WORLD HEALTH ORGANIZATION

ORGANISATION MONDIALE DE LA SANTÉ

a 63865

BIBLIOTHÈQUE OMS - 2 NOV. 1965 WHO LIBRARY

WHO/Vector Control/77
WHO/Mal/462
17 July 1964

ORIGINAL: ENGLISH

ASSESSMENT OF TWO POSSIBLE PRE-TREATMENT METHODS OF PREVENTING SORPTION OF INSECTICIDE RESIDUES BY DRIED MUD

by

A. B. Hadaway and F. Barlow
Department of Technical Co-operation
Tropical Pesticides Research Unit, Porton, United Kingdom

INTRODUCTION

Sorption of particulate insecticides from the surface of dried muds used in house construction in many tropical countries is accompanied by a reduction in their effectiveness against adult mosquitos resting on the surface, and the biological activity of the sorbed insecticide is influenced considerably by atmospheric humidity (Barlow & Hadaway, 1958a, 1958b). Many alkyl phenyl N-methylcarbamates that have a potential use as residual contact insecticides for adult mosquito control are sorbed more readily on a given soil than the chlorinated hydrocarbons DDT and dieldrin, and the influence of humidity on the availability of the sorbed carbamates is also greater (Hadaway & Barlow, 1963a).

Several attempts have been made to inhibit sorption of chlorinated hydrocarbons and increase the persistence of surface deposits by altering the insecticide formulation. For instance, Gerolt (1961) prepared new wettable powders based on ground solidified melts of dieldrin and an adjuvant such as coumarone resin, a synthetic resin Aroclor, or gilsonite, and laboratory tests showed that the persistence of dieldrin on a sorptive mud surface was greatly extended. The superiority of the dieldrin/resin formulations over the standard dieldrin wettable powder disappeared however, in field trials at Arusha, Tanganyika, when contact periods were unrestricted and the average relative humidity was comparatively high (van Tiel, 1961).

It would appear that with an insecticide such as dieldrin, with a high intrinsic toxicity to adult mosquitos and no irritant action, sorption is of little or no significance in practice provided that atmospheric humidity is high. However, there are situations where sorption of insecticides applied to dried mud walls may be an important factor in the failure to obtain adequate control of adult mosquitos and where the authorities are prepared to consider pre-treatment of walls in preference to the expensive alternatives of larviciding and mass drug administration. It is appreciated that pre-treatment of walls is a laborious procedure to be avoided if possible, but it was considered worthwhile to re-examine possible methods of preventing or delaying sorption.

MATERIALS AND METHODS

Plywood panels or dried mud bricks made from our standard sorptive red Babati soil, or similar test surfaces pre-treated as described later, were sprayed in a modified Potter tower with aqueous suspensions of wettable powder formulations at a dosage of 1 g active ingredient per m^2. They were stored and tested at 25°C and 50-55% relative humidity.

Mosquitos (Anopheles stephensi List.) were reared by standard methods at 25°C and 70-80% relative humidity. Batches of 12-15 females, 2-3 days old and blood-fed, were exposed on treated panels or dried mud bricks for known times by the method described previously (Hadaway & Barlow, 1963a) and were then transferred to paper-cup cages and stored for 24 hours before mortality counts were made.

PRE-TREATMENT WITH WHITEWASH

It is customary in some areas to coat the dried mud walls of houses with "whitewash", and if it could be shown that such a practice considerably extended the effective life of an insecticide then consideration could be given to the promotion of this practice in other areas before spraying programmes are embarked upon.

"Whitewash" is a general term, and the chemical nature of the deposit varies. Either calcium hydroxide or calcium carbonate may be the material first applied to walls. If the hydroxide is used, reaction with carbon dioxide in the air results in a slow conversion to the carbonate, and the stability of an alkali-labile insecticide

deposited on the surface is likely to vary according to the time elapsed since the hydroxide was applied. In this report, "limewash" will be used to describe deposits of calcium hydroxide, or slaked lime, and "whitewash" to describe those of calcium carbonate.

The chlorinated hydrocarbons DDT and dieldrin are stable on limewash, but the substituted phenyl N-methylcarbamates so far examined decompose rapidly when applied to fresh limewash and lose their toxicity to adult mosquitos (Hadaway & Barlow, 1963b). It was necessary, therefore, to check on the stability of such compounds on the less alkaline deposits of whitewash before investigating their persistence on whitewashed mud bricks.

Plywood panels were coated with whitewash or whitewash/size. The calcium carbonate used was "whiting" as defined in the specification of the British Whiting Federation. It was mixed with water in the ratio of 1.5:1 and the thick cream spread over a row of plywood panels with a spreader as used in thin-layer chromatography. The dried layer was about 0.25 mm thick and the average weight about 600 g/m^2. Where size was required the whiting was mixed with a 2% w/v animal size solution instead of water. The pre-treated panels, together with untreated ones, were sprayed with aqueous suspensions of wettable powders at a dosage of 1 g active ingredient per m^2.

All mosquitos died after an exposure of two minutes on all panels sprayed with a wettable powder of 6-chloro-3,4-xylyl N-methylcarbamate at 0, one, two, four and eight weeks after treatment, indicating at least no rapid decomposition of this persistent insecticide.

The percentage kills of mosquitos exposed on panels sprayed with a wettable powder containing 50% 3-isoprophylphenyl N-methylcarbamate are given in Table 1. They show that this more volatile carbamate is stable on whitewash, and that it had, in fact, a greater persistence on whitewash than on untreated plywood. This is probably due to sorption of some insecticide on the whitewash particles. Whitewash/size gave an intermediate persistence, probably because the size reduced the permeability of the whitewash and therefore its sorptive power.

TABLE 1. CONTACT TOXICITY TO A. STEPHENSI OF 3-ISOPROPYLPHENYL N-METHYLCARBAMATE AT A DOSAGE OF 1 g/m^2 ON TREATED AND UNTREATED PLYWOOD PANELS

Test surface	Age of deposit (weeks)	Mean percentage kill after contact of ... mins				
		2	5	15	30	60
Plywood	0	100				
	2	100				
	4	54	100			
	8		15	96		
	12			0	61	
	16				0	72
Plywood/whitewash	0	100				
	2	100				
	4	68	100			
	8		58	100		
	12			54	100	
	16			32	84	
Plywood/whitewash/ size	0	100				
	2	100				
	4	40	92			
	8		23	100		
	12			15	89	
	16				4	88

Dried mud bricks made from Babati soil were coated with whitewash by spraying with a suspension of 1:1 whiting and water. The average weight of the dried layer was about 200 g/m^2. These, together with untreated bricks, were sprayed with suspensions of wettable powders of 3-isopropylphenyl N-methylcarbamate, dieldrin, and 6-chloro-3,4-xylyl N-methylcarbamate at a dosage of 1 g active ingredient per m^2.

It can be seen from the results given in Table 2 that the coating of whitewash between the sorptive soil and the insecticide deposit delayed but did not prevent sorption. The presence of insecticide in the soil below the whitewash was confirmed chemically. Similar biological results were obtained when bricks were pre-treated with whitewash/size.

TABLE 2. CONTACT TOXICITY TO A. STEPHENSI OF INSECTICIDES AT A DOSAGE OF 1 g/m^2 ON BABATI BRICKS WITH AND WITHOUT PRE-TREATMENT WITH WHITEWASH

Insecticide	Pre-treatment	Age of deposit	Mean percentage kill after contact of ... minutes					
			2	5	15	30	60	120
3-isopropylphenyl N-methylcarbamate	None	0	100					
		1 day				0	38	
		2 days				0	0	
		1 week					0	0
3-isopropylphenyl	Whitewash	0	100					
		1 day		0	31	100		
		2 days				0	0	
		1 week					0	0
Dieldrin	None	0	100					
		1 week					0	20
		2 weeks					0	0
Dieldrin	Whitewash	0	98					
		1 week	100					
		2 weeks	58	100				
		4 weeks			0	0	19	
		8 weeks					0	23
6-chloro-3,4-xylyl N-methylcarbamate	None	0	100					
		1 week				0	0	
		2 weeks					0	0
6-chloro-3,4-xylyl N-methylcarbamate	Whitewash	0	100					
		1 week	100					
		2 weeks	96					
		4 weeks	34	84				
		8 weeks					0	0

It was considered of practical interest to determine whether the layer of whitewash prevented contact between mosquitos resting on the surface and insecticide sorbed in the dried mud. This was done by conditioning the bricks used in the above experiment for 24 hours at 80% relative humidity and then retesting at this humidity. One week after the application of 3-isopropylphenyl N-methylcarbamate no kills of mosquitos

were obtained when they were exposed on the bricks for two hours at 50% relative humidity, but after conditioning for 24 hours at 80% relative humidity, kills of 12% and 100% after exposures of one and two hours respectively were obtained on the standard bricks, and 27% and 100% respectively on the bricks pre-treated with whitewash. Eight weeks after the application of dieldrin 23% of the mosquitos exposed on the pre-treated bricks for two hours died, but after conditioning for 24 hours at 80% relative humidity the kills increased to 42% and 92% after exposures of half an hour and one hour respectively. The insecticides therefore can readily diffuse through the whitewash, and changes in a factor such as atmospheric humidity, which controls the availability of sorbed insecticides, are reflected in changes of mortality rates amongst exposed mosquitos.

Pre-treatment of dried mud bricks with whitewash, therefore, delays but does not prevent sorption of insecticides. The delay was insignificant with the relatively volatile, rapidly sorbed 3-isopropylphenyl N-methylcarbamate; but appreciable, about 6-8 times, with the less volatile 6-chloro-3,4-xylyl N-methylcarbamate and dieldrin. These experiments were deliberately carried out with a highly sorptive soil under relative humidity conditions where sorption is normally very rapid. It can be inferred that extension of the effective life of insecticides will be greater with thicker layers of whitewash, on less sorptive soils and at high humidities. Whitewashing should also give some benefit on relatively non-porous surfaces, such as thatch and wood, especially with the more volatile insecticides.

PRE-TREATMENT WITH SIZE AND POLYCEL

The simplest method of preventing sorption would be to block the capillaries of the sorbent with a colloidal material which dries to an impermeable layer. It was shown previously (Hadaway & Barlow, 1955) that treating Uganda mud bricks with a 2% solution of size in water delayed sorption of DDT for at least 15 days, but the availability of the insecticides to mosquitos (A. aegypti) was reduced. It was thought that the reduction in availability of more potent insecticides would not be so marked, and that the evaluation of cheap colloidal materials for the pre-treatment of dried mud was justified.

Dried mud bricks made from Babati soil were treated with size or Polycel, a commercial water-soluble adhesive based on etherified cellulose. The first method of application was by brushing with either two or four coats of solutions of 5% size or 1% Polycel in water, the bricks being alllowed to dry completely between coats. After storage for four days the bricks were sprayed with aqueous suspensions of a wettable powder containing 50% 3-isopropylphenyl N-methylcarbamate at a dosage of 1 g/m^2, and then stored and tested at 25°C and 50-55%. The surfaces of the treated bricks before spraying had a smooth shiny finish indicating that the dried polymers formed continuous layers which sealed the capillaries between the soil particles. The percentage kills of mosquitos exposed on the surfaces at different times after treatment are shown in Table 3.

TABLE 3. CONTACT TOXICITY TO A. STEPHENSI OF 3-ISOPROPYLPHENYL N-METHYLCARBAMATE APPLIED AT A DOSAGE OF 1 g/m^2 AS A 50% WETTABLE POWDER TO BABATI BRICKS PRE-TREATED BY BRUSHING

Pre-treatment	Age of deposit (weeks)	Mean percentage kill after contact of ... minutes				
		2	5	15	30	60
Size, 2 coats	0	100				
	1	100				
	2	87				
	4	84				
	8			0	38	96
	10					0
Size, 4 coats	0	100				
	1	100				
	2	100				
	4	98				
	8			25	85	
	10					0
Polycel, 2 coats	0	100				
	1	100				
	2	100				
	4	80				
	8			0	40	100
	10					0

TABLE 3 (continued)

Pre-treatment	Age of deposit (weeks)	Mean percentage kill after contact of ... minutes				
		2	5	15	30	60
Polycel, 4 coats	0	100				
	1	100				
	2	100				
	4	96				
	8			38	96	
	10					0

There was no apparent adverse effect of the pre-treatment on the immediate contact toxicity of this potent insecticide as 100% kills were obtained after a contact of only two minutes. This level of toxicity was maintained for about four weeks showing that the usual rapid sorption was prevented. It should be noted, however, that after four weeks the loss of effectiveness was greater than that shown by deposits on plywood panels (see Table 1). This may be explained by reference to a peculiarity of the residual action of this carbamate on plywood: the persistence as indicated by bioassay is longer than would be expected from the volatility of the insecticide on a completely non-permeable surface. Chemical analysis shows that cellulose fibres retain part of the insecticide in a condition, probably inside the fibres, where the evaporation rate is markedly reduced. The pre-treated mud bricks, however, will have essentially non-permeable surfaces and the insecticide particles will be lost by evaporation at a faster rate than on plywood.

Thus sorption can be prevented if the pores of the mud surface are completely sealed. Brushing, however, is too laborious and therefore costly as a method of practical application. It was necessary then to see if the same effect could be obtained by spraying the mud bricks with solutions of size or Polycel.

The size solutions up to say 5% can be readily sprayed but even a 1% Polycel solution has too high a viscosity and the concentration had to be reduced to 0.125% before a solution could be sprayed in our tower. Babati bricks were sprayed with 5% size or 0.125% Polycel solutions using volumes which are five times those used

for insecticide sprays: the surfaces were horizontal and would not have held this volume if they had been vertical. During the space of a few minutes the solutions were absorbed by the porous mud. The bricks were allowed to dry for several days and then sprayed with aqueous suspensions of wettable powder formulations of 3-isopropylphenyl, N-methylcarbamate, 6-chloro-3,4-xylyl N-methylcarbamate or dieldrin at a dosage of 1 g active ingredient per m^2. The mortality rates obtained in bio-assays are given in Table 4.

TABLE 4. THE CONTACT TOXICITY TO A. STEPHENSI OF INSECTICIDES APPLIED AT A DOSAGE OF 1 g/m^2 TO BABATI BRICKS PRE-TREATED BY SPRAYING

Insecticide	Pre-treatment	Age of deposit (weeks)	Mean percentage kill after contact of ... minutes				
			2	5	15	30	60
3-isopropylphenyl N-methylcarbamate	0.125% Polycel	0	100				
		1				0	0
3-isopropylphenyl N-methylcarbamate	5% size	0	100				
		1				0	0
6-chloro-3,4-xylyl N-methylcarbamate	5% size	0	50	96			
		1	4	31	42		
Dieldrin	5% size	0	88	100			
		1			0	23	52

Initially the contact toxicities of dieldrin and 6-chloro-3,4-xylyl N-methylcarbamate deposits were slightly reduced, and there was a slight delay in sorption but this was not of practical significance. Evidently either not enough colloid was applied or it was not distributed in the same way as when applied by brushing.

One per cent. solutions of various hydrophilic colloids were made and 10-ml samples spread thinly in Petri dishes. After the water had evaporated the resultant films were weighed and examined. All were dry but the film from size was very brittle, and this may be a reason for the inability of the sprayed size to seal the mud pores: unless a great excess is used, thin films of size across pores will break

on drying. Films from methyl ethyl cellulose, methyl cellulose and sodium carboxy methyl cellulose were much more pliable. As mentioned above, Polycel gives very viscous solutions or dispersions. Methyl cellulose, which is a similar compound to Polycel, gave an especially pliable film and is available in forms covering a wide range of intrinsic viscosities. The lowest viscosity grade, Celacol M20, was chosen as giving the highest solid content while still sprayable, and 1% and 2% solutions were sprayed on to Babati bricks at the rate of 200 g of spray liquid per m^2. After the bricks had dried for 24 hours they were sprayed with aqueous suspensions of 3-isopropylphenyl N-methylcarbamate at a dosage of 1 g/m^2. The 1% bricks wetted evenly with insecticide spray liquid but the 2% bricks wetted with difficulty and the water evaporated without any real penetration. All mosquitos died after a contact of two minutes with the treated surfaces initially, but none of those exposed for 60 minutes one week later were killed. Sorption had not been prevented, therefore.

A probable explanation is that if a colloid solution is of a sufficiently low viscosity to be sprayable it will readily penetrate the mud pores by capillary action. After drying, therefore, the solid colloid will be spread throughout a considerable depth of mud and at no level will the amount be enough to seal the pores completely. Very high viscosity solutions or dispersions, such as the 1% Polycel, can be spread by brushing but are too viscous to penetrate further into the pores than they are pushed by the mechanical forces of application. Consequently the colloid residue after drying will be left in a very thin superficial layer which will seal the pores more effectively.

CONCLUSIONS

Two possible pre-treatment methods of preventing the sorption of insecticide residues by dried soils have been examined; placing a barrier of a less sorptive material between insecticide and soil, and sealing the soil pores with a hydrophilic colloid.

"Whitewash" (calcium carbonate) applied to a highly sorptive dried mud caused a marked delay in the sorption of insecticides, such as dieldrin and 6-chloro-3,4-xylyl N-methylcarbamate, of low volatility. The beneficial effect of pre-treatment with whitewash would probably be much greater with less sorptive soils and at high

humidities, and field trials should be considered. The delay, however, was not sufficient to give any practical benefit when a more volatile, and therefore more readily sorbed, insecticide like 3-isopropylphenyl N-methylcarbamate was used. A coating of whitewash on relatively non-porous surfaces such as thatch and wood should also extend the effective life of deposits, especially those of more volatile insecticides.

Limewash, initially calcium hydroxide, should not be used as its greater alkalinity causes hydrolysis of carbamate insecticides and some organo-phosphorus compounds.

Sorption of all the insecticides tested was prevented by pre-treatment with a colloid solution providing that it could be applied at a concentration and in a way that gave a superficial layer of dried solid which completely sealed the pores. The only way of doing this found so far is to use a viscous solution and apply by brushing. Spraying a less viscous solution is not effective.

ACKNOWLEDGEMENTS

We are grateful for samples of Celacol (methyl cellulose) sent by J. M. Steel and Co. Ltd, London.

REFERENCES

Barlow, F. & Hadaway, A. B. (1958a) Bull. ent. Res., 49, 315

Barlow, F. & Hadaway, A. B. (1958b) Bull. ent. Res., 49, 333

Gerolt, P. (1961) Bull. Wld Hlth Org., 24, 577

Hadaway, A. B. & Barlow, F. (1955) Bull. ent. Res., 46, 547

Hadaway, A. B. & Barlow, F. (1963a) Bull. ent. Res., 54, 329

Hadaway, A. B. & Barlow, F. (1963b) Bull. Wld.Hlth Org., 28, 63

van Tiel, N. (1961) Bull Wld Hlth Org., 24, 593