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CYCLOPROTHRIN, AN ENVIRONMENTALLY SAFER PYRETHROID FOR INDUSTRIAL INSECT RESIST TREATMENT OF WOOL?

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SYNOPSIS

Dyebath addition is the simplest, cheapest, and most universally applicable method for applying insect-resist agent in the wool processing sequence, and this provides a treatment with optimum fastness properties. Unfortunately, this method cannot give 100% application efficiency even under the best industrial conditions, and some of the chemical must be discharged with the exhausted dyebath liquors. If this method of application is to be acceptable in the future, it must involve only biodegradable materials with a very low hazard to aquatic organisms of all kinds.

This paper reports laboratory and industrial results with a new synthetic pyrethroid, Cycloprothrin, that has the durability and fastness required for industrial insect-resist treatment of wool. Published data show that this compound has toxicities to a wide range of aquatic organisms, ranging from fish to invertebrates, that are three orders of magnitude safer than the currently used pyrethroids. Acceptance of Cycloprothrin will depend on economic factors and on the result of further detailed tests that will be required by environmental registering authorities.

INTRODUCTION

UK environmental authorities are currently exerting pressure on the British carpet industry because of their use of pyrethroids that are highly toxic to aquatic life, and Permethrin will be banned for mothproofing in the UK from 1993. The problems are summarised in a recent report from the Water Research Council[1]. Since Eulan WA new is no longer available, the main alternative existing insect-resist agent that will be usable in the forseeable future is the expensive Mitin FF.

Currently around 200 tonnes of mothproofing formulations[2] (representing more than 20 tonnes of various active ingredients) are used per year in the UK, treating some 45 million kg of fibre. Worldwide, around 230 million kg of wool is given an insect-resist treatment[3], but there is not the same environmental pressure to stop use of Permethrin in other countries as there is in the U.K. Part of the reason for this is that the industry is concentrated in three main centres[4] (Fig 1).

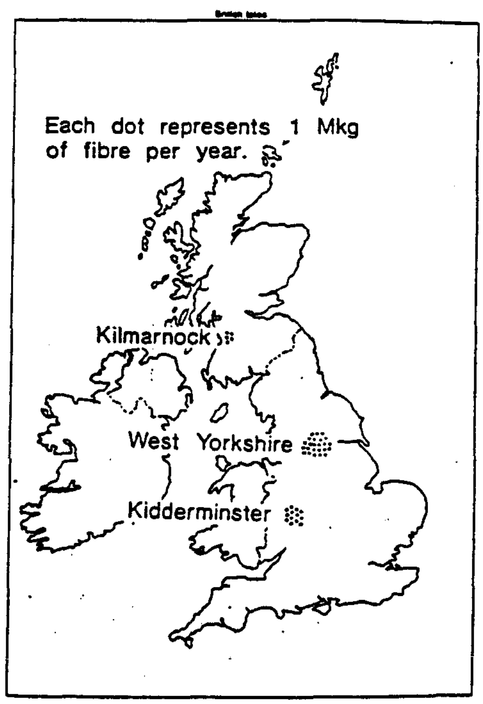

Fig. 1. Distribution of Carpet Processing Centres in U.K.[4]

In the carpet manufacturing process, the usual point of addition of the insect resist chemicals is in the dyebath along with the dyestuffs and other auxiliaries at the start of the dyeing operation. This is the simplest, cheapest, and most universal point of addition in the process, and this high temperature application usually provides a treatment with optimum fastness properties[5]. This method cannot give 100% application efficiency even under the best industrial conditions, and some of the insect-resist agent must be discharged with the exhausted dyebath liquors. With the industry localised as it is in the UK, these continuous discharges from each dyebath provide a significant toxic load to each of the affected sewage treatment plants and associated down-stream river systems. If this method of application is to be acceptable in the future, it must involve only biodegradable materials with a very low hazard to aquatic organisms of all kinds.

Fortunately there is a growing awareness in the agricultural chemical industry that there are market opportunities for synthetic pyrethroids with much lower toxicities to aquatic organisms than the highly active compounds that were developed in the late 1970's, and there has been a trend in recent years towards compounds that are environmentally less hazardous[6]. This paper describes the properties of one such material, Cycloprothrin, and shows that it has the dyebath exhaustion properties and durability required for industrial treatment of wool. Originally prepared by G.Holan of CSIRO, this material is manufactured by Nippon Kayaku and marketed as Cyclosal (Figure 2). It has a very safe mammalian toxicity (LD50 rat, mouse >5000mg/kg), and no irritant, carcinogenic, teratogenic or mutagenic properties have been observed[7]. This compound has toxicities to a wide range of aquatic organisms, ranging from fish to invertebrates, that are three orders of magnitude safer than the currently used pyrethroids (See Discussion)[7]. This combination of properties indicate that this material may have particular use for industrial insect-resist treatment of wool in environmentally sensitive areas.

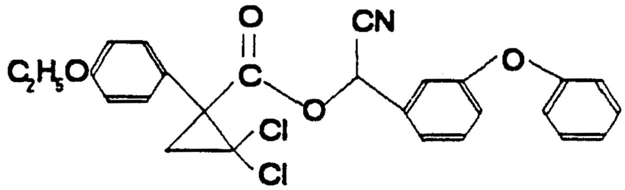

Fig. 2 Structure of Cycloprothrin

EXPERIMENTAL

Minimum Effective Concentration Values

A series of applications to plain weave wool fabric (135 g/m^2) were made with a self-emulsifiable formulation containing Cycloprothrin (20g/100g), xylene, Alkanate CS (10g/100g) and Lissapol TN450 (10g/100g). The insecticide formulation was applied to the fabric (20g) in an AHIBA Turbomat dyebath set at 313K with 4% ammonium sulfate and 1% acetic acid based on the weight of the wool; 500ml of liquor was used. The temperature was raised to 373K over 30 minutes, and held for an additional 30 minutes before rinsing in fresh cold water.

Fabric treatment levels were verified by chemical analysis. Insect testing to determine Minimum Effective Concentration values was essentially according to the Australian Test Method (1980)[8]

Measurement of Cycloprothrin in Dyebath and Rinse Liquors

Hot spent dyebath liquors and cold rinse liquors were spiked with Permethrin as an internal standard and 100 ml aliquots were then passed dropwise through Analytichem International BondElut C18 Solid Phase Extraction cartridges. The insecticide was stripped from the cartriges directly into the chromatographic sample vials by rinsing with ether and the dried residues were taken up in methanol for analysis.

Fabric Analysis

Methods for analyses of Permethrin on fabric using methanol as extraction solvent were used for cycloprothrin[10].

Chromatographic Analysis

A Varian Star HPLC system fitted with a diode array detector and a variable wavelength detector set at 215 nm was used. A Brownlee Labs Spheri-5 RP8S (10cm length, 4.6mmID) cartridge column was maintained at 313K and elution solvent was acetonitrile/water (85:15).

Lightfastness Testing

Accelerated exposure to light was conducted in fan-ventilated boxes equipped with 500W Phillips G-74 mercury-tungsten fluorescent lamps[11]. A thermostatically controlled fan was used to maintain the black body temperature at 340K.

DISCUSSION

Cycloprothrin Aquatic Toxicity

At present in Japan, Cycloprothrin is widely used in the aquaculture of rice for control of rice weevil, and registration of this compound in this difficult pest control situation demonstrates its aquatic and human safety. It is very safe to all marine organisms tested to date (Table 1).

TABLE I. Aquatic Toxicity of Cycloprothrin[7]

Common name	Species	48hr LC50
<u>Fish</u>		(mg/l)
Carp	*Cyprinus carpio*	>50
Goldfish	*Carassius auratus*	>10
Rainbow Trout	*Salmo gairdneri*	1.57
Ayu Fish	*Plecoglossus altivelis*	0.26
Cherry Trout	*Oncorhynchus masou*	2.0
Loach	*Misgurnus angiullicaudatus*	>10
Striped Mullet	*Mugil cephalus*	>10
<u>Invertebrates</u>		
Waterflea	*Moina macrocopa*	>200*
Waterflea	*Daphnia carinata*	>10*
FreshWater Crab	*Eriocheir japonicus*	>50
Pond Snail	*Cipangopaldina longispira*	>10
Japanese Littleneck	*Tapes philippinarum*	>10
Corbiculd	*Corbicula sp.*	>10

* 3 hour LC50

Significantly the list includes two water flea species and other aquatic invertebrates; these species are important in the environment as food sources for higher animals, and they also have an important role in preventing algal clogging in sewage treatment plants. In contrast to the data in Table 1, Permethrin has toxicities to a range of aquatic invertebrates from 0.00002 to 0.003 mg/l, and toxicities to fish species from 0.0004 to 0.03 mg/l[1,12].

Biological Activity of Cycloprothrin on Wool

Whereas Permethrin has higher activity against clothes moths than carpet beetles[11], Cycloprothrin has similar activities against both moth and beetle species (Table 2). Additionally, Cycloprothrin appears to be more active against wild dieldrin-resistant strains of *Tineola* than against our susceptible laboratory strains. Its activity against *Tineola* is strongly potentiated by piperonyl butoxide, indicating that microsomal oxidases may be responsible for the unusual spectrum of activity[13].

TABLE II. Minimum Effective Concentrations (MEC) after Application from a Boiling Dyebath, (313K, 0.5hr).

Insect Species	MEC
Susceptible *Tineola bisselliella*	0.04%
Dieldrin-Resistant *Tineola bisselliella*	<0.02%
Susceptible *Tinea translucens*	<0.02%
Dieldrin-Resistant *Tinea translucens*	0.03%
Anthrenus Flavipes	0.03%
Hofmannophila pseudopretella	~0.04%

To determine industrial application levels, the IWS has established protocols to determine recommended application levels (RALs) for particular end-uses and particular countries, depending on the major pest species encountered[14]. Losses under appropriate simulated end-use conditions are determined; for carpeting, the main requirement is that additional active ingredient is applied to ensure that an effective level remains after light exposure and shampooing. Cycloprothrin (Table 3) and Permethrin[11] have similar light fastness on fabric (Table 3), both losing 50-60% of their initial application levels after 4 weeks of exposure to MBTF lamps.

Cycloprothrin has similar chemical and physical properties to many other synthetic pyrethroids, and as a consequence, it has fastness properties (washing and drycleaning) that are similar to the other pyrethroids[11]. Both Cycloprothrin and Permethrin lost 55% of their initial application after simulated handwash cycles, they lost around 70% after 5 commercial dry-cleaning cycles and around 30% was lost after 5 carpet shampoo treatments.

TABLE III. Lightfastness of Cycloprothrin on Treated Fabric

Application Rate (%oww)	No Exposure	Cycloprothrin Light Exposure (%oww by Chemical Analysis) 1 Week (Blue 3)	2 Weeks (Blue 5)	3 Weeks (Blue 5)	4 Weeks (Blue6)*
0.150	0.140	0.110	0.083	0.071	0.058
0.100	0.095	0.065	0.061	0.053	0.050
0.075	0.072	0.045	0.040	0.037	0.036
0.050	0.037	0.026	0.026	0.017	0.016

* The 1, 3 and 4 week blue scale ratings correspond to grey scale contrast changes of 3-4. The 2 week sample colour change corresponded to a contrast of 2 on the grey scale.

Dyebath Exhaustion Efficiency

Because Cycloprothrin has similar water solubility properties to Permethrin, dyebath exhaustion levels similar to Permethrin are achievable. Cycloprothrin concentrations of 60-80 micrograms/litre in spent liquors were obtained in laboratory applications of 0.15% active ingredient, an application efficiency of 99.9% (25:1 L/W ratio). The higher application level of Cyclprothrin does not affect the level in spent dyebath liquors and similar Permethrin concentrations were obtained under these assistant-free conditions when it was applied at industrial levels.

As with all other non-polar insect resist agents, dyebath exhaustion of Cycloprothrin decreased substantially when surface active, solubilising dyeing assistants were used in the dyeing. Clearly, to optimise application of the insect resist agent and for economic reasons, these levelling agents should be used in minimum quantities.

Under industrial conditions, mills in Kidderminster and West Yorkshire discharged liquors with around 140-150 micrograms/litre of Permethrin in 1988[4]. Whereas liquors with this level of Permethrin would be highly toxic to aquatic species, Cycloprothrin liquors would be non-toxic even without any pretreatment or dilution.

Costs

At this stage it appears that Cycloprothrin may be more expensive for the industry compared with Permethrin as it would need to be applied at several times the amount of active ingredient, perhaps at 0.15% active ingredient on wool weight. At the moment increased cost appears inevitable at least in the UK as the expensive product Mitin FF may well be the only mothproofer available in 1993, and the market should be eager to buy any cheaper treatment.

CONCLUSION

Cycloprothrin, a new synthetic pyrethroid has the durability and fastness required for industrial insect-resist treatment of wool. It has toxicities to a wide range of aquatic organisms that are often three orders of magnitude better than the currently used pyrethroids.

With good quality control it should be possible for mills to discharge non-toxic dyebath liquors, and yet retain the benefits of cost, convenience and durability obtained by adding insect-resist chemicals to the dyebath along with the dystuffs and other auxiliaries at the start of the dyeing operation.

Acceptance of Cycloprothrin will depend on economic factors and on the result of further detailed tests that may be required by environmental registering authorities.

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