PESTICIDE DELIVERY FROM CULIGEL® SUPERABSORBENT POLYMERS: MOSQUITO AND COCKROACH CONTROL STUDIES

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Abstract—Several types of Culigel® superabsorbent polymers were evaluated as matrices for the controlled release and/or encapsulation of insect growth regulators, bacteria, or organophosphates for long-term control of immature mosquitoes or adult and immature cockroaches. Bioassays against mosquito larvae with Culigel®-insecticide granules indicated that insecticide formulation loading levels, controlled release profiles, and duration of efficacy in an aquatic habitat were regulated by the inert ingredients admixed with the insecticide formulations. Bioassays against German cockroach adults or nymphs with agglomerated wafer-like disquets that were fabricated by agglomerating admixtures of a Culigel® superabsorbent polymer, an insect growth regulator and/or organophosphate, and bait/inert materials suggested that single- or joint-action insecticide/bait formulations can be encapsulated within a solid Culigel® superabsorbent polymer matrix to provide slow, long-term cockroach control. Data indicated that insecticide release profiles and the duration of effectiveness were affected by the bait/inert ingredients incorporated in the disquets.

INTRODUCTION

Reviews of the patented (U.S. Patents 4,818,534; 4,983,389; 4,983,390; 4,985,251; U.S. and overseas patents pending) technology pertaining to the Culigel® controlled-release and pest-management systems are presented in a series of publications (Levy *et al.*, 1988, 1989, 1990a,b, 1991, 1992a,b,c,d, 1993a,b,c). These articles highlighted areas such as a general overview of patented Culigel® superabsorbent polymer formulation technology for pest control in aquatic and terrestrial environments, types of Culigel® acrylamide and/or acrylate superabsorbent polymers, manufacturing techniques for encapsulation or entrapment of bioactive agents in solid (e.g., granules or pellets) non-agglomerated/agglomerated and flowable variable-viscosity (water- or oil-based) Culigel® formulations, factors affecting bioactive agent loading in solid and flowable Culigel® formulations, environmental/habitat factors affecting controlled- release performance of Culigel® compositions, formulation factors affecting controlled-release performance and kinetics, bioassays and small-plot field trials, ground and aerial application techniques, Culigel® formulation potentials for control of aquatic and terrestrial pests, and techniques for utilization of Culigel® superabsorbent polymers exclusive of any bioactive agent(s) for pest control in aquatic and terrestrial habitats.

For the most part, research has focused on the potential for utilizing several types of granular Culigel® superabsorbent polymers as matrices for controlled release of dispersant- or dispersant complex-regulated bioactive agents for control of aquatic pests, particularly controlled release of insect growth regulators, bacteria, and an organophosphate against immature mosquitoes. Research in the aquatic area also focused on aquatic weed control (Levy *et al.*, 1993b,c). Although mosquito control continues to be our primary interest, formulation research was initiated to determine the potential for encapsulation and slow release of bioactive agents from Culigel® superabsorbent polymers for terrestrial pest management in urban and agricultural environments. Cockroaches were utilized as test organisms in these studies to initially evaluate the sustained pest-control potential of Culigel® solid or gel (variable-viscosity) formulations in a nonaquatic environment (Levy *et al.*, 1992a, 1993c).

The following paper reviews the literature and summarizes some bioassay results on the potential application of Culigel® superabsorbent polymer granules for controlled release of conventional and biological insecticides against mosquito larvae. The present study highlights the results of long-term bioassays against German cockroach adults or nymphs with solid Culigel®-based disquets composed of bait/inert formulations of an insect growth regulator and/or organophosphate.

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METHODS AND MATERIALS

Mosquito studies

Granule-transfer bioassay methodology for evaluating the efficacy of Culigel® controlled-release insecticide granules against mosquito larvae was described in previous reports (Levy *et al.*, 1992d, 1993a). In general, bioassays were conducted in glass pans containing 1000 ml of fresh, brackish, or polluted water (0.068 m^2 water surface), ten 2nd instar *Aedes* (e.g., *Ae. taeniorhynchus* or *Ae. aegypti*) or *Culex* (e.g., *Cx. quinquefasciatus*) larvae (i.e., one larval brood) and food (ground rabbit chow). Tests were conducted in a room maintained at ca. 26.6°C and 80% RH.

Larvae were challenged with one Culigel® Type I (Crosslinked Copolymer of Acrylamide and Sodium Acrylate), Type II (Lightly Crosslinked Potassium Polyacrylate), Type III (Partial Sodium Salt of a Lightly Crosslinked Polypropenoic Acid), or Type IV (Crosslinked Potassium Polyacrylate/Polyacrylamide Copolymer) granule (ca. 2-3 mm) that was loaded with a formulation composed of a dispersant or dispersant complex (e.g., one or more surfactants, alcohols, emulsifiers, salts, etc.), and an insect growth regulator formulation of methoprene (Altosid Liquid Larvicide), diflubenzuron (Dimilin 25W) or pyriproxyfen (Nylar 10% EC), a bacterial formulation of *Bacillus thuringiensis* var. *israelensis* (Vectobac TP) or *Bacillus sphaericus* (ABG-6184), and/or an organophosphate formulation of temephos (Abate 4-E) (3 replications/granular formulation).

Percent mortality was recorded at 24 hr post-treatment intervals. Culigel® insecticide granules in a bioassay were transferred to new test pans with new water, larval broods, and food if average mortality was 90% or greater. A bioassay was terminated if test adult emergence or control mortality was greater than 10%. Granule transfers were sequentially continued against new larval broods until average percent control was ineffective.

Bioassays mainly utilized a 10-day interval between granule transfers. During this 10-day period, granules were submerged in the test water with dead larvae/pupae for *Culex* studies (permanent water tests) before being transferred to a new test set-up. In *Aedes* studies (semipermanent water tests), granules were removed from the water and allowed to air-dry for varying periods before being transferred to new pans.

At the termination of a bioassay, mortality data for each replicate was averaged and plotted against time to determine a graphical controlled release profile for each Culigel®-insecticide formulation. The "10-day gaps" on the x-axis between data lines indicates inactive submergence periods between granule transfers. The duration of control and the number of larval broods controlled at a particular application rate were the main criteria used to evaluate the efficacy of specific Culigel®-insecticide granular formulations. Candidate granular formulations for field trials were selected on the basis of bioassay results.

Cockroach studies

Two series of disquet-transfer bioassays were conducted against German cockroach (*Blattella germanica*) nymphs and adults (Navy 3 strain, Virginia Polytechnic Institute and State University). Culigel® Type V (Crosslinked Potassium Polyacrylate/Polyacrylamide Copolymer) granules (100–350 microns) were agglomerated with a bait/inert formulation of an insect growth regulator and/or organophosphate into wafer-like disquets (35 × 10 mm or 35 × 4 mm).

One series utilized 0.5 gallon screen-covered plastic cups (ca. 16.5 cm diameter × 12 cm high) containing 10 cockroach nymphs or adults, a four-compartment petri dish (100 × 15 mm) with one ca. 2.5 or 7.0 g insecticidal disquet in one compartment, a petri dish (35 × 10 mm) with ca. 6 g of rabbit chow pellets (Purina), and a cotton-plugged 8 ml vial of water (Levy *et al.*, 1992a, 1993c). A second series utilized plastic trays (ca. 41 cm long × 23 cm wide × 17 cm high) as bioassay test chambers containing 25 German cockroach adults or nymphs, one 2.5 or 7.0 g Culigel®/insecticide/bait/inerts disquet in the center of a petri dish (50 × 9 mm) that was placed in a corner of the tray, one 2.5 or 7.0 g Culigel® /bait/inerts disquet in the center of a petri dish (50 × 9 mm) that was placed in a second corner, a petri dish (35 × 10 mm) of 6 g of rabbit chow pellets in the centre of a petri dish (50 × 9 mm) that was placed in a third corner of the tray, and a cotton-plugged vial

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of water (8 ml) that was in a square petri dish (100 × 15 mm) that was centrally located in the test tray. Each disquet formulation evaluated in a test series was replicated three times.

Disquets contained a single-action insect growth regulator formulation called Nylar technical (pyriproxyfen), a single-action organophosphate formulation called Dursban 4E (chlorpyrifos), or a joint-action formulation of both Dursban4E and Nylar technical. Imitation molasses, synthetic vegetable gums, and binder/dispersant components were utilized in each disquet formulation as bait and/or formulation compatibility ingredients.

The criteria used to evaluate the long-term efficacy of single- and joint-action disquet formulations were as follows. The average percent twisted wing/dark pigmentation abnormalities induced in adult cockroaches exposed to Culigel®-Nylar disquet formulations as nymphs was the main criterion used to evaluate growth regulator efficacy, while average percent mortality of adult cockroaches exposed to Culigel®-Dursban4E disquet formulations was the criterion used to evaluate organophosphate efficacy. Average percent mortality of nymphs and/or adults plus the average percent twisted wing/dark pigmentation abnormalities induced in adult cockroaches were used as combined criteria to evaluate the efficacy of joint-action Culigel®-Dursban4E/Nylar technical formulations that were exposed to the cockroaches as nymphs.

Mortality and/or twisted wing data was recorded in each test series at 24 hr post-treatment intervals. Twisted-wing adults and/or dead nymphs or adults were removed from the test chambers approximately twice a week to avoid errors in data recording. When criteria (i.e., % twisted wings and/or mortality) for a specific disquet formulation in a test series averaged 90% or greater (i.e., 10% or less of the cockroaches did not exhibit the desired insecticidal effect during exposure to the disquet formulations), the disquets were allowed to remain in the cups or trays for an additional 10 days before they were transferred to new test chambers containing new cockroach adults or nymphs, food, and water. Disquet transfers were sequentially continued (e.g., 2nd, 3rd, 4th, 5th, 6th, etc.) according to this procedure until greater than 10% of the cockroaches in a test series exhibited normal adult development (i.e., straight wings and/or no death after prolonged exposure to the single- and joint-action growth regulator and organophosphate disquet formulations). A test series was terminated if cockroach mortality in controls exceeded 10%.

Average percent mortality and/or twisted wings were plotted against time to determine the sustained controlled release profile and duration of effectiveness of each agglomerated disquet formulation against German cockroach adults or nymphs. The "10-day gaps" on the x-axis between data lines indicates inactive or resting periods before transfer of disquets to new test chambers to challenge new groups of cockroach adults or nymphs. Cockroach bioassays were shielded from direct light with black sheets of plastic in a room maintained at ca. 26.1–27.7°C and 68–77% RH.

RESULTS

Mosquito bioassays

Tests against larvae of *Cx. quinquefasciatus* in brackish water indicated that a variety of acrylamide and acrylate Culigel® Type I, II, III, or IV superabsorbent polymer granules can be utilized as matrices for encapsulation and prolonged controlled-release of insect growth regulators, bacterial larvicides, or an organophosphate larvicide (Fig. 1). Our data indicated that optimum loading levels and controlled-release profiles for each insecticide formulation were mainly dependent on the inert dispersant or dispersant complex (e.g., sulfonate- or alcohol-based) admixed with the insecticide (Levy *et al.*, 1988, 1989, 1990a,b, 1991, 1992a,b,c,d, 1993a,b,c). Selection of an appropriate dispersant or dispersant complex was also shown to compensate for extreme variations/fluctuations in insecticide release rates due to habitat water quality.

A range in the duration of effective insecticide release from Culigel® Type I-IV microporous granules (i.e., fast, slow, or delayed insecticide delivery) was obtained by simply altering the type of Culigel® superabsorbent polymer matrix or the type and/or concentration of dispersant or dispersant complex formulated with the insecticides (Fig. 2). In general, the controlled release performance of Culigel® granules was formulation dependent.

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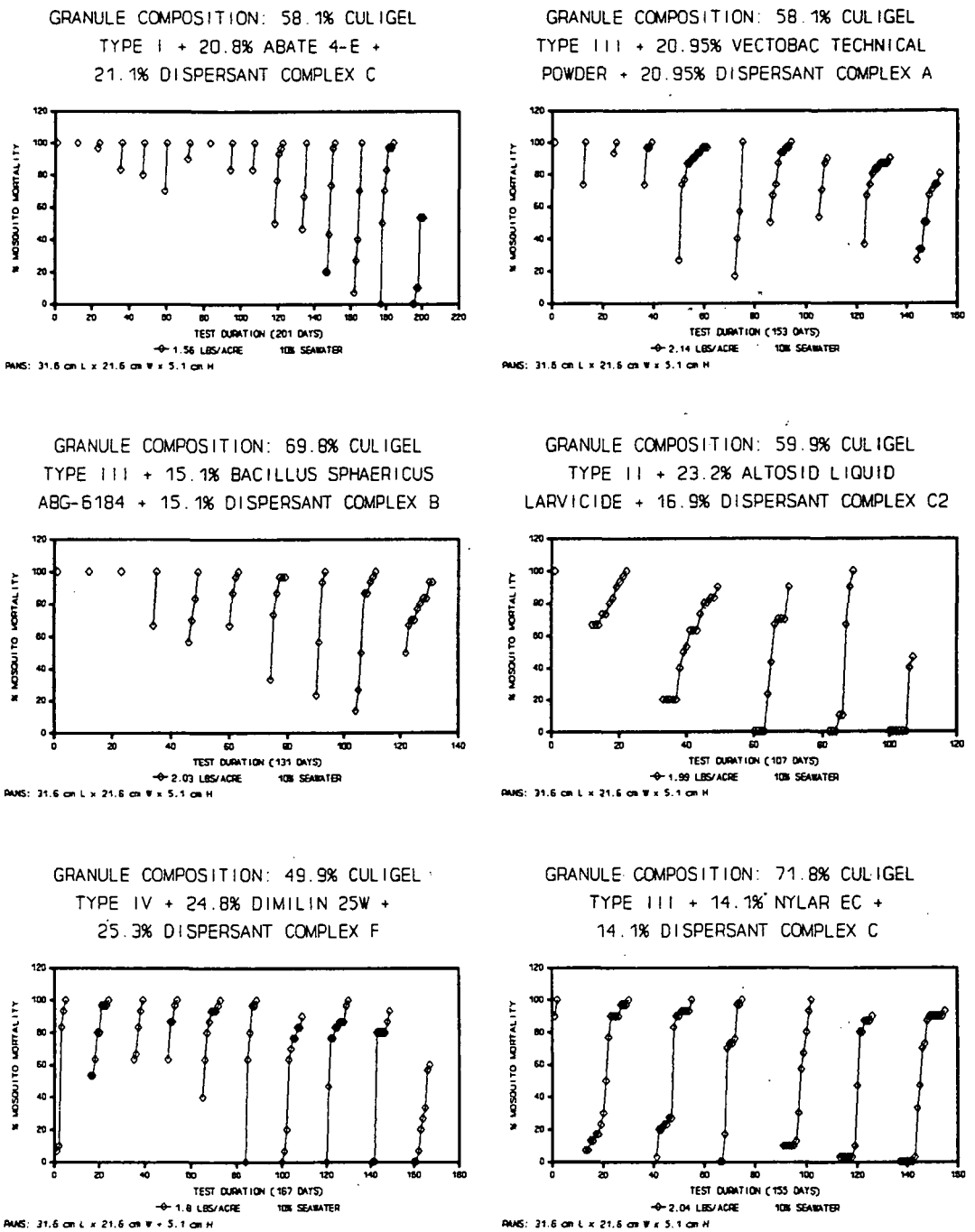

Fig. 1. Controlled-release profiles of several dispersant complex-regulated formulations of mosquito larvicides from Culigel® Type I-IV superabsorbent polymer granules. Granules evaluated against 2nd instar larvae of *Culex quinquefasciatus*.

Cockroach bioassays

Preliminary tests (Levy *et al.*, 1992a, 1993c) in plastic cups against German cockroach adults or nymphs with single-action Culigel® Type V insecticide/bait disquets indicated that slow, long-term cockroach control can be obtained with encapsulated organophosphate or growth regulator

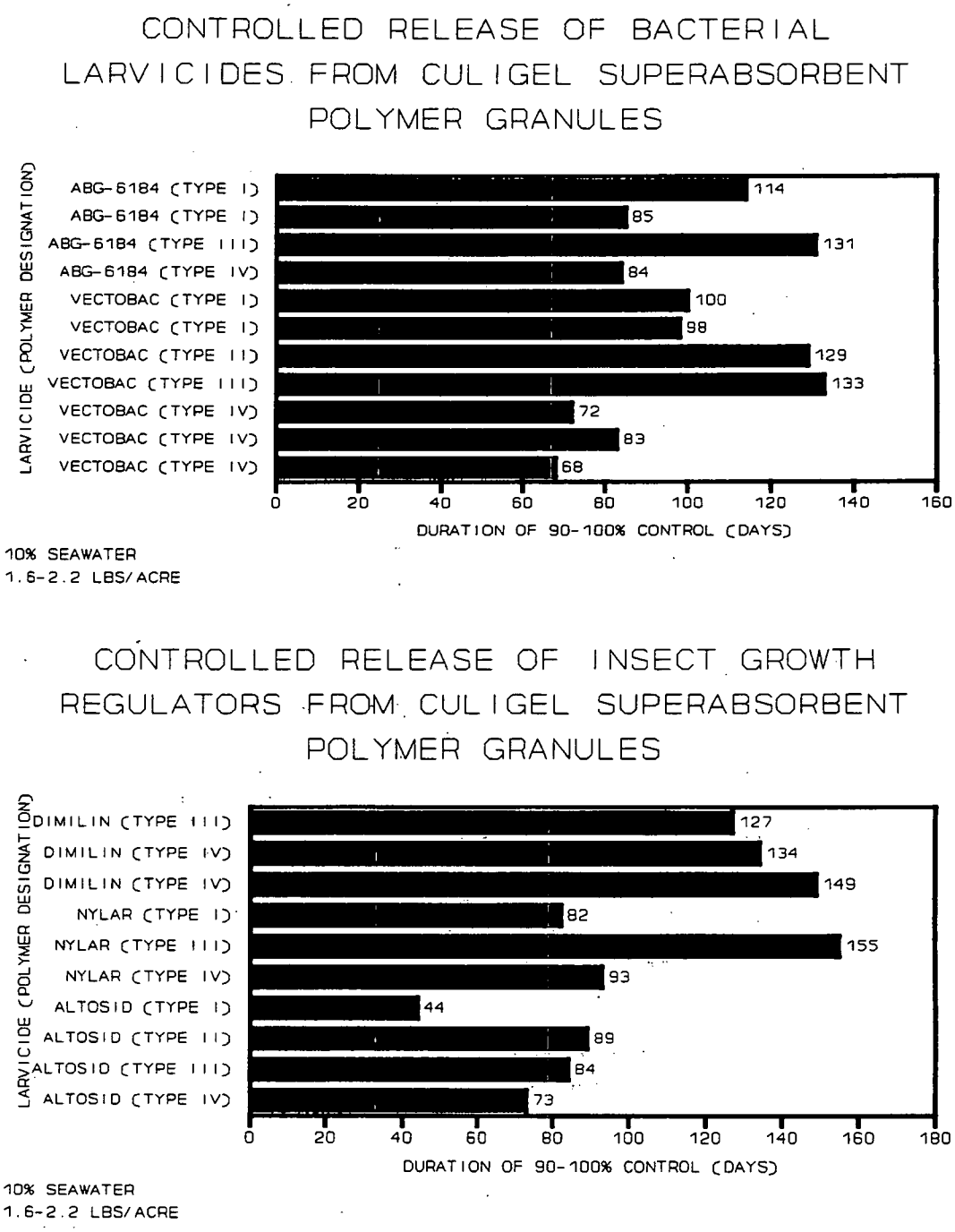

Fig. 2. Sustained delivery of several dispersant- or dispersant complex-regulated formulations of mosquito larvicides from Culigel® Type I-IV superabsorbent polymer granules. Granules evaluated against 2nd instar larvae of *Culex quinquefasciatus*.

formulations (Fig. 3). Results suggested that the concentration of bait/inerts admixed with an insecticide formulation could affect controlled-release profiles, duration of insecticide delivery, and/or the number of cockroach groups controlled with a disquet.

Comparative bioassays in trays against German cockroach adults and nymphs with single-action Culigel®-based (Nylar or Dursban) disquets formulated with and without bait/inerts indicated that these ingredients were important in providing sustained release of the insecticidal agents for

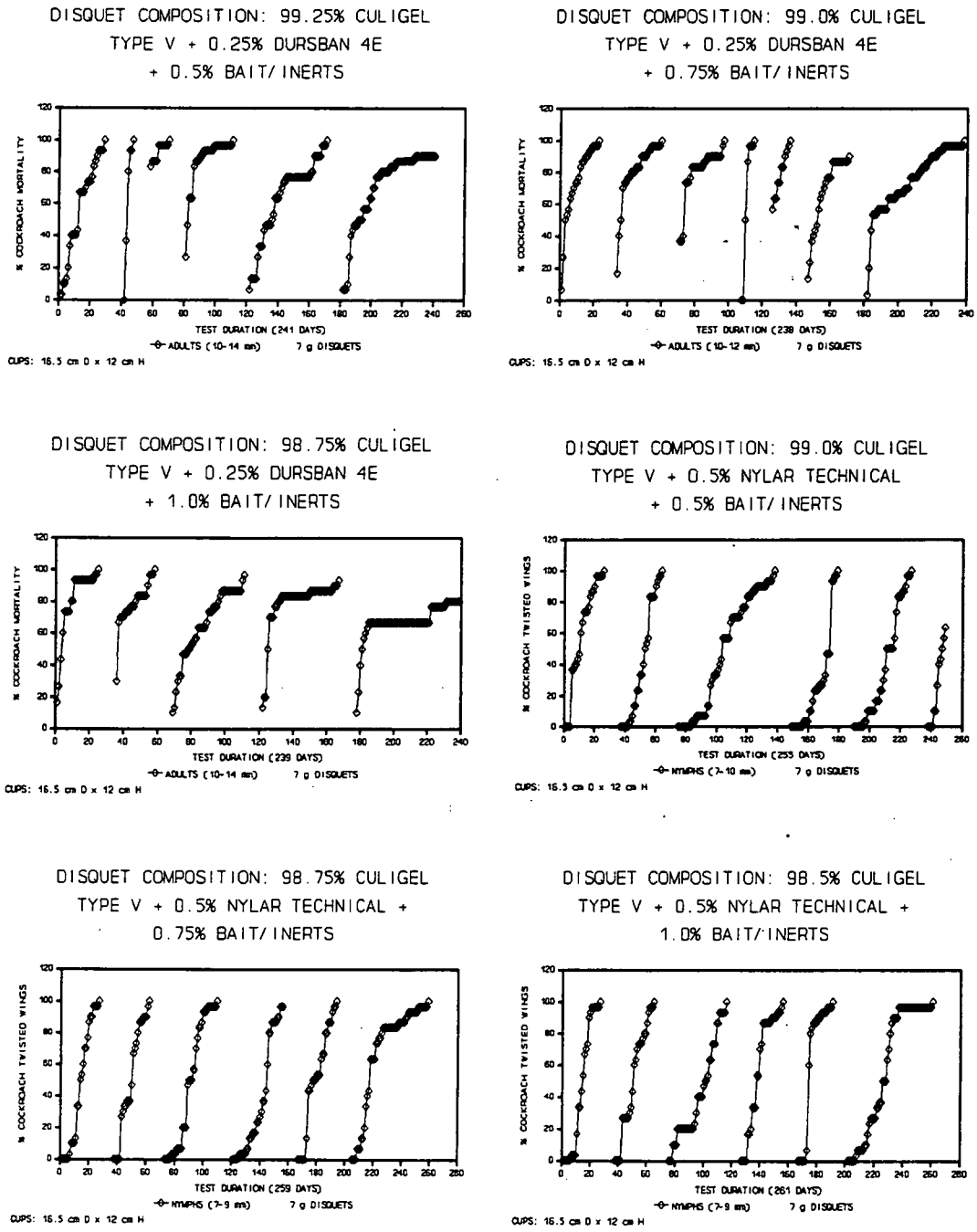

Fig. 3. Long-term delivery profiles of single-action cockroach insecticide-bait formulations encapsulated in Culigel® Type V-based superabsorbent polymer disquets. Disquets evaluated against German cockroach (*Blattella germanica*) nymphs or adults.

prolonged cockroach control (Fig. 4). In general, control trends in trays were significantly slower than observed in cup tests with a comparable disquet formulation. This observation was presumed to be related to differences in test chamber surface area, the number of cockroaches in a bioassay, and to the presence or absence of a bait/inert disquet as an additional food/attractant source. Bioassays with insecticide/bait diquets are currently in progress.

Bioassays against cockroach nymphs were also conducted in trays with joint-action Culigel®-

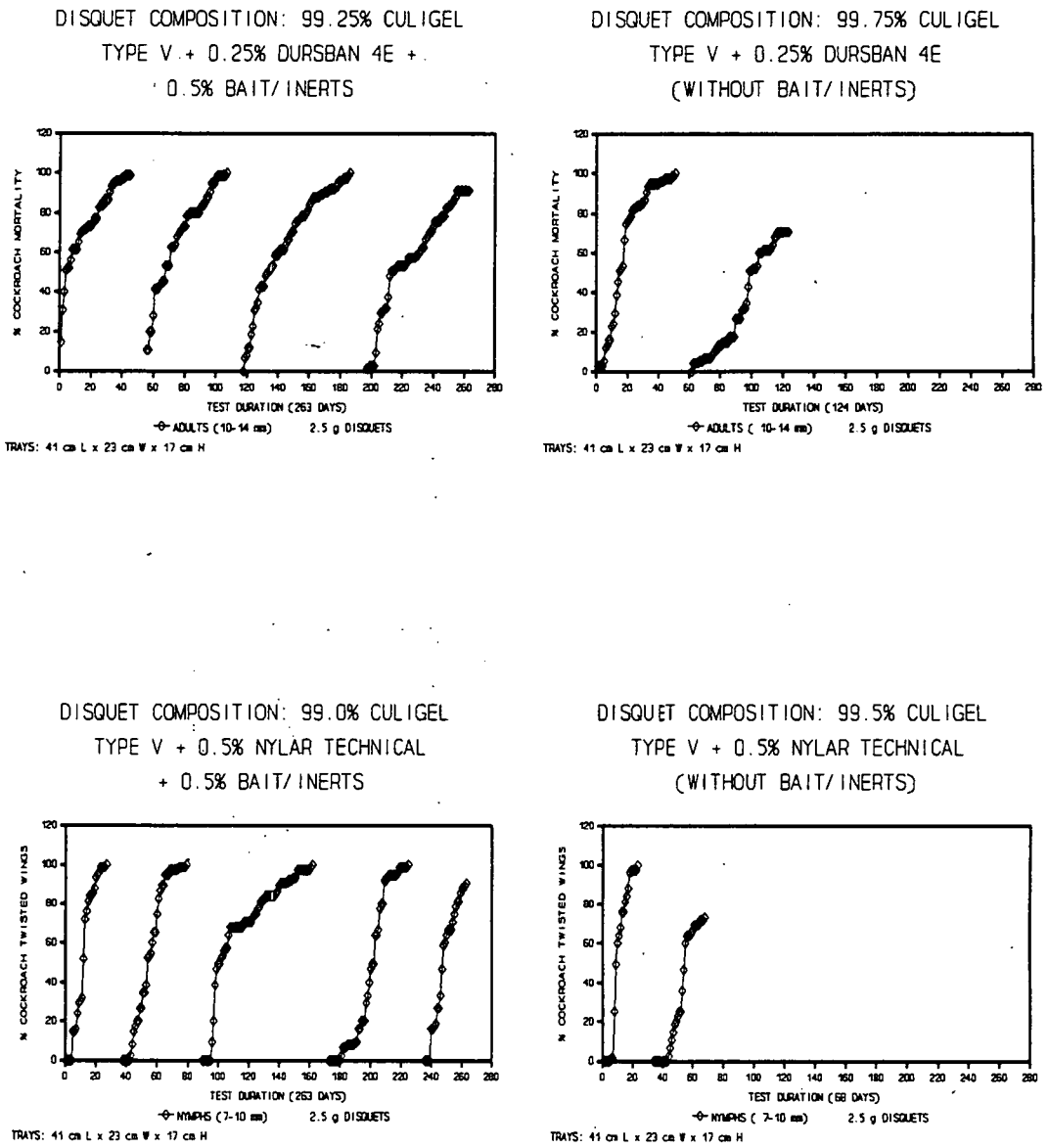

Fig. 4. Long-term delivery profiles of single-action cockroach insecticides encapsulated in Culigel® Type V-based superabsorbent polymer disquets formulated with and without bait ingredients. Disquets evaluated against German cockroach (*Blattella germanica*) nymphs or adults.

based disquets containing Dursban 4E, Nylar technical, and bait/inert ingredients (Fig. 5). The data indicated that joint-action insecticide release profiles were affected by the concentration of bait/inerts in a disquet. Joint-action disquets formulated with half the growth regulator and organophosphate concentration of a standard joint-action disquet produced significantly lower levels of cockroach control when evaluated in comparative bioassays.

In general, results suggested that joint-action Culigel®-based disquet formulations could provide slow, long-term simultaneous control of both adults and nymphs. The dual action of the two insecticidal agents in the disquets (i.e., produced varying percentages of dead nymphs, twisted wing adults, dead normal adults, and dead, twisted wing adults) exhibited a faster rate of cockroach control than disquets formulated with either Nylar or Dursban; however, at a higher combined insecticide application rate. Joint-action bioassays, with the exception of the low rate disquet, are currently in progress.

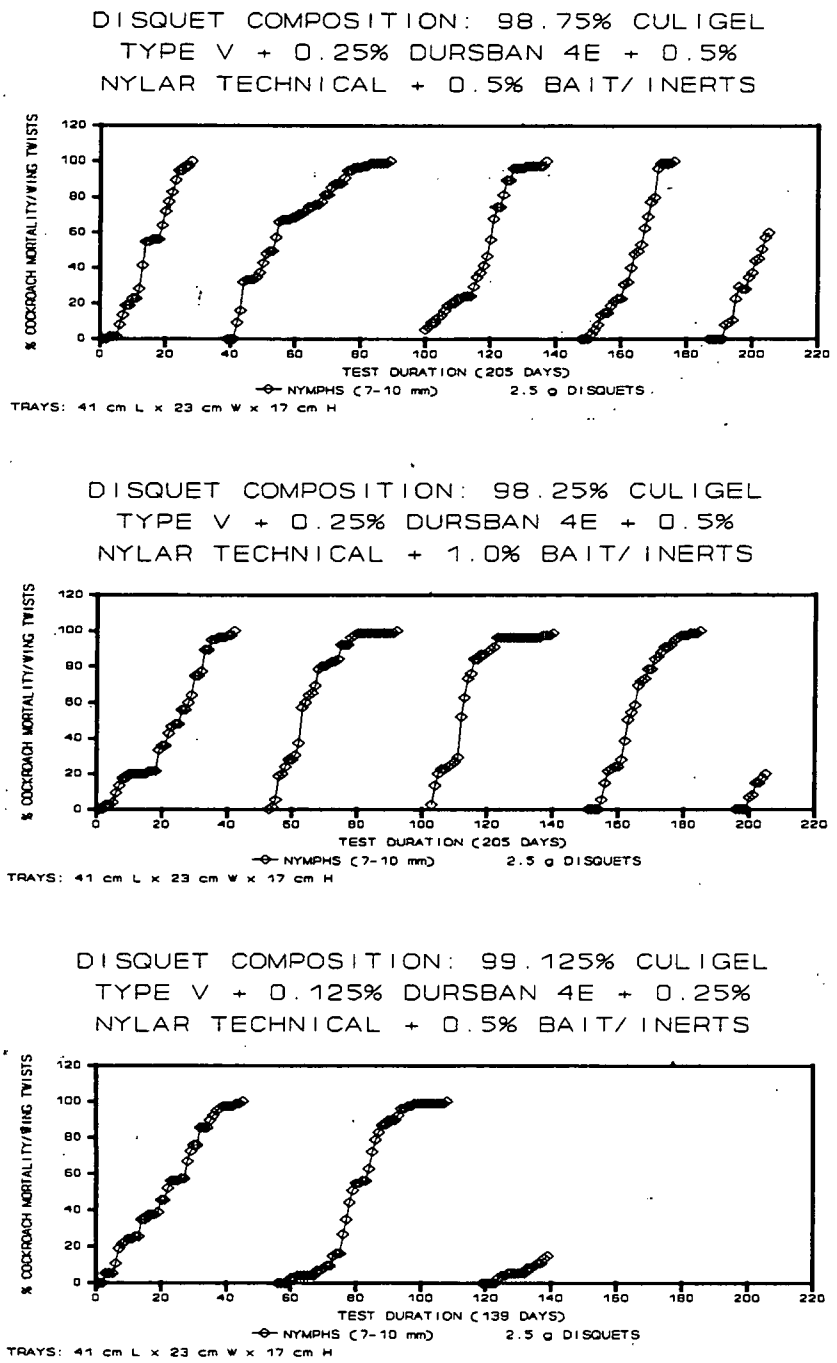

Fig. 5. Long-term delivery profiles of joint-action cockroach insecticide-bait formulations encapsulated in Culigel® Type V-based superabsorbent polymer disquets. Disquets evaluated against German cockroach (*Blattella germanica*) nymphs.

DISCUSSION

Several types of Culigel® superabsorbent polymer granules (i.e., Type I-IV) can serve as effective encapsulation and controlled-release matrices for a variety of bioactive agents used to control immature mosquitoes in aquatic environments. Inert formulation ingredients can be used as dispersants or dispersant complexes to provide optimum controlled release characteristics (e.g., first-order or square-root-of-time kinetics) for specific insecticides. Shelf-life studies and bioassays

have suggested that the granular matrices can effectively protect the bioactive agents from degradation during typical storage periods (i.e., 3–12 months).

Culigel® Type V superabsorbent polymer can serve as an encapsulation/entrapment matrix for fabricating (via agglomeration) single- or joint-action insect growth regulator and/or organophosphate and bait/inert formulations into wafer-like disquets for use as German cockroach bait-stations. Cockroach adults and nymphs were observed to travel over and feed on the Culigel®-based bait- insecticide disquets; however, the materials utilized as a bait in the bioassays did not exhibit strong feeding attractancy when compared to the standard food. The bait/inerts could also serve as a formulation compatibility ingredient to improve distribution, migration, or release characteristics of the insecticidal agent(s) in or from a solid disquet composition. Comparative bioassays against cockroaches with new and old insecticidal disquets indicated that the shelf-life of the disquet formulations would be satisfactory over typical storage and use periods (i.e., 3-12 months). Single- and joint-action gel formulations are also being evaluated.

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