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EVALUATION OF EFFICACY OF CHLOROPICRIN AS A WARNING AGENT TO PREVENT UNAUTHORIZED ENTRY DURING STRUCTURAL FUMIGATION

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CONTRACTING LABORATORY

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8770 Highway 25
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LABORATORY PROJECT NO.

BR393.1,2,3,4,5:93

STUDY DATES

May 11 - 24, 1993

PROJECT INFORMATION

STUDY TITLE:	EVALUATION OF EFFICACY OF CHLOROPICRIN AS A WARNING AGENT TO PREVENT UNAUTHORIZED ENTRY DURING STRUCTURAL FUMIGATION
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PROTOCOL:	EVALUATION OF EFFICACY OF CHLOROPICRIN AS A WARNING AGENT TO PREVENT UNAUTHORIZED ENTRY DURING STRUCTURAL FUMIGATION
BOLSA PROJECT NO:	BR393.1,2,3,4,5:93
TEST MATERIALS:	Methyl Bromide, Chloropicrin, and Vikane
SOURCE OF TEST MATERIALS:	Soil Chemicals Corporation

CHEMICAL DESCRIPTION:

Chemical Name:	Methyl Bromide 99.5%	Chloropicrin	Vikane
Chemical Formula:	CH_3Br	CCl_3NO_2	SO_2F_2
Physical Form:	Liquid under pressure	Liquid	Gas
Nominal Purity:	99.5%	99+%	99%

TEST DATES:	May 11 - 24, 1993
STUDY START DATE:	May 11, 1993
STUDY COMPLETION DATE:	December 15, 1993
DATA ARCHIVED AT:	Bolsa Research Associates, Inc. 8770 Highway 25 Hollister, CA 95023

STUDY PERSONNEL

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I. OBJECTIVE

The purpose of this study was to evaluate under controlled conditions the efficacy of chloropicrin as a warning agent to prevent unauthorized entry during structural fumigation. It involved monitoring gas concentrations over time in residences undergoing fumigation for the control of drywood termites.

II. SUMMARY

A total of 290 chloropicrin samples were taken from 10 houses after being fumigated with either 99.5% Methyl Bromide + 0.5% Chloropicrin, or Vikane + Chloropicrin, under normal application rates. Over a period of 24 hours, the samples were collected at 6 intervals after the introduction of the fumigant. Although 3 samples exceeded 16 ppm in concentration, all samples were found to be less than the theoretical amount, based on application rates. The chloropicrin concentration levels were found to be higher in those houses fumigated with Vikane than those fumigated with 99.5% methyl bromide. In some cases the average chloropicrin level in a house rose during the first few sampling intervals, but overall the levels declined over time. 25 % of the samples were at or below 1.0 ppm in concentration, but 61 % were above 2 ppm, a level considered sufficient to deter illegal entry.

III. INTRODUCTION

A study conducted by employees of SCC Products in 1984 demonstrated that chloropicrin concentrations of 1.6 to 2.0 ppm (0.09 oz. to 0.12 oz/ft^3) were high enough to evacuate people from a house [Ref. 1]. The lowest rate allowable by law is 1 oz/15,000 ft^3, equivalent to 17.3 ppm. The pre-mixed fumigant Methyl Bromide 99.5% at an application rate of 1.5 lb/1000 ft^3 should result in a chloropicrin concentration equivalent to 1 oz/15,000 ft^3 at equilibrium. The highest rate of chloropicrin permissible by law is 1 oz/10,000 ft^3 and equivalent to 26 ppm. This rate can be more difficult to aerate following fumigation so fumigators generally opt for the lower application rate.

Because of a number of deaths from premature or unauthorized entries into residences under fumigation, there has been concern as to whether chloropicrin is an effective warning agent at the current rate of 1 oz/15,000 ft^3 of fumigated space.

The Worker Health and Safety Branch of CDPR (California Department of Pesticide Regulations) made a survey of fumigated homes throughout the state in 1990 [Ref. 2]. The goal was to determine levels of chloropicrin beneath the tarpaulins of residences under fumigation.. From this study it was concluded that at certain times during the fumigation, the concentration of

chloropicrin may not have always been adequate to act as a proper warning agent due to the fact that:

1. There was a wide variation in the levels of chloropicrin measured under the tarpaulins at fumigation sites; levels ranged from none detected to 9.9 ppm, and over one third of the residences has less than 1 ppm of chloropicrin in the house-tarp interspace (HTI).
2. The chloropicrin concentration in the HTI at all sites tested was less than the theoretical level, based on applications rates.
3. The chloropicrin concentrations were lowest in residences where the chloropicrin was added separately, as must be done when Vikane (Sulfuryl fluoride) is the fumigant used.
4. There was no correlation drawn between chloropicrin concentration and time since application.

The present study, as outlined in the Protocol (Appendix 1), was designed to attempt to answer the questions raised in previous experimentation and to enable the finalization of a dosage of chloropicrin which would indeed serve to prevent unauthorized entry into residences under fumigation until they are fully aerated and safe for human entry.

IV. TEST MATERIALS AND DOSAGE

Two fumigants were used for the study: Methyl Bromide 99.5% (containing 0.5% chloropicrin) at a dosage of 1.5 lb/1000 ft^3, and Vikane (Sulfuryl Fluoride) plus a separate application of chloropicrin at the rate of 1 oz/15,000 ft^3.

V. TEST SITES

Ten residences were selected for the study: 5 to be treated with Methyl Bromide 99.5%, and 5 with Vikane plus chloropicrin. The homes were selected so that as far as possible, they were similar in size, number of stories, type of construction (slab versus crawl space, siding versus stucco, etc.), roof type, furnished versus unfurnished, and integrity of tarp seals. Actual fumigation techniques were standard industry practice for the fumigant used. The addresses of these ten residences are listed in Appendix 2.

VI. APPLICATION PROCEDURES

The structures were tarped and sealed using fumigation clips on the tarp seams and sand or water snakes to seal the tarps to the ground. When Vikane was the fumigant used, a small shallow pan containing some cotton was placed on the floor behind a 5000 CFM fan located within the structure, and the chloropicrin dosage was poured on the cotton in the pan. Where

Methyl Bromide 99.5% was used, the gas was generally discharged into the HTI with a nearby window being open into a room where a 5000 CFM fan had been placed to help circulate the fumigant throughout the house.

In each structure, the access door to the attic was open during the exposure period, and a 5000 CFM fan was set on the floor directing air up towards the opening, or was connected directly to the attic opening with a plastic duct running from the cage of the fan to the periphery of the attic access.

All of the residences treated with Vikane were occupied and contained furnishing. Of those treated with Methyl Bromide 99.5%, only one was occupied and contained furnishing.

During the study, wind speed and direction and outdoor temperature were recorded at each sampling time. Air temperature inside the fumigated residences was monitored only prior to closing the tarpaulins and again following removal of the tarpaulins after aeration.

Reporting forms were designed from air sampling data sheets as well as sample transmittal sheets to document chain of custody for each sample collected. A copy of each sheet is attached in Appendix 3. Diagrams of each structure in the study were drawn prior to the fumigation showing the location of possible points of entry into the structure, and the location and designation of each of the gas sampling lines. These are found in Appendix 4.

At each test site, gas sampling lines consisting of 0.25" OD Tygon tubing were put in place just before the fumigation crews started to tarp the structure. Five gas sampling lines were used at each test site and all lines were extended out so each would be accessible outside the tarpaulin enclosure. Lines were located and marked so samples could be drawn from each of the following points:

Line A - Inside the residence, close to the point at which the fumigant was to be discharged.
Line B - Inside the residence, at a point most distant to the point at which the fumigant was to be discharged.
Line C - Outside the residence in the house-tarp interspace (HTI) on the upwind side of the structure and approximately 4 feet above ground level.
Line D - Outside the residence in the HTI on the downwind side of the structure and approximately 4 feet above ground level.
Line E - Outside the residence in the HTI on a crosswind side of the structure and approximately 4 feet above ground level.

Gas samples were taken using SKC personal sampling pumps (# 222-3,4) set at a rate to draw about 1 liter of air per minute, and each was run for about 15 to 20 minutes per sample. The sampling pumps were attached to XAD-4 sampling tubes (SKC # 226-93) for chloropicrin samples and to sorbent charcoal tubes (SKC # 226-38-02) for methyl bromide samples. No

readings of Vikane levels were attempted. At each test site where Methyl Bromide 99.5% was used, the chloropicrin samples were taken first at each sampling period, followed by the samples for methyl bromide.

The air volume sampled is determined from the air sampling conditions and pump information. These are included in the tabulated spreadsheets (Tables 1 and 2).

Gas samples were collected from each line in each residence at 1 hour, 2 hours, 4 hours, 8 hours, 12 hours, and 24 hours after the introduction of the fumigant. Each sampling line was purged using a 1-liter syringe prior to its being connected to the sampling pump for each sample collected. Immediately after each gas sample was collected, the gas sampling tube was tagged, sealed at both ends, and placed in an ice chest where it was frozen. Sample tubes remained frozen while they were bunched into plastic ziploc bags and shipped by air on dry or blue ice to the Bolsa laboratory in Hollister for analysis.

VII. SAMPLE LABELING

Each sample was assigned an X-Y-[A,B,C,D, or E]-Z code. X refers to the day of sampling; there were 8 days in all. Y refers to the first (1) or second (2) house sampled on the Xth day. A,B,C,D, and E refer to the lines that identified the sampling sites, as explained in Section 6, p. 8. Z refers to the sampling interval, as explained in Section 6, p. 9. Methyl bromide samples were indicated by the prefix "M".

VIII. ANALYTICAL METHOD AND METHOD VALIDATION

Bolsa Analytical Method BR-AP-002 was used for the analysis of methyl bromide sampled in sorbent charcoal tubes. A Hewlett-Packard 5890 Series II gas chromatograph equipped with an electron capture detector was used in the analyses. Details are given in Appendix 5. The method has been amply validated for field monitoring on two separate experiments (Appendix 6), from which an average recovery of 79.2% was derived. All methyl bromide values in Table 2 have been adjusted using the 69.5% "lab desorption efficiency" determined from an earlier study on methyl bromide adsorbed on charcoal sorbent tubes (Appendix 7).

For chloropicrin, the sampling method using XAD-4 tubes was validated in Hollister in early May 1993 using the procedures outlined in Appendix 6 for methyl bromide. A recovery of 78.5% was obtained; as detailed in Appendix 8. The 78.5% figure was used to adjust the chloropicrin data in Table 1.

IX. SAMPLE EXTRACTION AND STORAGE OF TEST SAMPLES

Samples were shipped on dry ice or blue ice to Bolsa laboratory. After log in, the samples were either extracted immediately with 4 mL of ethyl acetate or temporarily stored in a freezer.. The extracted samples were then analyzed by GC/ECD with a fresh set of standards. After analysis, the samples were returned to the freezer for storage. In many instances, the concentrations of the samples exceeded the saturation limit of the ECD. In those cases, the samples were diluted and reanalyzed. The dilution factor is included in the tabulated spreadsheets.

X. RESULTS

Representative chromatograms are shown in Appendix 9. The chloropicrin concentrations measured from the five sampling locations taken from each of the 10 houses are plotted in Figures 1 to 10. These plots do not reveal any correlations between concentration levels and sampling locations or interval. However, the average concentrations calculated from each set of five sampling locations per interval (shown in Figures 11 to 20) generally exhibit a monotonic decline over time--with few exceptions. In 6 out of 10 cases, the concentrations rose before declining. The chloropicrin concentration levels reached at the final sampling interval tended to be higher in the 5 houses where vikane was used concurrently. In only one instance--probably due to sampling error at the house located on Gardenia in Long Beach--the chloropicrin level dropped almost to zero during the second sampling interval.

In the 5 houses where methyl bromide was also sampled, the decline curves for both chloropicrin and methyl bromide were compared in Figures 21 to 25. As expected the decline curves correlated fairly well, exhibiting a gradual decrease over time. Because vikane was not analyzed for in this study, it is not known whether the decline curves for vikane would have exhibited a similar correlation.

XI. DISCUSSION

From this study a total of 290 chloropicrin samples were taken. The distribution of concentration levels is indicated in Figure 26. It might be instructive to compare these results with those of Gibbons and McLean, which are reproduced in Figure 27.

There were a number of striknq similarities between the results from the two studies, among them:

1) The concentrations at all sampling locations in all the residences monitored were less than the theoretical amount, based on application rates.
2) A sizeable proportion of the samples (25 % in this study and 50 % in Gibbons and McLean's) were < 1.0 ppm, but about 61 % in this study (versus 41.7% in Gibbons

and McLean's) were above 2.0 ppm, a level considered sufficient to deter illegal entry.

However, there were difference between the results from the two studies, among them:

1) In our study, the chloropicrin concentration levels were found to be higher in those houses fumigated with Vikane than those fumigated with 99.5% Methyl Bromide. The reverse was observed in Gibbons and McLean's study.
2) In our study there were 26 samples, or 0.09 % of all samples, with chloropicrin levels exceeding 10 ppm. Gibbons and McLean found none above 9.9 ppm.
3) In our study a general decline of chloropicrin concentration was observed over time. Gibbons and McLean did not find such a correlation from their study.

XII. CONCLUDING REMARKS

From the two studies mentioned it has been observed that the chloropicrin concentrations were nowhere near the theoretical level, based on application rates. The results were gathered from a total of 367 samples from 37 houses (from the two studies combined). The results appear to be conclusive, at least for applications of chloropicrin with methyl bromide and vikane as described in these two studies. The conclusions are probably not likely to be any different if more samples had been taken from the same or additional sampling sites.

XIII. DATA ARCHIVES

The GC raw data, sampling forms, and other original documents pertaining to this study are temporarily archived at Bolsa Research Associates, Inc., 8770 Highway 25, Hollister, CA 95023 (408) 637-976, pending final decision from the Sponsor.

REFERENCES

1. Soil Chemicals Corporation, in-house study, 1984.

2. Dennis Gibbons and Steve McLean, "A Survey of the Warning Agent Concentration (Chloropirin) Present Immediately Behind the Tarpaulin of Residences Undergoing Fumigation", April 27, 1990, a Report to the Structural Pest Control Board.