EVALUATION OF ALIPHATIC AMINE CONCENTRATES AGAINST IMMATURE MOSQUITOES

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ABSTRACT. Several aliphatic amines were formulated as concentrates in various solvents with surfactants and evaluated against mosquito larvae and pupae. These concentrate formulations were diluted with water and the emulsion was added to cups in the laboratory or sprayed on the surface of mosquito breeding sources. The most promising formulations were: 25% Armeen L-15 [*beta*-RNH_2 primary beta amine (R = 15 C)] and 25% Duomeen L-15 [*beta*-RNH $(CH_2)_3$ NH_2 *beta*-diamine (R = 15 C)] in automotive diesel oil containing 2% of surfactants. Most formulations produced complete mortality of larvae of *Culex pipiens quinquefasciatus* Say at 2 ppm in the laboratory, and yielded excellent control of larvae and pupae of *C. tarsalis* Coquillett in experimental ponds at the rate of 0.5 lb/A. Some other formulations were also effective in controlling field populations of *Culex* species.

INTRODUCTION

A number of aliphatic amines evaluated against larvae and pupae of the southern house mosquito *Culex pipiens quinquefasciatus* Say in the laboratory showed good biological activity (Mulla 1967a, 1967b). Some of the most effective aliphatic amines also showed good activity against the immature stages of *Aedes aegypti* Linnaeus, *Aedes nigromaculis* Ludlow, and *Anopheles albimanus* Wiedemann (Mulla et al. 1970). In field studies, aerial application of 50 percent concentrates of several aliphatic amines in petroleum oils failed to control larvae of the pasture mosquito *A. nigromaculis* at the rate of 32 oz/A. Ground application of these formulations, however, yielded excellent control of larvae and pupae of *C. tarsalis* Coquillett, *A. nigromaculis* and *C. peus* Speiser at the rate of 0.5–1.0 lb/A (Mulla and Darwazeh 1971a, 1975). Some of the formulations gave poor results, attributed to the incompatibility of the amines with the solvents or surfactants. The less effective formulations either gelled or formed a powdery film upon contact with water.

Currently, several formulations of aliphatic amines in petroleum oils are being used operationally by mosquito control agencies in California. At the rate of 2.0 gal/A, aerial application of these low-concentrate formulations (1–5 percent) provided satisfactory control of larvae and pupae (Darwazeh 1973). Application of such large volumes of petroleum oil-aliphatic amine formulations is costly in terms of materials, application, loading and ferrying time of aircraft. Therefore, there is a great need for the evaluation and development of high-concentrate formulations which can be diluted with water and applied by ground and aerial equipment. The current studies were undertaken to develop emulsifiable concentrate formulations of aliphatic amines which could produce adequate larval and pupal control, especially in areas where resistance in mosquitoes to organophosphorus compounds is critical, as Mulla et al. (1970), and Georghiou et al. (1969) found no cross tolerance to aliphatic amines in populations resistant to chlorinated hydrocarbons and organophosphorus larvicides. In addition, these materials have little or no effects on nontarget aquatic organisms (Mulla and Darwazeh 1971b).

METHODS AND MATERIALS

LABORATORY. Each of the aliphatic amines and surfactants listed (Table 1) was formulated in xylene, ethanolamine, automotive diesel No. 2 and Chevron larvicidal base oil (Chev. 74R–2895) with (2 percent) and without surfactant; 25 grams of technical grade material were placed in 100 ml beaker, the solvent and 2 grams of surfactant were added to bring the volume to the 100 ml level.

Each EC formulation was diluted with water to yield 1 percent stock suspension and series of further dilutions were prepared as needed. All materials were tested at 1, 2 and 3 ppm of the amine against larvae. For evaluation, 20 4th-stage larvae of *Culex p. quinquefasciatus* Say were placed in 4 oz. paper cups containing 100 ml of tap water. The required amount (1 ml or less) of aqueous toxicant suspension was added to each cup, and mortality was taken 24 hours after treatment. Each test was repeated twice, utilizing 2 replicates per concentration. Along with each test, an equal amount of the solvent with surfactant was added to the check without the amine.

FIELD. Following evaluation of the aliphatic amine formulations in the laboratory, the most effective formulations were selected for further evaluation under semi-field conditions in experimental ponds.

The tests were conducted in experimental ponds located at the Aquatic Research Facility (Midgeville) at the University of California, Riverside. Detailed description of these facilities is reported elsewhere (Mulla and Dawarzeh 1971a). Each formulation was applied at the rate of 0.25, 0.5 and 1.0 lb/A of the amine, utilizing 2 ponds per rate, and 2 ponds left untreated as checks. The required amount of a formulation was mixed with 100 ml of water and applied from the sides of the pond with an all-purpose 1 qt. household sprayer (Smart and Final Iris Co., Los Angeles, Calif. 90058).

For larval and pupal assessment, 5 dips per pond were taken prior to and 24

Table 1. Aliphatic amines and surfactants utilized in larvicidal formulations.

Material	Supplier	Chemical Composition
	Aliphatic Amines	
Armeen L-15	Armak Chemicals Division	Beta-RNH_2 primary beta-amine (15 carbons)
Armeen DML-15D	Armak Chemicals Division	n-alkyl (15–20 carbons) diemthyl tertiary amine
Duomeen L-15	Armak Chemicals Division	Beta-RNH $(CH_2)_3$ NH_2 beta diamine (15 carbons)
Adogen 462	Archer Daniels Co.	Dimethyldicoco ammonium chloride
	Surfactants	
Pluronic L-101 L-121	Wyandott Chemical Corp.	Condensates of propylene oxide with propylene glycol
Arlatone T	Atlas Chem. Industrial Inc.	Polyoxyethylene polyol fatty acid ester
Tween 20	Atlas Chem. Industrial Inc.	Polyethylene sorbitan monolaurate (polysorbate 20)
Agrimul 70A	Nopco Chem. Co.	Alkyl aryl polyether alcohol

hours after treatment, and percent reduction was based on the number of 3-4 stage larvae and pupae recovered in the pre- and post-treatment counts. Mosquito populations in the ponds consisted of *C. tarsalis* and *C. peus*.

RESULTS AND DISCUSSION

LABORATORY. The aliphatic amine formulations in ethanolamine with or without 2 percent surfactants were unstable, and the amines separated from the solvents soon after vigorous agitation. However, the formulations emulsified when they were added to water. Armeen L-15 and Adogen 462 showed increased activity with some of the surfactants, but Duomeen L-15 yielded best results without the incorporation of a surfactant (Table 2, Test A). Due to the low solubility of the aliphatic amines in ethanolamine, high concentrate formulations are not feasible to be formulated in this solvent.

Automotive diesel No. 2, and Chevron Research 74R-2895 larvicidal base oil were efficient solvents for the aliphatic amines evaluated. Activity of the amines formulated in these solvents was enhanced noticeably by the addition of surfactants. Armeen L-15 with all surfactants produced almost complete mortality at 2 ppm (Table 2, Test B, C). Similar results were also obtained with Duomeen L-15 formulated in either solvent with Arlatone T or Tween 20. Xylene and Armeen L-15 performed exceptionally well with all surfactants used, and produced complete mortality at 2 ppm (Table 2, Test D). Adogen 462 without surfactant and Armeen DML-15D with Tween 20 were also equally effective.

From the laboratory data presented here, automotive diesel type oils appear to be the best, cheapest and readily available solvents for Armeen L-15 and Duomeen L-15 formulations. Fatty acid ester surfactant (Arlatone T) enhanced the performance of the primary beta amine (Armeen L-15) markedly, while polyethylene sorbitan (Tween 20) enhanced the activity of the beta diamine (Duomeen L-15) in the automotive diesel oil formulations.

EXPERIMENTAL PONDS. At the rate of 0.5 lb/A, Armeen DML-15D in xylene with (2 percent) Pluronic L-121 produced complete control of *C. peus* larvae and pupae in experimental ponds. At the same rate, this formulation produced only 83 percent reduction in the *C. tarsalis* population. Similar results were obtained with this material when formulated in xylene and 2 percent Tween 20, and in automotive diesel No. 2 and 2 percent Arlatone T (Table 3).

Duomeen L-15 in xylene with Arlatone T performed well in the laboratory, but poor results were obtained at the rate of 1.0 lb/A against *C. tarsalis* in the experimental ponds (Table 4). Excellent results, however, were obtained with this

Table 2. Evaluation of aliphatic amine concentrates (25%) in various solvents with and without surfactants (2%) against 4th stage *C. p. quinquefasciatus* in the laboratory.[a]

Amines	Conc. ppm	Avg. (%) 24-hr mortality with and without surfactants				
		w/o	PL-101	Arlatone T	Tween 20	Agrimul 70A
		Test A—Ethanolamine				
Armeen DML-15D	1	30	75	69	0	75
	2	59	80	79	80	85
	3	85	85	88	100	100
Duomeen L-15	1	90	35	20	0	0
	2	100	50	70	25	20
	3	100	85	100	35	60
Armeen L-15	1	30	70	90	0	70
	2	90	100	100	80	100
	3	100	100	100	100	100

Table 2 (continued)

Amines	Conc. ppm	Avg. (%) 24-hr mortality with and without surfactants				
		w/o	PL-101	Arlatone T	Tween 20	Agrimul 70A
Adogen 462	1	65	90	60	15	0
	2	85	100	95	65	10
	3	100	100	100	100	65
Test B—Automotive Diesel No. 2						
Armeen DML-15D	1	56	65	78	60	75
	2	64	93	85	90	85
	3	76	100	93	100	100
Duomeen L-15	1	35	35	75	70	20
	2	75	80	95	100	70
	3	100	100	100	100	90
Armeen L-15	1	25	50	70	40	95
	2	80	98	100	95	100
	3	100	100	100	100	100
Adogen 462	1	20	35	10	10	15
	2	80	85	75	50	50
	3	95	95	90	85	80
Test C—Chevron 74R-2895						
Armeen DML-15D	1	23	83	65	50	50
	2	48	88	75	80	60
	3	80	100	85	90	75
Duomeen L-15	1	60	50	70	40	20
	2	85	85	100	100	60
	3	100	100	100	100	95
Armeen L-15	1	20	60	70	80	80
	2	75	100	100	100	100
	3	100	100	100	100	100
Adogen 462	1	5	0	0	25	10
	2	70	30	70	65	50
	3	90	70	95	75	80
Test D—Xylene						
Armeen DML-15D	1	28	80	76	70	50
	2	54	90	80	100	85
	3	58	98	95	100	95
Duomeen L-15	1	45	45	70	30	60
	2	85	80	95	95	90
	3	100	100	100	100	100
Armeen L-15	1	20	90	30	85	80
	2	85	100	100	100	100
	3	100	100	100	100	100
Adogen 462	1	70	25	5	50	30
	2	100	70	75	75	70
	3	100	90	100	85	85

[a] No mortality in checks.

Table 3. Evaluation of Armeen DML-15D (25 percent) concentrate in various solvents and surfactants applied as aqueous spray against mosquito larvae and pupae in experimental ponds.

Rate lb/A	Solvent	Surfactant (2%)	Avg. no. of larvae and pupae 5/dips: Pre-treat L	Pre-treat P	Post-treat (24 hr) L	Post-treat (24 hr) P	(%) Reduction
			May 7, 1974[a]				
0.25	Xylene	PL-121	84	6	18	1	79
0.50			43	3	0	0	100
Check	...	...	12	2	17	1	0
			Sept. 9, 1975[b]				
0.25	Xylene	PL-121	57	17	22	10	55
0.50			79	38	14	6	83
0.25	Xylene	Tween 20	53	6	13	3	73
0.50			79	35	6	4	91
0.25	Auto. diesel	Arlatone T	50	14	18	12	54
0.50	No. 2		81	26	6	7	88
Check	...	...	46	6	49	8	0

[a] Population consisted of *C. peus*.
[b] Population consisted of *C. tarsalis*.

material when formulated in automotive diesel No. 2 and Sunland automotive diesel with the surfactant Tween 20. This formulation produced 95–100 percent reduction at the rate of 1.0 lb/A.

Armeen L–15 in xylene, automotive diesel No. 2 and Sunland automotive diesel with PL–101 and Arlatone T as surfactants produced excellent control of larvae and pupae. The diesel type sol-

Table 4. Evaluation of Duomeen L-15 (25%) concentrate in various solvents and surfactants applied as aqueous spray against larvae and pupae of *C. tarsalis* in experimental ponds.

Rate lb/A	Solvent	Surfactant (2%)	Avg. no. of larvae and pupae 5/dips: Pre-treat L	Pre-treat P	Post-treat (24 hr) L	Post-treat (24 hr) P	(%) Reduction
			Aug. 8, 1975				
0.25	Xylene	Arlatone T	26	3	61	2	0
0.50			40	9	58	3	0
1.00			37	17	39	4	20
Check	...	...	14	1	24	1	0
			Aug. 4, 1975				
0.25	Auto. diesel	Tween 20	31	5	21	1	39
0.50	No. 2		54	27	4	0	95
1.00			51	14	0	0	100
Check	...	...	18	4	32	2	0
			Aug. 14, 1975				
0.50	Sunland	Tween 20	33	6	4	2	85
1.00	Auto. diesel		28	3	2	0	94
Check	...	..	6	3	8	2	0

Table 5. Evaluation of Armeen L-15 (25%) concentrate in various solvents and surfactants applied as aqueous spray against larvae and pupae of *C. tarsalis* in experimental ponds.

Rate lb/A	Solvent	Surfactant (2%)	Avg. no. of larvae and pupae 5/dips				
			Pre-treat		Post-treat (24 hr)		(%) Reduction
			L	P	L	P	
			July 7, 1975				
0.25	Xylene	PL-101	100	30	55	10	50
0.50			155	59	21	10	86
1.0			70	53	3	4	94
0.25	Auto. diesel	Arlatone T	180	57	35	11	81
0.50	No. 2		103	88	3	1	98
1.00			104	47	0	0	100
Check	...	...	50	4	47	7	0
			Aug. 4, 1975				
0.50	Sunland	Arlatone T	24	3	3	0	89
1.00	Auto. diesel		32	6	0	0	100
Check	...	...	6	3	8	2	0

vents with Arlatone T gave the best results. At 0.5 lb/A, the formulation in automotive diesel No. 2 was slightly more effective than the others producing 98 percent reduction in the population (Table 5).

From these studies, it is apparent that Armeen DML-15D (at 0.5 lb/A) concentrates formulated in xylene and the surfactants PL-121, Tween 20 and Arlatone T, yield good control of *Culex* species in water impoundments devoid of vegetation. Duomeen L-15 on the other hand, when formulated in xylene and Arlatone T, yielded no control of *C. tarsalis* at the rates of up to 1 lb/A. This material, however, when formulated in 2 types of automotive diesel with the surfactant Tween 20, produced excellent control at 0.5 lb/A. Armeen L-15 concentrates in xylene and 2 diesel type solvents yielded good control of *C. tarsalis* in the experimental ponds. This material was more effective when formulated in the diesel type solvents and Arlatone T as the surfactant. It is evident that Duomeen L-15 and Armeen L-15 are the most effective materials formulated in the diesel type solvents containing the surface active agents Tween 20 and Arlatone T respectively, and their concentrates are stable and yield stable emulsions when mixed in water.

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