

## **Air Concentrations of Chlorpyrifos (Dursban®) from a 2% Slow-release Paint-on Formulation vs. a Standard 0.5% Emulsion Spray**

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The slow-release or controlled-release formulations of insecticide for structural pest control use are limited to an impregnated adhesive tape containing 10% propoxur (Insecttape<sup>TM</sup> manufactured by Hercon<sup>®</sup>) and two paint-on formulations containing 1% and 2% chlorpyrifos (Killmaster<sup>TM</sup> and Killmaster II<sup>TM</sup> manufactured by Positive Formulators, Inc.).

These unique products were registered by the EPA for up to six months cockroach control for the 1% chlorpyrifos paint-on in December, 1974 and for the 10% propoxur tape in February 1976. The 2% chlorpyrifos paint-on was registered in March 1977 for up to 12 months of cockroach control.

It was the purpose of these experiments to compare the air concentrations resulting from use of the 2% slow-release vs. the 0.5% emulsion spray of chlorpyrifos when applied in a closed room according to label directions.

### **MATERIALS AND METHODS**

The room selected for testing was an office of the University of Arizona, whose dimensions were 19' X 10'6" X 11'6" (2294 ft<sup>3</sup>), equipped with 2 windows and one door. It contained the usual desks, book cases, chairs, and shelving. The floor was vinyl asbestos floor covering, and all walls molded with 4" vinyl molding.

After completely blocking off both air ducts to stop ventilation, a 1-hr control air sample was collected by scrubbing the air at 25 SCF/hr through 2 tandem, ethylene glycol air scrubbers. The first scrubber was equipped with a fritted disc, the second with a constricted glass tube, in series with a glass-ball rotometer between the second scrubber and the pump. Each scrubber contained 190 ml of reagent grade ethylene glycol. The temperature remained at 24.5°C and the relative humidity was 56%.

A 1-hr treatment air sample was collected, beginning with the application of the 2% chlorpyrifos paint-on formulation. The material was applied with a 4" paintbrush, following the recommended

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procedures, and required 9 minutes and 100 ml of the formulation. All treated surfaces were dry to the touch in 15 minutes. The scrubbers were operated at 25 SCF/hour for an additional 51 minutes for a total of 1 hour. The air intake of the sampler was located in the center of the room 40" above the floor.

A 1-hr post treatment air sample was then collected while the ventilation system remained sealed. The scrubbers were recharged with fresh ethylene glycol and operated at 25 SCF/hour, 24°C and 57% RH.

A 14-hr post-treatment air sample was collected the following morning. The windows had been left open and only the exhaust vent of the ventilation system left uncovered for that 14-hr period, prior to sampling, to simulate natural ventilation. The windows and exhaust vent were closed and the air scrubbers were operated for 2 consecutive hours at 25 SCF/hr, 23°C, and 58% RH.

Eight days later the same room was treated with a standard 0.5% chlorpyrifos emulsion spray commonly used in homes by the pest control industry. Prior to treatment, a 2-hour control air sample was collected at 23.5°C and 53% RH.

After blocking the ventilation system, a 1-hr treatment air sample was collected, beginning with the application of 0.5% chlorpyrifos emulsion spray. A B and G compressed air sprayer was used, and operated at 20 PSI. The spray application was made to the same locations treated previously with the paint-on formulation and required 6 minutes and 340 ml of spray. Temperature and humidity during the sampling period were 23.5°C and 53% RH.

One-hour and 15-hr post-treatment samples were collected for 1- and 2-hrs, respectively under the conditions described for the paint-on air sampling series. Temperature and humidity were 23°C and 54% for both tests.

Analytical Methods - Air scrubbing samples, trapped in ethylene glycol, were refrigerated from time of collection until analysis. The volumes of ethylene glycol from each scrubber were measured and transferred to one-liter separatory funnels. One hundred mls of redistilled benzene were added to each funnel and the contents vigorously shaken for several minutes. The funnels were allowed to stand until the two layers were perfectly clear (about 1/2 hr). At this time an extremely sharp boundary existed between the two layers.

Ten ml aliquots of the benzene layers were concentrated to one ml and analyzed by gas chromatography using a flame photometric detector in the phosphorus mode. Recovery standards were prepared by pipetting 2 ml of a benzene solution, containing 8.0 micrograms chlorpyrifos per ml, into a volumetric flask, evaporating off the benzene using only an air stream, and then adding 100 ml of ethylene glycol. The volumetric flasks were

inverted numerous times and allowed to stand for 24 hrs. Thirty ml of this ethylene glycol solution plus 70 additional ml of ethylene glycol were partitioned with 100 ml of redistilled benzene.

The gas chromatograph was a Micro Tek MT-220 equipped with a flame photometric detector, on phosphorus mode, a 4' Pyrex column, 4 mm I.D., packed with 5% SE 30 on 100/120 mesh Chromosorb W (HP) and nitrogen carrier at 40 PSI and 70 ml/min. Air flow was 40 ml/min; oxygen, 20 ml/min; and hydrogen, 200 ml/min. The column temperature was held at 195°C. Quantitation was by peak height, utilizing 2 to 8 µl of sample or standard. The values presented in the tables represent an average of at least two injections per sample.

Table 1. Chlorpyrifos volatilization resulting from a paint-on application of 2% slow-release formulation of chlorpyrifos (KILLMASTER II) 9/28/76.

Sample	Period of Sampling	Total µg in Scrubber	µg/ft <sup>3</sup>	µg/M <sup>3</sup>	PPB in Air
Control					
Scrubber 1	1 hr	<<0.50	<<0.02		
Scrubber 2		<<0.50			
Treatment					
Scrubber 1	1 hr	5.34	0.21	7.41	0.51
Scrubber 2		<0.50			
1-hr Post Treatment					
Scrubber 1	1 hr	6.10	0.24	8.47	0.59
Scrubber 2		<0.50			
14-hr Post Treatment					
Scrubber 1	2 hr	13.4 <0.50	0.27	9.53	0.66
			<u>Theoretical</u>	<u>% Recovery</u>	
Recovery Standard 1		262	240		109
Recovery Standard 2		264	240		109

No detectable chlorpyrifos found in any of the second scrubbers.

Table 2. Chlorpyrifos volatilization resulting from a standard spray application of 0.5% water emulsion of chlorpyrifos (10/5/76).

Sample	Period of Sampling	Total $\mu\text{g}$ in Scrubber	$\mu\text{g}/\text{ft}^3$	$\mu\text{g}/\text{M}^3$	PPB in Air
Control					
Scrubber 1	2 hr	2.58	0.05	1.77	0.12
Scrubber 2		<<1.56			
Treatment					
Scrubber 1	1 hr	12.1	0.43*	15.2*	1.06*
Scrubber 2		<<1.56			
1-hr Post Treatment					
Scrubber 1	1 hr	14.0	0.51*	18.0*	1.26*
Scrubber 2		<<1.56			
15-hr Post Treatment					
Scrubber 1	2 hr	25.8	0.47*	16.6*	1.16*
Scrubber 2		<<1.56			

No detectable chlorpyrifos found in any of the second scrubbers.

\*Corrected for the pre-treat or Control values.

## RESULTS

Results of air sampling from these two tests are shown in Tables 1 and 2. The 100 ml of 2% paint-on formulation contained 1.74 g, while the 340 ml of 0.5% emulsion contained 1.70 g of chlorpyrifos, yet the spray resulted in an approximate two-fold increase of air-borne chlorpyrifos over the paint-on formulation.

The parts per billion (PPB) values shown in the tables were derived using the following equation:

$$\text{PPB} = \frac{\text{observed concentration } (\mu\text{g/liter}) \times 24,450}{\text{molecular weight of compound}}$$

where 24,450 ml, is the gram molecular volume of a gas at a temperature of 25°C and a pressure of 760 mm of mercury.

Threshold limit values (TLV) of the American Conference of Governmental Hygienists are standards for respiratory exposure in work situations. These standards for permissible concentrations of industrial chemicals in air are intended for the protection of workers and assume an 8-hour working day and 40-hour work week.

The American Conference of Governmental Hygienists' (1973) threshold limit value (TLV) for Dursban<sup>®</sup> (chlorpyrifos) is 0.2 mg/M<sup>3</sup>. This compares with the highest measured air level of chlorpyrifos in an unventilated situation from the 2% paint-on formulation of 0.0095 mg/M<sup>3</sup> and from the 0.5% emulsion spray of 0.018 mg/M<sup>3</sup>. This represents a 21-fold reduction below the TLV for the paint-on formulation and an 11-fold reduction for the 0.5% emulsion spray.

## REFERENCES

American Conference of Governmental Industrial Hygienists (1973). TLVs: Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1972. ACGIH, Cincinnati, Ohio.