The Role of Chlorinated Polyphenyls in Improving Lindane Residues[1]

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The use of lindane and other volatile insecticides to leave toxic residues on surfaces presents several problems. With lindane deposits the following problems may be encountered:

(1) The appearance of a crystalline deposit may be objectionable.
(2) It evaporates so rapidly that repeated treatments may be necessary.
(3) The crystals may be removed by mechanical contact.
(4) Weathering may remove the toxicant in outdoor applications.
(5) On very porous surfaces there may be a rapid loss of toxicity through sorption of the insecticide.
(6) The cost of lindane is high.

A film-forming material in which the insecticide is soluble will prevent crystallization, reduce the volatilization rate, and if the proper material is chosen, provide a tight bond to the surface being treated. The problem of cutting down sorption on porous surfaces is essentially one of finding appropriate methods of application.

Prolonged insecticidal effectiveness has been obtained by incorporating the toxicant in a nonvolatile oil. However, on porous surfaces this oil solution penetrates rapidly and toxicity is soon lost, and on nonporous surfaces a wet oily film is left which may be very undesirable.

Lindquist *et al.* (1945), Campbell & West (1944a, b), and others have suggested the incorporation of DDT in paints. Block (1948) has made a comprehensive survey of the field of insecticide coatings. In general, oil films, oil-modified resins, or rosin derivatives produced coatings with DDT having poor insecticidal quality. Among paint vehicles from natural products an asphalt varnish derived from gilsonite appeared to be satisfactory. Water-dispersible vehicles, such as casein and glue, were found not to be so toxic as expected. Various synthetic resins including urea-formaldehyde appeared promising.

In these insecticidal paints and coatings the insecticide is of low solubility in the film-forming material. It is assumed that the mechanism of prolonging their toxicity consists essentially in the formation of a supersaturated solution, which crystallizes at the film surface only. This crystallization lowers the concentration of insecticide in solution at the film surface and results in a diffusion of insecticide from the body of the coating to this surface. If we are dealing with a metastable equilibrium such as exists in supersaturated solutions, a scratch or a blow may cause crystallization within the coating, and the slow diffusion of insecticide to the surface will stop and the toxicity of the film will quickly drop. If the surface becomes case-hardened with time, as do many paints and coatings, this diffusion process can no longer take place and again the toxicity of the surface quickly drops.

Suitable Properties of Chlorinated Polyphenyls.—It has been found after a number of trials that a mixture of chlorinated terphenyls available commercially appears to have the physical properties that make it suitable as a film-forming carrier for lindane. This material is produced by the pyrolysis of benzene to yield a mixture containing 80 per cent of biphenyl and 20 per cent of isomeric terphenyls, separation of the terphenyl fraction, and chlorination until a 60 per cent chlorine content is attained. This material is available as Aroclor 5460 and is inexpensive in bulk quantities. It has been safely used for a variety of industrial purposes. However, as a precautionary measure pharmacological studies should be made to determine possible toxicity.

The properties of this product that make it particularly suitable are as follows:

(1) It is a good solvent for lindane, and thereby contributes to the lowering of its vapor pressure and prevents its crystallization.

(2) It is inert, resistant to oxidation, nonflammable, and does not afford a medium for fungus growth. Once the film has been deposited and the solvent evap-

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orated, no further change in the physical properties of the film is to be expected.

(3) When properly applied, a 1:1 or a 1:2 mixture of lindane and chlorinated terphenyls provides a surface that is slightly tacky. Insects passing over such a surface appear to pick up the insecticide more readily than when they travel across a hard surface. Thus, when lindane is incorporated in a vinyl-type polymer, a clear transparent film results but because of the surface hardness the insect toxicity is quite low.

DECREASED VOLATILITY OF LINDANE IN MIXTURES WITH CHLORINATED TERPHENYLS.—The rate of volatilization of lindane at a given temperature is a function of its vapor pressure, the surface area available for evaporation per unit mass, and the concentration of lindane in the air surrounding the deposit. The last factor depends largely on the air exchange in the area treated.

The reduction in vapor pressure in lindane-chlorinated terphenyl mixtures accounts in part for the extended life of the material. Of importance too is the decrease in surface area per unit mass of lindane. The relatively large surface associated with lindane crystals is no longer available for vaporization. Instead evaporation takes place from a relatively smooth film having considerably less exposed surface.

In contrast to crystallization from a supersaturated film, it is the evaporation of lindane that creates the lack of balance in concentration that keeps lindane diffusing to the surface from the body of the coating. Thus, higher concentrations of insecticide can be utilized completely and longer lasting residues are obtainable.

COMPARATIVE TOXICITY OF LINDANE AND LINDANE-CHLORINATED TERPHENYL MIXTURES.—In previous tests we compared the effectiveness against the American cockroach, *Periplaneta americana* (L.), of deposits of 100 mg. of lindane per square foot with and without 200 mg. of chlorinated terphenyls on aluminum surfaces (Sullivan & Hornstein 1953). Lindane alone gave a 36 per cent kill after 30 days, a 3 per cent kill after 60 days and no kill at the end of 90 days. The lindane-chlorinated terphenyl mixture still gave 80 per cent kill at the end of 90 days. Tsao *et al.* (1953) obtained similar results against house flies, *Musca domestica* L. On masonite, a porous surface, similar deposits gave only about a 20 per cent kill of American cockroaches after 10 days. Other porous surfaces, such as carpeting and plywood also gave poor results when lindane or lindane-chlorinated terphenyl mixtures were applied.

Our knowledge of the ability of lindane-chlorinated terphenyl mixtures to withstand outdoor weathering is limited. However, the following experiment is of interest. A low-pressure aerosol containing 5 parts each of lindane and chlorinated terphenyls, 40 parts of methylene chloride and 50 parts of *Freon-12* (by weight) was sprayed on the leaves of a small willow tree and subjected to the summer weather conditions prevailing at Beltsville, Maryland. At the end of 30 days a leaf sample was found on analysis to contain 250 micrograms of lindane per square inch. There were no obvious ill effects on the leaves. At the end of 60 days, another leaf sample contained about 200 micrograms of lindane per square inch. At the end of 70 days flies caged around a portion of a treated branch showed 90 per cent mortality and all those on untreated check branches were alive.

Although the fumigating effect of lindane vapors is materially cut down by the lowered rate of vaporization, it is by no means eliminated. Two weeks after lindane chlorinated terphenyl mixtures were painted on the inside of a large glass vessel 50 per cent of caged flies not in contact with the treated surface were killed after a 10-minute exposure.

METHODS OF APPLICATION TO POROUS SURFACES.—We have tried in several ways to obtain better surface coatings on porous materials and have selected unpainted plywood as a typical porous surface for test purposes.

Wetting the surface down with water and then applying as a spray a solution of lindane and chlorinated terphenyls in a low-boiling solvent appears promising. The water prevents the oil from wetting and therefore penetrating the porous surface, and the solvent quickly evaporates to leave a surface deposit of lindane-chlorinated terphenyls.

Pressurized sprays containing low-boiling solvents give good surface deposits. By adjustment of the concentration of a very volatile solvent, such as methylene chloride, in the pressurized-

spray formulation, most of the solvent will evaporate before the lindane-chlorinated terphenyl mixture reaches the surface. The highly viscous particles of this mixture will then have little tendency to penetrate into the porous material.

The lindane-chlorinated terphenyl mixture may be precipitated out of solution just as it hits the surface. A nearly saturated solution of this mixture in acetone-water is prepared. The surface to be treated is wetted down with water. In this instance it is not the repellency of the oil and water, but the solubility of the acetone in water that gives the desired result. The water precipitates the lindane-chlorinated terphenyl mixture out of the acetone solution. After evaporation of the acetone and water, the lindane-chlorinated terphenyl mixture will be left as a spotty but adherent deposit; however, for many purposes, where appearance is not of prime importance, this may prove a useful method of application.

A homogenized suspension of a xylene solution of lindane and chlorinated terphenyls in water also gave promising results. To obtain a fairly stable homogenized suspension, a xylene solution having a specific gravity of 1 was prepared by adding 15 parts each of lindane and chlorinated terphenyls to 60 parts of xylene (all parts by weight). The closer the densities of the mutually insoluble phases the more stable will be the homogenized suspension. This solution was then homogenized with water so that the final suspension contained about 2 per cent each of lindane and chlorinated terphenyls and a water-to-xylene ratio of about 10 to 1. When such a homogenized suspension is sprayed on a surface, it has a tendency to break quickly. Again the initial repellency of oil and water appears to give a good surface coating before much of the insecticide penetrates. This phase of the work is being continued. The surface deposits made as described appear to be heavier than those obtained by direct application of solutions or emulsions.

LINDANE VAPOR PRESSURE IN MIXTURES WITH CHLORINATED TERPHENYLS.—The lindane vapor pressure in various mixtures of lindane and chlorinated terphenyls has been measured (table 1). The lindane was recrystallized from 95 per cent ethanol and had a melting point of 112.5°C. The chlorinated terphenyl was the same product used in the previous tests.

The mixtures were prepared by dissolving the desired amount of lindane and chlorinated terphenyls in acetone. Wads of glass wool were dipped in the solution, then removed and air-dried for 48 hours.

The apparatus consisted of a train having in series a drying bottle filled with anhydrous calcium sulfate, two gas-saturation bottles with fritted glass discs through which the air was pulled and packed with the coated glass wool, an alumina column for adsorbing lindane, a diaphragm-type pump, and a calibrated gas meter. The apparatus was adjusted so that 1 cubic foot of air per hour was pulled through the train. At the completion of the run the lindane adsorbed on the alumina was eluted with acetic acid and the lindane determined colorimetrically (Hornstein & Sullivan 1953).

Table 1.—Vapor pressure of lindane in mixtures with chlorinated terphenyls at 25° C.

LINDANE-CHLORINATED TERPHENYL RATIO		VOLUME OF SATURATED AIR SAMPLE (CUBIC FEET)	VAPOR PRESSURE (MICRONS)	
Weight	Mole		Measured	Theoretical
1:0	1:0	2.5	0.059	—
1:2	1:1.6	4.0	.029	0.023
1:5	1:4.0	5.0	.017	.012
1:10	1:7.9	6.0	.0073	.0067

The vapor pressures were calculated from the results as described by Thomson (1949). The theoretical vapor pressures were calculated on the assumptions that the chlorinated terphenyl had a molecular weight of 368 and that the vapor pressure of lindane was proportional to the mole fraction of lindane in the film.

SUMMARY.—Lindane residues can be made to last longer and look better if the lindane is applied in chlorinated terphenyl coatings. The vapor pressure of lindane in these films is lowered, but the fumigating action of lindane is not eliminated.

A general method of prolonging the residual effectiveness of volatile insecticides by preparing concentrated solutions in chlorinated polyphenyl film-forming materials has been described.

An attempt has also been made to apply insecticides on porous surfaces in a manner designed to minimize absorption.

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Methyl Bromide Fumigation of Soil for Destruction of White-Fringed Beetle Larvae

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The white-fringed beetle (*Graphognathus* spp.) is now known to occur in eight Southern States. The larvae are present in the soil throughout the year (Young & App 1939). Tests for control measures led not only to the use of methyl bromide to fumigate nursery stock and potting soil under confinement (Hawkins 1939, Livingston 1940) but also to the fumigation of soil areas *in situ*.

Use of methyl bromide and of carbon disulfide in quarantine work was first approved by this Bureau in January 1942 (BEPQ 503, 4th rev.) largely on the basis of tests made at Monroeville, Alabama (Livingstone & Swank 1942).[1] The approved treatment of soil plots and plunging beds provided for an application of methyl bromide at the rate of 4.7 ml. per square foot (7 ml. per 1.5 square feet injected 6 inches into the soil at points 15 inches apart each way. It further provided that the fumigated area should be covered with asphalt builders' paper for 6 days at soil temperatures at the 6-inch level between 45° and 62°F., or for 4 days at temperatures above 62°. It was considered impractical to reduce the permissible minimum soil temperature below 45°, for as the 40° boiling point of methyl bromide was approached this fumigant volatilized less readily and ice crystals from soil moisture were formed which obstructed orifices in the injector. Subsequent to this approval, testing was continued first at Gulfport, Mississippi, and later at Burgaw, North Carolina, in an attempt to improve the treatment schedules and reduce their cost.

METHODS OF APPLICATION.—Technical methyl bromide was applied with a specially built injector (Foster & Dunn 1942) which delivered a fixed amount of 7 ml. per injection. Because the output was not adjustable, it was necessary to vary spacings between injections in order to apply different dosages per square foot. An applicator suitable for injecting small measured amounts in rapid succession is difficult to make, because of the necessity for a closed system capable of retaining vapors under pressure. This system must also include a quick-acting two-way valve. Such a valve permits liquid methyl bromide to pass from storage into the injector chamber while its outlet is closed; then the inlet is closed and the outlet opened so that the charge can escape into the soil through the hollow injection needle. A pressure gauge shows when the chamber is filled or emptied. Pressures up to 90 p.s.i. have been used.

To obviate the mechanical inconveniences of a closed system, volatile liquid vehicles having boiling points above normal outdoor temperatures were tested. Aqueous emulsions were unsatisfactory, but certain organic solvents were found suitable. A proprietary product containing 10 per cent of methyl bromide and 90 per cent of ethylene dichloride was tested

[1] Most of this work was done by G. R. Swank; later he and E. E. Rogers continued this work and made preliminary tests on the field use of methyl bromide solutions.