

TCN

**TEXTILE
CONSERVATION
NEWSLETTER**

WARNING!

Dichlorvos Resin Strip Fumigation

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Introduction

Dichlorvos (DDVP) impregnated polyvinylchloride strips such as Vapona or S.W.A.T. are used worldwide for sustained space fumigation in museums (Hammick, 1989). The suitability dichlorvos is queried because it can cause artifact damage and health problems.

Health Hazards

Exposure to dichlorvos can result in acute toxicity or chronic illness. General symptoms of toxicity occur when plasma cholinesterase in the blood is depressed to 75% of the pre-exposure value. Repeated sub-clinical doses may result in overt symptoms at exposures well below the levels expected to produce an effect in an unexposed individual. Constant biotic exposure by inhalation, ingestion, and dermal absorption poisons insect and mammalian nervous systems by inhibiting acetylcholinesterase enzymes (AChE) at the synaptic gap of nerves with the subsequent accumulation of toxic levels of the neurotransmitter acetylcholine.

Loss of AChE activity leads to a range of physiological effects that are a result of excessive nervous stimulation (WHO, 1986; Matsumura, 1985). These include nausea, headache, tension, blurred vision, tightness in the chest, mental confusion, and muscle twitching. Insidious long term effects such as leukocytosis, neutrophilia, decreases in lymphocytes and monocytes, paralysis, neuropathy, and liver damage are recognized in current reports of accidental or occupational poisonings. Experimental data from microbial assays and animal studies imply that dichlorvos is mutagenic, carcinogenic and teratogenic (WHO, 1986; ACGIH, 1986).

Dermal exposure to dichlorvos is an immense problem because of its lipophilicity, volatility, extremely high toxicity, and rapid speed of action (Eto, 1974). Most occupational toxicity is ascribed to dermal exposure which includes contact with contaminated surfaces.

Damage to Materials

Materials in contact with the resin strips or highly concentrated vapours are damaged. Dichlorvos is corrosive to iron, steel, brass, silver, tin, lead, baked enamel, and silver. It causes pigments and dyes to fade, resins and glues to become tacky, dissolves polystyrene, yellows silk, and degrades leather (Armes, 1984; Williams & Walsh, 1989; Stanfield, 1985; Spivak *et al.*, 1981; Nakamoto, 1984; Reagan *et al.*, 1984; Young, 1987). Dichlorvos is readily absorbed by both water soluble and insoluble proteins in grain (Rowlands, 1975). Selective absorption in morphological areas such as the aleurone in grains where high concentrations of oils and lipoproteins are located is reported to occur. The affinity and translocation of dichlorvos in organic substances such as fibers and grain are reported to be accompanied by

extensive binding and redistribution. McGaughey (1973) reports that repeated applications increased the amount of residue remaining on textiles such as burlap. The potential for damage to artifact material is immense.

Research on Wool

Introduction

Keratin fibers such as wool are among the most vulnerable materials to be infested and damaged by museum pests. Few studies have been conducted to determine the effect of dichlorvos resin strips on textiles materials (Spivak et al., 1981; Reagan et al., 1984).

Experimental

Exploratory research was conducted to determine the effects of dichlorvos resin strip (S.W.A.T.) fumigation on Merino and Corriedale wool fibers and Merino yarn at the University of Alberta (Hammick, 1989). Tests were conducted on unheated and heated controls, and fibers fumigated with concentrated vapours at 50° C in glass desiccators in a dark oven for 7, 21 and 35 days. In a 2.5 L desiccator, 11 grams of wool fiber and yarn were suspended over a 50 g strip of S.W.A.T. All fibers were washed at 25 + 3° C with Shurgain anionic detergent, rinsed in distilled water, air dried and conditioned at 65% RH and 21° C. Separate sets of fibers were given a 20 minute soak in methanol to extract residual lanolin following the Shurgain wash and rinse, and rinsed in distilled water to remove methanol and air dried.

Series of tests, adapted from basic and applied research literature (Merkel, 1984; Garner, 1966; ASTM, 1981; Zhao & Johnson, 1986), were conducted to find useful test methods for detecting fumigation damage. Methods were selected by exposing laboratory scoured fibers to possible by-products of dichlorvos resin strip degradation such as mono-, di-, trichloroacetic acid, hydrogen chloride, phthalic acid, phosphoric acid, and hydrogen peroxide. In addition, textiles and fibers from a collection fumigated in situ, and laboratory fumigated fibers and yarns were used to select, tests and develop suitable methods. Preliminary tests were conducted on S.W.A.T fumigated wool fibers and controls to refine possible testing methods. A summary of the tests used, and purpose of the tests is given in the results. Details for experimental methods and fumigation procedures are available elsewhere (Hammick, 1989).

Results

The results of tests conducted on fumigated wool are given in Table 1.

Table 1. Summary of Test Methods, Purpose of Test, and Observed Changes in Fibers exposed to S.W.A.T. Fumigation in a Dark Oven at 50° C for 7, 21, and 35 Days.

Test	Test Indicates	Results
Load-extension	inter/intra bonds	extension changes
Colour change	chemical change	yellowing
pH extract	ionic balance	increased acidity
Lead Acetate	cystine oxidation	oxidation of -SSH
Bromine water	epicuticle integrity	epicuticle damage
Krais-Viertel	acid damage, epicuticle integrity	acid damage epicuticle damage
Methylene Blue	mechanical damage acid damage, chlorination	change dye uptake, ionic charge and surface damage
Kiton Red	oxidation, mechanical damage	change dye uptake, oxidation/acid damage
Orange 14 Fluorescence	acid damage	localized acid damage
EDX	presence of contaminating elements	sorption chlorine and phosphorous species
SEM	topographical changes	fiber degradation, topographical changes

Discussion of the Results

Both heat and scouring methods affected the results. Unheated controls (scoured wool not exposed to fumigant vapours) showed no damage, heated controls showed slight or no observable changes. Heating wool to 50° C causes oxidative damage and slight changes in amino acids. Wool fumigated with dichlorvos resin strips showed observable changes. Wool soaked in methanol before fumigation at 50° showed highly observable changes.

The extreme resistance of normal keratin fibers to degradation by chemicals and enzymes is attributed to the complementary inertness of the various components. The laminar overlapping cuticular structure consists of several layers such as the outer resistant keratinous exocuticle and inner non-keratinous endocuticle (Praser *et al.*, 1972). The presence of grease, suint and a proteinaceous contaminant layer (PCL) on the cuticular surface provide additional protection to wool fibers.

In this study removal of methanol soluble components from the surface prior to fumigation accelerated the physical and chemical changes in the fibers fumigated with S.W.A.T. The inherent resistance to fumigants can be destroyed by simple conservation treatments with solvents which remove the oily protective film on wool fibers.

Normal wool fibers have the capacity to sorb 810 to 860 $\mu\text{mol. g}^{-1}$ of acid (measured by titration with 0.02M HCl) at the isoelectric point. Fibers fumigated for 7 days at 50° C increased in acidity. The aqueous extract decreased by 1 pH unit (6.8 to 5.8 pH) in Shurgain scoured fibers and 3 pH units (6.4 to 3.4) in methanol and Shurgain scoured fibers. Under the experimental conditions used the increase in acidity is attributed to chlorine absorption.

Changes in pH were reflected in dye, fluorescent microscopy and extensibility tests. The colour difference between wool fibers scoured in Shurgain, and scoured in Shurgain and soaked in methanol and then fumigated for 7 days at 50° C are given in Figure 1. It is interesting to note that the color difference given in Figure 1 represents a marked decrease in dyeability and lead acetate staining for the fumigated fibers soaked in methanol to remove suint peptides. In the lead acetate test a change in the oxidation state of hydrodisulfide is manifest by reduced staining.

Although 7 day heated Shurgain scoured controls, stained a deeper shade than the unheated controls, longer heating periods inhibited staining with the acid dye Kiton Red and basic dyes Methylene Blue and Orange 14. According to Menefee and Yee (1965), oxidative damage at elevated temperatures cause acidic and basic groups to decrease. In the fumigated samples a marked decrease in dyeability is attributed to the removal of negative sites by complexing, and dissociation of acids which produce free H⁺ ions which compete with dye cations for the electronegative sites. Metachromasia in fumigated fibers stained with Methylene Blue is indicative of oxidation reactions where the removal of N-methyl groups produces an aqua colour. Ion binding is often associated with spectral shifts. Other studies have found that modification of tyrosine and replacement of carboxy groups by carboxyl complexes repress Methylene Blue staining (Whewell *et al.*, 1971; Hewish & French, 1986). In summary, several factors such as decreased pH, changes in electronegativity and modification of amino acid groups, and pesticide conjugated or bound proteins are suggested to decrease dyeability after fumigation with S.W.A.T. Caution must be used in interpreting test results because complex interactions do not produce linear results. Initial increases in staining, tensile strength and elongation were followed by net decreases in these properties.

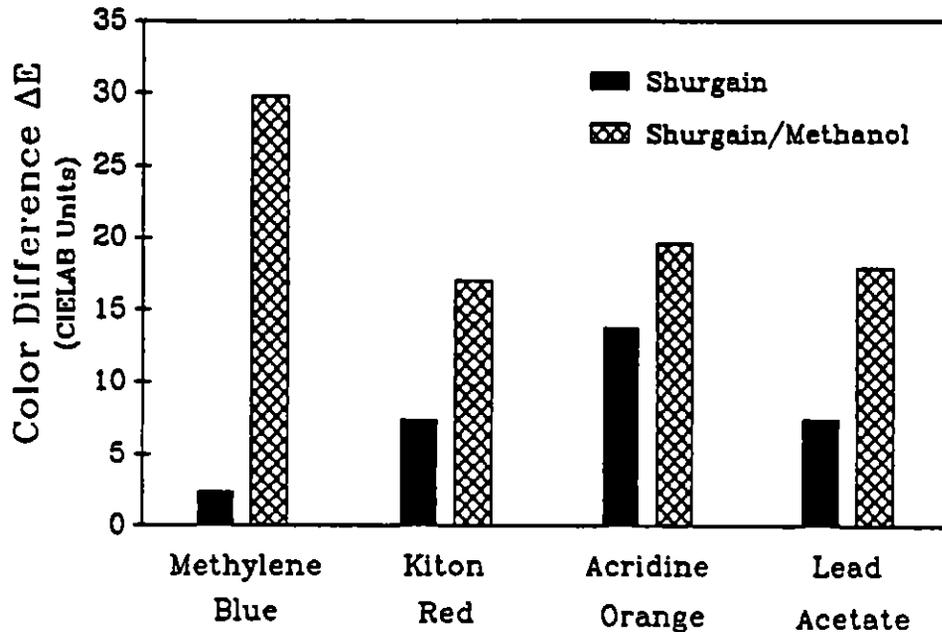


Figure 1. A comparison of reagent reactivity measured by colour difference (CIELAB Units) between Shurgain scoured and Shurgain and methanol scoured fibers fumigated at 50° C with 50 g of S.W.A.T. in a desiccator in a dark oven for 7 days.

Levels of phosphorus and chlorine were used to determine the amount of dichlorvos absorption. The relative amount of chlorine and phosphorus sorbed was based on the known element sulfur which was assumed to be constant. Natural surface contaminants (PCL) such as suint peptides which were not removed by the Shurgain scour appear to retard chlorine and phosphorus absorption (Figure 2). Energy-dispersive X-ray microanalysis indicated that when chlorine and phosphorus from the fumigant were absorbed only negligible amounts could be removed by distilled water and methanol washes. The resistance to removal suggests that the fumigant is bound to amino acids.

In another study (Jones, 1983) phosphate esters insecticides were found to bind to wool. Only a small proportion of the insecticides were removable by Soxhlet extraction with dichloromethane, methanol and water.

Chlorine attacked the cementing matrix between cuticular scales causing the scales to become visco-elastic or plastic. Chlorine also generates osmotically active degradation products from oxidizable cystine, which is found in abundance in the A-layer of the exocuticle (Makinson, 1979). The appearance of fibers in SEM micrographs suggests dissolution and outward diffusion of denatured protein which formed a viscous-like coating. Although damage was observed using SEM in wool fibers scoured with Shurgain and methanol no observable damage was seen on fibers scoured only in Shurgain after 7 days of fumigation. However, Shurgain scoured fibers were visibly damaged during the 21 and 35 day fumigation periods.

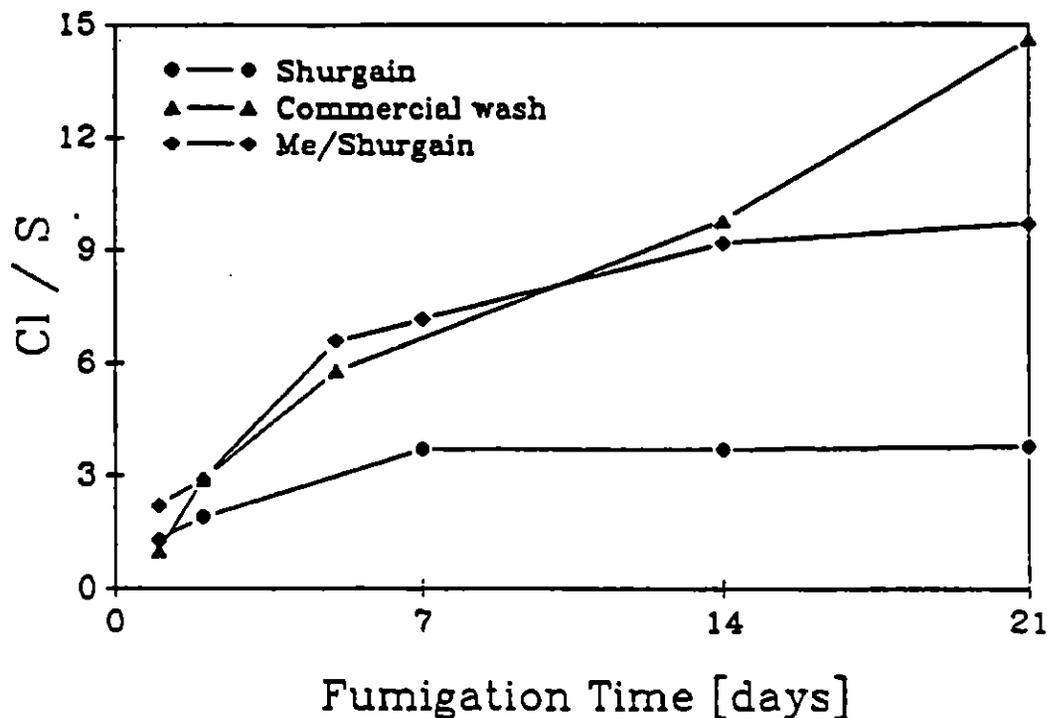


Figure 2. The effect of scouring pretreatment on chlorine sorption of wool fibers fumigated with S.W.A.T. at 50° C in a desiccator in a dark oven for 7, 14 and 21 days.

Yellowing of wool is attributed to changes in amino acids such as tryptophan, tyrosine and cystine residues by chlorine and peroxides. Instrumental colour difference readings showed that commercially scoured and methanol soaked fibers yellowed much more during fumigation than fibers washed only in Shurgain (Figure 3). More yellowness occurred in Shurgain/methanol scoured fibers fumigated for 2 days than in Shurgain scoured fibers fumigated for 21 days.

Yellowing in heated controls that were scoured in Shurgain only, is attributed to oxidation of greasy surface contaminants (Figure 4). The coloring agent in suint responsible for yellowing is methyl 10-(2,5-dihydroxyphenyl)-decanoic acid which is associated with nitrogenous beta-ketone (Fraser & Truter, 1960). Post fumigation washing with Shurgain removed most of the yellowness from heated control fibers. However, the yellowness in fumigated fibers was neither removable by Shurgain nor solvents.

Under different test conditions more phosphoric acid may be present during fumigation (Williams & Walsh, 1989). Since phosphoric acid is a bleaching agent, it is possible that yellowing may be retarded.

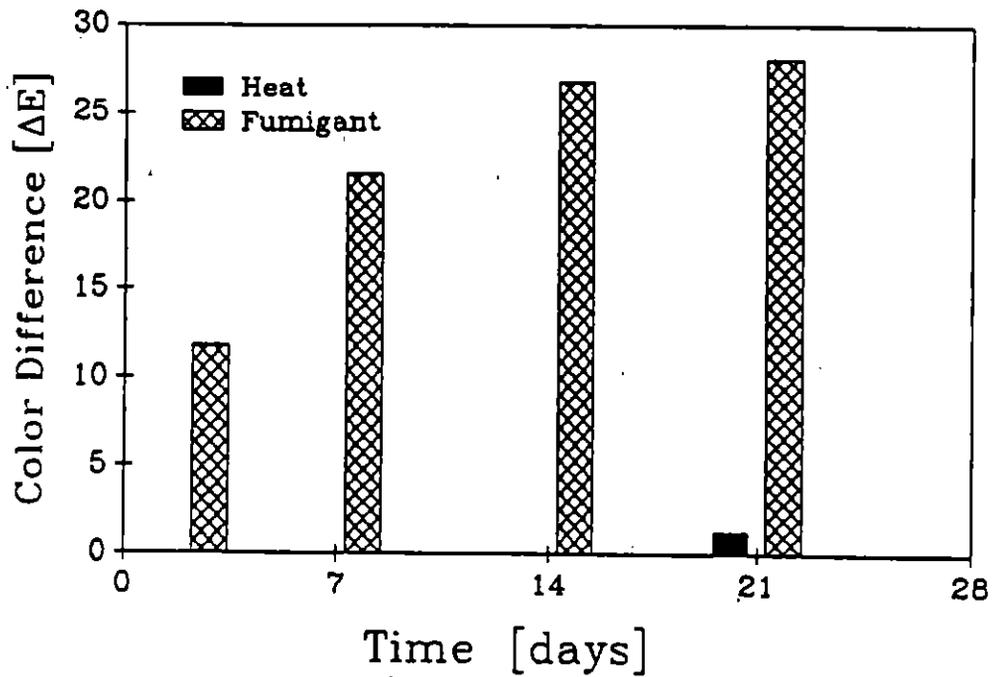


Figure 3. Total colour difference (CIELAB units) of methanol/Shurgain scoured wool fibers fumigated with S.W.A.T. in a desiccator in a dark oven compared with the heated control.

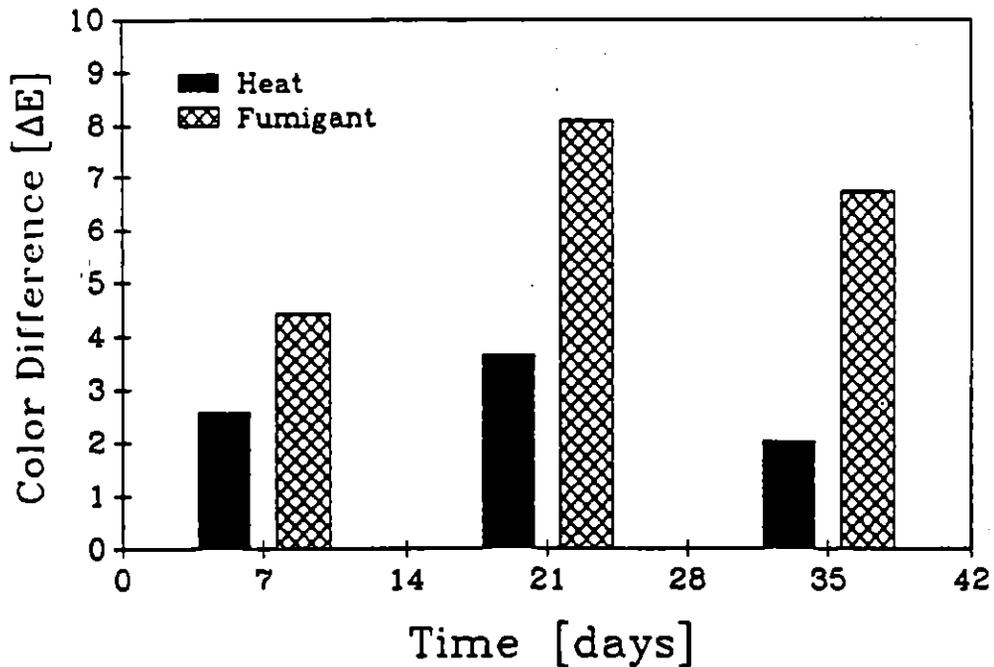


Figure 4. Total colour difference (CIELAB units) of wool fibers scoured only in Shurgain after fumigation with S.W.A.T. compared with the heated control.

Textiles and furs may be damaged by residual acid from dichlorvos resin strip space fumigation in storage or display. Damage by residual acid is reported in the literature. Haley and Hafey (1975) found that a combination of scouring with 0.1% Lissapol non-ionic detergent and a mild 2% acid (sulfuric) treatment caused fiber damage, whereas, scouring or acid treatment without scouring caused no damage. These researchers also found that wool stored in an acidified state (pH 3.5-4) was degraded. In this research acid damage was apparent in the fluorescent photomicrographs of fumigated fibers which were stained with Orange 14 fluorescent dye. Suint, wax and other PCL components apparently neutralize acids and protect wool.

Conclusion

It is apparent that dichlorvos resin strip fumigation can cause extensive damage to wool fibers. Scanning electron micrographs of the fumigated fibers showed changes such as erosion and a viscous exudate similar to over-chlorinated fibers as described in other studies (Makinson, 1979). Removal of protective oils from the wool fibers increased the rate of fumigation damage.

Physical tests such as tensile strength, and staining tests such as lead acetate, Kiton Red, Orange 14, and Methylene Blue may give distorted results because of complex chemical reactions during fumigation or in the pre-history of the fiber. Spivak et al. (1981) recorded increased tensile strength after fumigation with dichlorvos resin strips and Williams & Walsh (1989) found that polyethylene showed an increase in pH at the end of the post-fumigation period with the DDVP impregnated polyvinylchloride strips.

As an alternative to dichlorvos fumigation the Royal British Columbia Museum, has adopted an integrated systems approach and freezing methods for insect control (Florian, 1987). This system is effective and safe.

Post Script

Textile conservators should note any damage that may have occurred during fumigation with dichlorvos. The author would appreciate information about damage such as colour change, corrosion, tackiness, tendering and persistent odors.

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