demonstate the effectiveness of carbonyl sulphide against adult wheat mites and psocids (species Liposcelis bostrychophilus). The methodology of the assays of adult external stages of stored-product insects, described above in Example 1, was used, except that 3 grams of wheat (containing 18 per cent moisture) and approximately 100 mg of brewers yeast were added to the glass jars before the addition of approximately 200 psocids. After exposure of the psocids to carbonyl sulphide for either six hours or 24 hours, the sealing caps were removed from the jars and, after 1 hour of airing, the jars were closed with thin plastic material. The assays were conducted at 25°C, 75 per cent relative humidity. The number of mobile mites was counted at the end of the exposure to the carbonyl sulphide and the mortality was assessed after a holding period of five days.

The results of these experiments with adult psocids and mites (Lepidoglyphus destructor) are shown in Tables 9 and 10, with some of the information obtained from this data being included in Table 2.

In a separate experiment, 200 psocids in a glass container were exposed to a dose of 5 mg per litre of carbonyl sulphide for one hour. At the end of that one hour exposure to carbonyl sulphide, all 200 of the psocids were dead.

Example 4 - The efficacy of carbonyl sulphide in the control of fruit flies.

Bioassays of the effect of carbonyl sulphide on the external immature stages of the Queensland fruit fly, Bactrocera tyroni (Diptera: Tephritidae) were conducted in the same manner as the assays of the immature external stages of stored-product insects in Example 1, except that

(a) when using eggs, the filter paper strips were damp when subjecting the eggs to a dose of carbonyl sulphide, and

(b) one drop of water was added to each jar for larvae prior to the addition of the insects.

The assays with eggs, feeding larvae and pupae of B.tyroni were conducted at 30°C. The results are shown in Tables 11, 12 and 13 for, respectively, pupae, late instar larvae and eggs of B. tyroni.

<u>Example 5 - The use of carbonyl sulphide to control termites</u>

Adult termites and nymphs of the species *Coptotermes acinaciformis* (Froggat) (Isoptera, Rhinotermitidae), and *Cryptotermes domesticus* (Haviland, Isoptera, Kalotermitidae) were exposed to carbonyl sulphide in the same manner as the adult stored-product insects in Example 1, except that damp filter paper (Whatmans No 1, diameter 4.25 cm) was added to each jar before the addition of insects. The results obtained with this series of experiments with adults and nymphs of *Coptotermes acinaciformis* are recorded in Tables 14 and 15.

<u>Example 6 - The effect of carbonyl sulphide on seed germination</u>

To investigate whether carbonyl sulphide affects the germination of seeds, grains of Australian standard white wheat and malting barley were conditioned to 12 per cent and 16 per cent moisture, as determined by the ISO air oven method. The grain samples were each dosed for 24 hours with carbonyl sulphide in concentrations of 0.5 per cent V/V, 1.0 per cent V/V and 5.0 per cent V/V. At these concentrations, the corresponding nominal concentration x time products were 300 mg hours per litre, 600 mg hours per litre and 3,000 mg hours per litre.

In all of these experiments, no effect on seed germination or vigour was detected. Table 16 records the results obtained with wheat at 16 per cent moisture content.

<u>Example 7 - The sorption of carbonyl sulphide on grains</u>

Sorption studies using grains of Australian standard white wheat and Calrose rice were carried out using glass serum vials of capacity 120 ml, each equipped with a cap having a "Mininert" valve to permit gas injection. The moisture contents of the grain samples were measured with an electronic meter (a Marconi meter). The samples of grain were then used to fill the vials to levels of, respectively, 25 per cent, 50 per cent and 95 per cent. The vials were then held at 25 ± 1°C. A volume of air equal to the fumigant dose to be used was removed from each vial, then the same volume of carbonyl sulphide was added to the vial. The concentration of carbonyl sulphide was measured with time and analysed to evaluate the decay of carbonyl sulphide.

An example of the raw data obtained in the course of these experiments is provided in Table 17. It will be noted that for a filling ratio of 0 per cent (that is, no wheat in the vial), recoveries 0.25 hour after dosing were 98.4 per cent of the calculated applied dose. This is a very high level of recovery. The decline in fumigant concentration from vials containing no grains, after 93.9 hours of testing, in replicated experiments, was always in the range of from 1.2 per cent to 1.5 per cent, which indicates a high degree of sealing of the vials. The results obtained from these experiments are consistent with a rapid initial uptake of some fumigant by the grain, followed by declining residues of fumigant, in a manner proportional to the amount of grain in the vial.

Similar experiments were conducted with methyl bromide and phosphine as the fumigant, to obtain comparative sorption data. The results are shown in Figure 1. Clearly carbonyl sulphide is absorbed much less strongly than methyl bromide, and slightly more strongly than phosphine. This indicates that carbonyl sulphide may be used for long exposure fumigation.

Example 8 - The effectiveness of carbonyl sulphide as a mould inhibitor

In a test of the effectiveness of carbonyl sulphide as a mould inhibitor, a number of samples of wheat, containing 31 per cent moisture (w/w, wet basis) were placed in sealed containers (glass jars). Some containers held only the wheat sample and air. Other containers held the wheat sample and air containing from 2.5 per cent to 10.0 per cent (by volume) of carbonyl sulphide. All of the sealed containers were kept at 35°C for seven days. After two days of this storage, some of the wheat in the sealed containers which held no fumigant was noticeably discoloured. After seven days, all of the wheat in the containers without fumigant was discoloured by growth of mould on the grains. However, no discolouration occurred of the wheat which was in the containers which also held carbonyl sulphide in concentrations in the range from 4.5 per cent to 10.0 per cent (by volume).

Example 9 - Investigation of how the period of exposure affects the concentration of carbonyl sulphide.

Samples of a mixed culture of Sitophilus oryzae were exposed to different concentrations of carbonyl sulphide for periods ranging from 6 hours to 168 hours, using the same technique as that described in Example 2. The results of this series of experiments are shown in Table 18. It will be seen that carbonyl sulphide is an effective control of this insect over a large range of concentrations and for a wide range of exposure periods.

Example 10 - Investigation of the use of carbonyl sulphide to fumigate soil

Three samples of soil - designated samples A, B and C - were taken from a vegetable garden. Sample A was taken from a compost heap in the garden. The moisture contents of the samples A, B and C were, respectively, 29.4 per cent, 25.8 per cent and 27.1 per cent.

Three glass vials (jars), each of capacity 120 mL, were approximately half-filled with soil from each of the samples A, B and C. Each vial was then fitted with a "Mininert" valve. Carbonyl sulphide was applied to two of the three vials containing soil from a sample. The third vial or jar was left untreated, as a control. In addition, 1 kilogram of soil from sample B was placed in a glass jar of capacity 1.8 L, fitted with a lid having a septum through which carbonyl sulphide was injected.

All of the jars (that is, the vials of 120 mL capacity and the 1.8 L jar) were stored at 27°C for 20 hours. During this storage period, the concentration of carbonyl sulphide in each jar was measured. From the measurements of the concentration of carbonyl sulphide during the storage period, the following results were obtained:

(a) two minutes after the injection of carbonyl sulphide, the concentration of carbonyl sulphide had an average value of 62 per cent of the calculated initial concentration, indicating a rapid uptake of carbonyl sulphide by the moist soil;

(b) five hours after the injection of carbonyl sulphide, the jars contained (on average) 18 per cent of the calculated initial concentration; and

(c) after 20 hours, the average concentration of carbonyl sulphide was 5.9 per cent of the calculated initial concentration.

At the end of the storage period, the lids or caps were removed and the jars were left open to the air. The efficacy of the carbonyl sulphide was assessed by comparing the number of nematodes in the controls with those in the fumigated soils. The results obtained are summarised in Table 19.

It is clear from Table 19 that carbonyl sulphide effectively removes nematodes from soil.

Example 11 - Assessment of carbonyl sulphide as a fumigant relative to phosphine and methyl bromide

It was noted in the introduction to this specification that there is no "ideal" fumigant. The selection of a fumigant is made by assessing its advantages and disadvantages. The present inventors have ranked the commonly used fumigants methyl bromide and phosphine with carbonyl sulphide in respect of mammalian toxicity, insect toxicity (short and long exposures), environmental safety and flammability.

For each parameter, 1 was taken as the best ranking and 3 the worst ranking. The results of this assessment are as follows:

Parameter	Relative ranking		
	Methyl bromide	Phosphine	Carbonyl sulphide
Mammalian toxicity	3	2	1
Insect toxicity -			
short exposures	1	3	2
long exposures	2	1	3
Environmental safety	3	2	1
Flammability	1	3	2

The mammalian toxicity ranking was based on TLV values, and the flammability was assessed by reference to flammability limits in air. Methyl bromide was ranked last in the category "environmental safety" because of its effect on the ozone layer, and carbonyl sulphide was ranked above phosphine in this category because there is an absence of knowledge about the environmental fate of phosphine and reaction mechanisms of phosphine in the environment.

It is clear that carbonyl sulphide is a viable alternative to methyl bromide and phosphine as a fumigant. It can be used for short term fumigation (which is not possible with phosphine) and for long periods - up to 35 days or more (which is not possible with methyl bromide). In addition, it will be apparent to entomologists that registration of carbonyl sulphide as a "new" fumigant should be a relatively inexpensive exercise in view of the extensive knowledge already obtained regarding carbonyl sulphide.

Table 1

Concentration x time products of certain fumigants required for the control of various species of insects

Insect	*Oryzsephilus surinamensis*	*Rhyzopertha dominica*	*Sitophilus granarius*	*Sitophilus oryzae*
Insect Fumigant	Adults LC_{95} 6 h.21°C	Adults LC_{95} 6 h.21°C	Adults LC_{99} 5 h.25°C	Adults LC_{95} 6 h.21°C
Acrylonitrile	8.4	8.4	11.0	10.8
Carbon disulphide	408.0	294.0	325.0	300.0
Carbon tetrachloride	-	-	495.0	220.0
Chloropicrin	19.2	15.6	150.0	23.4
Ethylene dibromide	19.2	37.2	34.5	60.0
Ethylene dichloride	462.0	636.0	230.0	738.0
Ethylene oxide	60.0	69.6	38.0	62.0
Hydrogen cyanide (HCN)	7.2	15.6	67.5	60.0 (LD_{90}) 5 h 25°C
Methyl bromide	40.8	33.0	28.0	30.0 (LD_{90})
Phosphine (24 hr exposure 27°C)	0.96 (LD_{90})	0.6 (LD_{90})	1.01	0.36 (LD_{90})
Sulphuryl fluoride	-	-	17.5	-

Table 1 (continued)

Concentration x time products of certain fumigants required for the control of various species of insects

Insect	Tenebroides mauritanicus	Tribolium confusum	Tribolium castaneum	Trogoderma granarium
Insect Fumigant	Larvae LC_{99} 5 h.21°C	Adults LC_{99} 5 h. 25°C	Adults LC_{90} 6 h.24°C	Larvae LC_{95} 8 h.21°C
Acrylonitrile	40.0	19.5	-	48.0
Carbon disulphide	828.00	560.00	-	696.0
Carbon tetrachloride	400.00*	025.0	600.0	-
Chloropicrin	58.00	57.5	14.0	96.0
Ethylene dibromide	125.00	31.0	22.0 (LD_{99}) 4 h. 27°C	80.0
Ethylene dichloride	1728.0	365.0	462.0	2080.5
Ethylene oxide	175.0	127.5	135.0**	176.0 5 h. 25°C
Hydrogen cyanide (HCN)	68.5	5.55	2.4 (LD_{99})	26.4
Methyl bromide	115.0	64.0	62.0 (LD_{99})	136.0 h. 27°C
Phosphine (24 hr exposure 27°C)	5.0 approx.	0,48	11.5	331.0 100% mort. 72 h 21°C
Sulphuryl fluoride	81.5	55.0	-	-

*LD_{50} **LD_{99}

Table 2

Toxicity of carbonyl sulphide to insects and mites

Species	Stage	Exposure (h)	Temperature (°C)	LC_{95} (mg h L^{-1})	Minimum effective tested dose (mg h L^{-1})
R. dominica	adult	6	25	38	68.7
T. castaneum		6	25	82	108
		24		297	
S. oryzae		6	25	99	112
		24		264	
O. surinamensis		6	25	198	240
		24	30		240
T. confusum		6	25	111	146
L. destructor		6	27		120
		24		240	
psocids (*L. bostrychophilus*)		6	25		22.5
T. castaneum	pupae	6	30	290	360
		24	30	490	600
E. cautella		24	27		480
B. tyroni		6	27		360
		24	27	440	600
T. castaneum	larvae	6	25	270	300
		24	30		480
E. cautella		6	30		240
		24		410	480
O. surinamensis		6		210	300
B. tyroni		6	27		180
		24	27		360

10069

Table 2 (continued)

Toxicity of carbonyl sulphide to insects and mites

Species		Stage	Exposure (h)	Temperature (°C)	LC_{99} (mg h L^{-1})	Minimum effective tested dose (mg h L^{-1})
B. dominica	eggs	0-1d	24	30	145	192
			6		102	144
		2-3d	24			144
		4-5s	24			120
T. castaneum		0-1d	24		520	600
			6		430	480
			48			360
O. surinamensis		0-1d	24		495	600
			6			420
B. tyroni		2-6h	24		460	600
E. cautella		0-1d	24			600
			6			720
S. oryzae		0-1d	24			600

Table 3

Control of immature stages of R. dominica at 25°C or 30°C after 24h exposure

Time after dosing before emergence (days)	Dose Low (mg L-1)	Dose High	Temp (°C)	No. emerging in Control	No. emerging in Low dose	No. emerging in High dose	% reduction Low dose	% reduction High dose
0-7	8	16	25	0	0	0	-	-
7-14	8	16		95	0	0	100	100
14-21				294	12	0	95.9	100
21-28				343	3	0	99.1	100
28-35				360	4	0	98.8	100
0-35				1092	19	0	98.3	100
0-7	15	45	25	77	4	0	94.8	100
7-14				121	15	0	87.6	100
14-21				123	4	0	96.7	100
21-28				928	2	0	99.8	100
0-28				1249	25	0	98.3	100
0-7	8	24	25	0	0	0	-	-
7-14				69	0	0	100	100
14-21				284	8	0	97.2	100
21-28				253	11	0	95.6	100
28-35				184	6	0	95.7	100
7-35				790	25	0	96.8	100
0-7	8	25	30	14	1	0	92.8	100
7-14				284	24	0	90.9	100
14-21				234.	6	0	97.4	100
21-28				265	2	0	99.2	100
0-28				797	33	0	95.9	100
0-7	8	25	25	131	29	0	77.9	100
7-14				265	84	1	68.3	99.6
14-21				244	38	0	84.4	100
21-28				240	20	1	91.7	99.6
38-35				252	33	0	86.9	100
7-35				1132	204	2	82.0	99.8
0-7	8	25	25	298	22	0	92.7	100
7-14				301	47	0	84.4	100
14-21				385	15	0	96.1	100
21-28				294	6	0	98.0	100
28-35				380	7	0	98.1	100
0-28				1658	97	0	94.1	100

Table 4

Effect of increasing the exposure period, to a single dose, on immature stages of R. dominica

Time after dosing before emergence (days)	Dose (mg L^{-1})	Exposure period Short (h)	Exposure period Long (h)	No. emerged Control (short)	No. emerged Short dose	No. emerged Control (long)	No. emerged Long dose	% reduction Short dose	% reduction Long dose
0-7	25	6	24	24	3	14	0	87.5	100
7-14				164	28	284	0	82.9	100
14-21				181	11	234	0	93.9	100
21-28				169	5	265	0	97.0	100
28-35				180	7	355	1	96.1	99.7
0-35				718	54	1152	1	92.4	99.91
0-7	8	24	48	131	29	298	22	77.9	92.7
7-14				265	84	301	47	68.3	84.4
14-21				244	38	385	15	84.4	96.1
21-28				240	20	294	6	91.7	98.0
28-35				252	33	380	7	86.9	98.1
0-35				1132	204	1658	97	82.0	94.1
0-7	25	24	48	131	0	298	0	100	100
7-14				265	1	301	0	99.6	100
14-21				244	0	385	0	100	100
21-28				240	1	294	0	99.6	100
28-35				252	0	380	0	100	100
0-35				1132	2	1658	0	99.8	100

Table 5

Control of immature stages of S. oryzae at 25°C or 30°C after 24H exposure

Interval after dosing (days)	Dose Low mg L⁻¹	Dose High	Temp (°C)	No. emerged in Control	No. emerged in Low dose	No. emerged in High dose	% reduction Low dose	% reduction High dose
0-7	24	48	25	24	6	0	75.0	100
7-14				136	34	3	76.1	97.8
14-21				106	5	0	95.3	100
21-28				102	38	0	62.7	100
28-35				55	59	0	-7.3	100
7-35				423	142	3	66.4	99.3
0-7	15	45	25	79	79	49	0	38.0
7-14				65	73	26	-12.3	60.0
14-21				236	183	8	22.4	96.7
21-28				1424	778	202	45.3	85.8
0-28				1804	1113	285	38.3	84.2
0-7	24	64.5	25	0	0	0	-	-
7-14				69	0	0	100	100
14-21				284	8	0	97.2	100
21-28				253	11	0	95.7	100
28-35				184	6	0	96.7	100
0-35				790	25	0	96.8	100
0-7	25	66	30	2	1	0	50	100
7-14				156	76	38	49.3	74.6
14-21				139	38	30	72.7	78.4
21-28				147	12	13	91.8	91.1
28-35				107	40	12	62.6	88.8
0-35				545	169	93	69.4	82.9
0-7	25	66	25	131	25	0	80.9	100
7-14				265	67	7	74.7	97.4
14-21				244	4	0	98.4	100
21-28				240	4	0	98.2	100
28-39				252	16	0	93.7	100
0-35				1132	116	7	89.8	99.4

Table 6

Effect of increasing the exposure period, to a single dosage, on the immature stages of S. oryzae

Interval after dosing (days)	Dose (mg L^{-1})	Exposure period		No. emerged				% reduction	
		Short (h)	Long (h)	Control (short)	Short dose	Control (long)	Long dose	Short dose	Long dose
0-7	66	6	24	22	2	2	0	90.9	100
7-14				143	48	150	38	66.4	74.6
14-21				152	14	139	30	90.8	78.4
21-28				151	17	147	13	88.7	91.1
28-35				82	65	107	12	20.7	88.8
0-35				550	146	545	93	73.4	82.9
0-7	66	24	48	93	0	40	0	100	100
7-14				135	7	70	10	94.8	85.7
14-21				82	0	60	0	100	100
21-28				70	0	53	0	100	100
28-35				74	0	167	0	100	100
0-35				454	7	390	10	99.5	97.4
0-7	25	24	48	93	25	40	49	73.1	-22.5
7-14				135	67	70	25	50.3	64.2
14-21				82	4	60	2	95.1	96.7
21-28				70	4	53	7	94.3	86.7
28-35				74	16	167	45	78.4	73.1
0-35				454	116	390	128	74.3	67.2

Table 7

Effect of increasing the exposure period, to a single dosage, on the immature stages of S. oryzae

Interval after dosing (days)	Dose (mg L^{-1})	No. emerged after exposure period				Control No.
		6	24 (h)	48	72	
0-7	60	0	0	0	0	1
7-14		1	0	0	0	85
14-21		15	0	0	0	178
21-28		27	0	0	0	119
28-35		40	1	0	0	58
0-7	91	0	-	0	0	2
7-14		13	-	1	0	84
14-21		10	-	0	0	139
21-28		13	-	0	0	97
28-35		38	-	0	0	60

Table 8

Comparison between carbon disulphide (CS_2), ethyl formate (EtF) and carbonyl sulphide (COS) in single dosing of wheat for 24h at 25°C

Interval after dosing (days)	Species	Dose mg L^{-1}	No. emerged in			% reduction		
			Control	CS2	EtF	CS2	EtF	COS[a]
0-7	*S. oryzae*	24	59	11	54	81.4	8.5	
7-14			266	102	226	61.7	15.0	
14-21			205	29	187	85.9	8.8	
21-28			131	19	155	85.5	-18.3	
28-35			66	49	42	25.8	36.3	
0-35			727	210	664	71.1	8.7	80.6[a]
0-7		42	118	11	80	90.6	32.2	
7-14			194	61	147	68.6	24.2	
14-21			125	24	96	80.8	24.8	
21-28			118	2	35	98.3	70.3	
28-35			92	6	33	93.5	64.1	
0-35			647	104	391	83.9	65.4	
0-7	*R. dominica*	8	126	107	128	15.0	-1.6	
7-14			630	423	516	32.8	18.1	
14-21			421	357	488	15.2	15.9	
21-28			527	326	302	38.1	42.7	
28-35			267	274	284	-2.6	-6.3	
0-35			1971	1487	1718	24.5	12.8	93.2[b]
0-7		15	186	144	157	22.6	15.6	
7-14			270	175	285	35.1	-5.5	
14-21			265	231	245	12.8	7.5	
21-28			290	150	116	48.2	63.4	
28-39			244	116	95	52.4	61.1	
0-35			1255	816	898	35.0	28.4	98.3[c]

a. Mean of 4 replicates at this dose
b. Mean of 5 replicates at this dose
c. One replicate at this dose

Table 9

Toxicity of carbonyl sulphide to adult psocids (*Liposcelis bostrychophilus*)

Temperature (°C)	Exposure period (h)	Dose (mg h L^{-1})	Mortality		Corrected mortality (%)
			Treated (a)	Control	
30	6	5.4	28/200	0/200	14.0
		10.8	100/200		50.0
		22.5	200/200		100
		45	200/200		100
	24	180	200/200	5/200	100

(a) Numbers estimated

Table 10

Toxicity of carbonyl sulphide to adults of *L. destructor*

Temperature (°C)	Exposure period (h)	Dose (mg h L^{-1})	Mortality		Corrected mortality (%)
			Treated (a)	Control	
25	6	120	43/43	10/135	100
	24	360	35/35	3/53	100
		240	241/241	7/167	100
		120	339/340		99.7

Table 11

Toxicity of carbonyl sulphide to pupae of B. tyroni

Temperature (^oC)	Exposure period (h)	Dose (mg h L^{-1})	Mortality		Corrected mortality (%)
			Treated	Control	
30	6	600	40/40	0/40	100
		360	60/60		100
		300	55/60		91.7
		240	33/60		55.0
		180	11/80		13.8
	24	600	40/40	0/40	100
		540	59/60		98.3
		480	59/60		98.3
		420	71/80		88.8
		366	32/60		53.3
		300	5/55		9.1

Table 12

Toxicity of carbonyl sulphide to late instar larvae of *B. tyroni*

Temperature (°C)	Exposure period (h)	Dose (mg h L^{-1})	Mortality		Corrected mortality (%)
			Treated	Control	
30	24	600	60/60	2/17	100
		360	60/60		100
		120	13/31		37.1
	6	360	60/60		100
		120	15/78		12.6
	24	240	4/36	–	–
		180	9/38	–	–
	6	240	37/37	18/47	100
		210	34/34		100
		180	33/33		100
		150	32/33		
		120	41/50		

Table 13

Toxicity of carbonyl sulphide to eggs of B. tyroni

Age (d)	Temperature (°C)	Exposure period (h)	Dose (mg h L^{-1})	Mortality		Corrected mortality (%)
				Treated	Control	
0.08-0.3	30	24	600	116/116	23/111	100
			540	130/133		97.1
			480	90/92		97.3
			420	80/104		70.9
			360	92/112		77.5
			180	60/515	17/239	4.9
			240	101/401		19.5
			300	356/521		65.9
		6	240	265/407	17/343	63.2
			360	373/399		93.1
			480	517/521		99.19
			600	450/452		99.53
		6	720	483/484	17/285	99.73
			870	118/126	81/327	93.3
			180	198/336		45.4
			150	122/349		13.5

Table 14

Toxicity of carbonyl sulphide to adults of *Coptotermes acinaciformis*

Temperature (°C)	Exposure period (h)	Dose (mg h L^{-1})	Mortality		Corrected mortality (%)
			Treated (a)	Control	
25	24	600	165/165	0/100	100
		288	110/110		100
		192	0/165		0
	6	120	11/113		9.7
		96	3/110		2.7

Table 15

Toxicity of carbonyl sulphide to nymphs of *Coptotermes acinaciformis*

Temperature (°C)	Exposure period (h)	Dose (mg h L^{-1})	Mortality		Corrected mortality (%)
			Treated (a)	Control	
25	24	600	30/30	0/30	100
		192	0/30		0

Table 16

Effect of carbonyl sulphide on germination of wheat of 16.0% moisture content

Concentration %, V/V	% Germination	
	First count (4 days)	Final count (10 days)
0	85 90 87	90 91 87
0.5	93 91	96 93
1.0	93 89	93 92
5.0	89 93	93 93

Table 17

Raw data for absorption of carbonyl sulphide on wheat of 11.7% moisture content, at 25°C, and at initial concentrations of 48-52 mg L^{-1}

Time after dosing (h)	Concentration for degree of fill (mg L^{-1})							
	0%		25%		50%		95%	
Applied	45.0	44.9	47.7	47.5	49.2	48.4	52.2	51.5
0.25	44.3	44.2	45.7	45.6	45.9	45.7	46.4	46.0
0.75	44.8	44.8	45.4	45.2	43.6	43.5	44.9	44.8
1.28	44.9	44.8	45.0	45.0	42.0	41.8	43.6	43.5
3.35	44.5	44.5	43.5	43.3	40.7	40.2	40.3	39.8
21.7	44.8	44.9	43.1	43.0	37.0	36.6	30.8	30.6
27.5	44.8	45.0	44.1	44.0	36.8	36.8	29.5	29.3
42.5	44.7	44.0	41.2	41.3	35.4	35.2	24.5	24.5
50.0	44.0	44.0	40.5	40.6	33.6	33.8	22.2	22.0
68.3	43.7	43.7	39.0	39.1	33.1	33.1	17.8	17.7
73.5	43.7	43.0	39.7	39.7	32.5	32.5	16.7	16.6
93.9	43.8	43.9	37.0	37.1	31.1	30.8	13.4	13.3

Table 18

Toxicity of carbonyl sulphide to a mixed culture of *S. oryzae* with various concentrations of carbonyl sulphide for various exposure periods

Days after dosing	Number of insects emerging from culture for exposure (in hours) x concentration (in mg L^{-1})			
	6 x 200	6 x 120	24 x 80	24 x 60
7	0	3	0	0
14	3	5	0	0
21	0	2	0	0
28	0	3	0	0
35	2	6	0	0

Table 18 (continued)

Toxicity of carbonyl sulphide to a mixed culture of *S. oryzae* with various concentrations of carbonyl sulphide for various exposure periods

Days after dosing	Number of insects emerging from culture for exposure (in hours) x concentration (in mg L^{-1})			
	48 x 60	48 x 40	48 x 30	Control
7	0	0	0	8
14	0	0	2	93
21	0	0	0	87
28	0	0	0	36
35	0	0	0	36

Table 18 (continued)

Toxicity of carbonyl sulphide to a mixed culture of *S. oryzae* with various concentrations of carbonyl sulphide for various exposure periods

Days after dosing	Number of insects emerging from culture for exposure (in hours) x concentration (in mg L^{-1})			
	72 x 40	72 x 30	72 x 20	168 x 30
7	0	0	0	0
14	0	0	3	0
21	0	0	1	0
28	0	0	0	0
35	0	0	3	0

Table 18 (continued)

Toxicity of carbonyl sulphide to a mixed culture of *S. oryzae* with various concentrations of carbonyl sulphide for various exposure periods

Days after dosing	Number of insects emerging from culture for exposure (in hours) x concentration (in mg L^{-1})		
	168 x 20	168 x 10	Control
7	0	1	8
14	0	0	93
21	0	1	87
28	0	36	36
35	0	27	36

Table 19

Control of nematodes in soil with carbonyl sulphide

Soil Sample	Quantity (grams)	Calculated concentration of COS(mg L^{-1})	% kill of nematodes
A1	30	28	42.6
A2	30	280	89.5
A control			0
B1	39	28	54.4
B2	38	560	37.8
B3	1000	28	94.0
B control			0
C1	40	140	7
C2	40	28	28
C control			0

CLAIMS

1. A fumigant comprising carbonyl sulphide.

2. A fumigant as defined in claim 1, including a diluent gas.

3. A fumigant as defined in claim 2, in which the diluent gas is selected from the group consisting of air, carbon dioxide and a flammability inhibitor.

4. A method of fumigating a stored product, timber, soil or a space, said stored product including grains and other durable foodstuff, and fruit and other perishable foodstuff, said method comprising applying a dose of carbonyl sulphide to the stored product, timber, soil or space.

5. A method as defined in claim 4, in which a stored product is fumigated, the stored product comprises grain or other durable foodstuff, and the dose of carbonyl sulphide is applied for a period in the range of from 1 hour to 35 days, at a concentration that is sufficient to control selected food pests.

6. A method as defined in claim 5, in which the control comprises achieving a mortality of 95 per cent at 25°C, and in which
   (a) when the selected food pest is adult <u>Rhyzopertha dominica</u>, the dose comprises at least 68 mg h. L^{-1};

(b) when the selected food pest is adult Tribolium castaneum, the dose comprises at least 108 mg h. L^{-1};

(c) when the selected food pest is adult Sitophilus oryzae, the dose comprises at least 112 mg h. L^{-1};

(d) when the selected grain pest is adult Tribolium confusum, the dose comprises at least 146 mg h. L^{-1};

(e) when the selected food pest is adult Oryzaephilus surinamensis or Lepidoglyphus destructor, the dose comprises at least 240 mg h. L^{-1};

(f) when the selected pest comprises pupae, larvae and eggs of R.dominica, T. castaneum, S. oryzae, T. confusum and O. surinamensis, the dose comprises at least 600 mg h. L^{-1}; and

(g) when the selected food pest is psocids, the dose comprises at least 22.5 mg h L^{-1}.

7. A method as defined in claim 4, in which a stored product is fumigated, the stored product is fruit or another perishable foodstuff, and the carbonyl sulphide is applied for at least 6 hours at a concentration that is sufficient to control all immature stages of fruit fly.

8. A method as defined in claim 4, in which timber, a wood product or a building containing wood is fumigated, and in which the carbonyl sulphide is applied at a concentration sufficient to control termites or other timber pests.

9. A method as defined in claim 4, in which soil is fumigated and in which the carbonyl sulphide is applied at a concentration sufficient to control nematodes.

Br. n°

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION

planche 1/1

10069

1/1

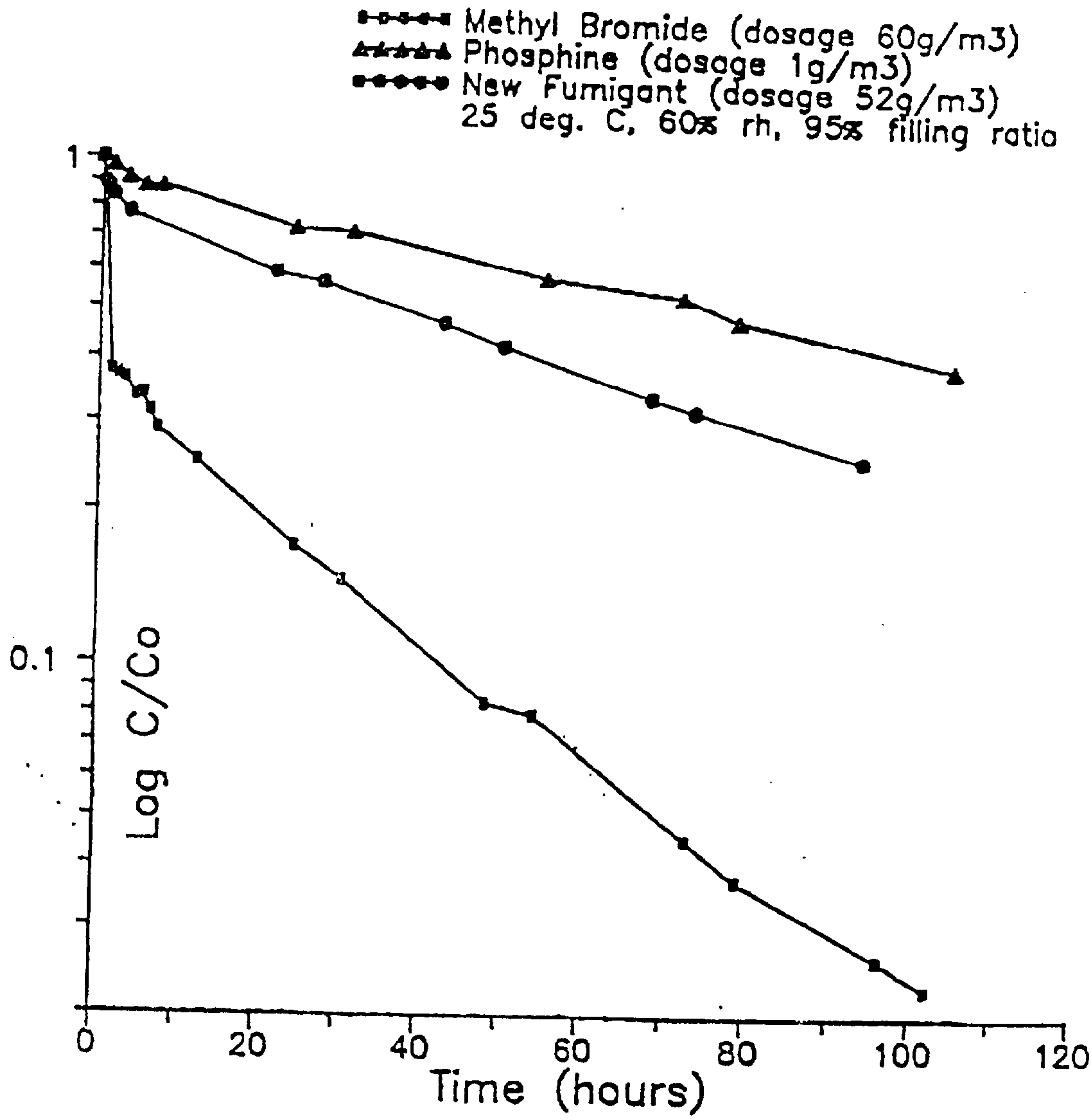

FIG. 1