

Original Article

Improvement of Insecticidal Efficacy of Carbaryl Emulsifiable Concentrates by Isobornyl Thiocynoacetate*

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An emulsifiable concentrate of carbaryl was developed and its efficacy improved by synergization with isobornyl thiocynoacetate. The formulations exhibited satisfactory physico-chemical characteristics. Emulsions (up to 0.2% carbaryl) from these concentrates exhibited no phytotoxicity against *Vicia faba*, *Daucus carrota*, *Brassica oleracea*, *Gossypium hirsutum*, *Raphanus sativus*, *Brassica juncea* and *Lycopersicum esculentum*. The synergized concentrate, however, showed phytotoxicity against *Solanum tuberosum* and *Hibiscus esculentus*. Isobornyl thiocynoacetate showed a factor of synergism of 2.5 at the 1 : 1 synergized concentrate. For a comparable bioefficacy with the commercial WDP, only 1/3 to 1/5 of carbaryl from these concentrates was required. Their 0.05% emulsions controlled the bollworm complex in cotton, increased seed cotton yield and left no detectable residues in lint and seed at harvest. In insect control and yield increase, the 0.05% emulsions from the synergized EC matched 0.2% carbaryl from WDP and 0.02% fenvalerate emulsions. Carbaryl WDP and fenvalerate, however, left detectable residues at harvest.

Carbaryl (1-naphthyl *N*-methyl carbamate) is one of the earliest and most popular amongst carbamate pesticides. Its low mammalian toxicity, environmental degradability and a broad spectrum of insect toxicity are responsible for its extensive usage throughout the world. A number of its solid and liquid formulations are commercially available and these could be referred to in literatures. No information on an emulsifiable concentrate (EC) formulation of this toxicant was traceable in literatures although such formulations are stated to be in use in Japan (personal communication). This paper embodies the results of emulsifiable concentrates of carbaryl developed by us. The efficacy of carbaryl in such concentrates has been improved by using isobornyl thiocynoacetate as a synergist.

MATERIALS AND METHODS

1. Materials

Technical carbaryl (97% a.i.) and 50% commercial carbaryl (Sevin) water dispersible powder were obtained from M/s Union Carbide (India) Ltd., Bhopal, Madhya Pradesh, India. Fenvalerate (Sumicidin 20% EC) was obtained from M/s Rallis India Ltd., Bangalore, Karnataka, India. Isobornyl thiocynoacetate was procured from M/s Camphor and Allied products Ltd., Bareilly, Uttar Pradesh, India. Various solvents, surfactants and other auxiliaries were commercial grade, indigenously available materials.

2. Preparation of Emulsifiable Concentrates and Determination of Physico-chemical Characteristics

The concentrates (carbaryl 10% w/v) were prepared as per method reported earlier.¹⁾

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The synergized concentrate contained the insecticide and isobornyl thiocynoacetate (synergist), at 1 : 1. Emulsion characteristics, cold test (low temperature stability) and acidity or alkalinity were evaluated before as well as after heat stability requirement; flash point and visual description were noted only before the heat stability requirement. Recommended ISI²⁾ test methods were followed. More severe test conditions compared to those prescribed²⁾ were also investigated and these are appropriately indicated in the text.

3. Phytotoxicity

Different carbaryl concentrations from both the normal and the synergized concentrates were sprayed as emulsions over bean (*Vicia faba*) at flowering and pod formation, over carrot (*Daucus carota*) at full carrot formation, over cauliflower (*Brassica oleracea*) at flowering, over cotton (*Gossypium hirsutum*) 11–17 days old in pots and 7 week old in the field, over okra (*Hibiscus esculentus*) 15 days old, over potato (*Solanum tuberosum*) at tuber formation, over raddish (*Raphanus sativus*) at full raddish formation, over rapeseed (*Brassica juncea*) at flowering and pod formation and over tomato (*Lycopersicum esculentum*) at flowering. Solvent emulsions at 2 and 5% were sprayed as controls. The plants were generally oversprayed by completely drenching them with the spray. Only visual observations indicating any adverse effect on the plants were recorded. Observation period ranged between 10–40 days.

4. Bioassay

Isobornyl thiocynoacetate was evaluated as a carbaryl synergist (carbaryl : synergist, 1 : 5) initially by the filter paper impregnation technique³⁾ and subsequently in the emulsifiable concentrates (carbaryl : synergist, 1 : 1) by the Potter's direct spray technique.⁴⁾ Acetone solutions (0.5 ml) of carbaryl and/or synergist were impregnated on pieces of filter paper (dia 7 cm) without using any fixative oil. After placing the ground glass rings, 10 insects per paper were released in 3 replications. Spraying details by the Potter's technique are already reported.⁵⁾ A comparison of these concentrates with the commercial 50%

carbaryl water dispersible powder (WDP) was also done by the spray technique.⁴⁾ Appropriate untreated, solvent, solvent water emulsions, etc. controls were maintained as required. Laboratory reared, 15 days old adult red flour beetle, *Tribolium castaneum* Herbst. was the test insect. The mortality counts, recorded 72 hr after the treatment were subjected to probit analysis⁶⁾ and factor of synergism⁷⁾ or carbaryl units for the same bio-efficacy worked out.

5. Field Experiment

Cotton, *Gossypium hirsutum* Linn. "Selection 95" was sown in 10 m² plots on 25th May, 1980 on the farm of the Institute. A randomized block design was employed and each treatment was replicated four times. Five sprays each of carbaryl WDP (0.2% suspension), carbaryl and synergized carbaryl EC (0.05% emulsion each) and fenvalerate EC (0.02% emulsion) were made @ 500 l/ha/spray at 10 days interval commencing from 11th August, 1980, on the day when bollworms first appeared.

6. Efficacy of Insecticidal Treatments

Starting with the 2nd spray, 8 plants per plot were randomly selected before each spray, number of healthy and affected bolls were counted and infestation expressed as % damage.

7. Residue Determination

The residues were estimated in leaves (at 1 hr and 10th day after each spray) and lint and seed (at harvest, 20th October). Carbaryl residues were extracted with methylene chloride, filtered through Hyflo Super Cel and cleaned.⁸⁾ Carbaryl in cleaned extracts was hydrolyzed with strong alkali, derivatized with 1-fluoro-2,4-dinitrobenzene and estimated by GLC⁹⁾ using Tracor MT 220 gas chromatograph.

Fenvalerate residues were extracted in acetone, cleaned up by passing through a neutral alumina column and analyzed by GLC.^{10, 11)}

Various GLC parameters for both insecticides were: detector ⁶³Ni electron capture; column 3% OV-17 on Chromosorb W (HP);

temperatures (°C) -column 225, inlet 250, detector 275; carrier gas (N) 80 ml/min. Three microlitre sample was injected.

RESULTS AND DISCUSSION

1. Physico-chemical Characteristics

The physico-chemical characteristics of the concentrates are reported in Table 1 (a, b and c). As it is apparent, the formulations generally complied with the requirements prescribed for emulsifiable concentrates. To the best of informations, no specifications for a carbaryl EC are as yet available; leaving no scope for comparisons.

IS: 6940²⁾ prescribes conducting of the emulsion stability test at 30°C for 1.0 hr whereas CIPAC¹²⁾ prescribes a period of 24 hr followed by re-emulsification after that period. The present samples were left at room temperature (~20°C) after 8 hr. As it is apparent from Table 1a, these formed stable emulsions and at 24 hr, little (often unmeasurable) solid settled at the bottom. Re-emulsification of the samples at 24 hr left this solid dispersed up to the final observation period.

In India, as a normal agricultural practice, pesticide emulsions are sprayed within 1–2 hr of their preparation. The present concentrates can thus be safely recommended.

A cold test at 10°C for 1 hr is the usual ISI prescription.²⁾ CIPAC¹²⁾ prescribes conducting this test at 0±1°C with occasional shaking for 1 hr and subsequently keeping and observing the samples for 7 days at this temperature. In these studies, the conditions as stated in Table 1b were maintained. Under these, the test samples performed satisfactorily. Slight solid settling, whenever observed, vanished when the samples were brought back to above 20°C.

The flash point of both the formulations was above 24.5°C and acidity as H₂SO₄, though marginally above the usually prescribed limit of 0.05%, was not expected to have any adverse effect on this active ingredient.

2. Phytotoxicity

The 0.1% carbaryl emulsions prepared from any one of these concentrates showed no phytotoxicity against any test plant except

Table 1 Physico-chemical characteristics of carbaryl emulsifiable concentrates.

a) Emulsion characteristics^{a)} (values in ml).

Particular	Initial emulsification	Emulsion stability on standing												Final emulsion stability after re-emulsification at 24 hr			
		30 min and 1 hr				2 hr				24 hr							
		C.L.	O.L.	S.S.	F.L.	C.L.	O.L.	S.S.	F.L.	C.L.	O.L.	S.S.	F.L.	C.L.	O.L.	S.S.	F.L.
Carbaryl EC	Instant, V. good	Nil	Nil	Nil	Nil	<1.0	Nil	Nil	Nil	Nil	Nil	Slight fluffy	Nil	Nil	Slight	Nil	
Synergized carbaryl EC	Instant, V. good	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Slight fluffy	Nil	Nil	Nil	Nil	

(to be continued)

Table 1 (continued)

b) Cold test^{b)} (low temperature stability).

Particular	Pre-heat storage test					Post-heat storage test				
	Temp. (°C)	Period (upto)	O.M.	Turb.	S.S.	Temp. (°C)	Period (upto)	O.M.	Turb.	S.S.
Carbaryl EC	0-1	2 hr	Nil	Nil	Nil	10	7 hr	Nil	Nil	Nil
	3	6 hr	Nil	Nil	Nil	6	96 hr	Nil	Nil	Nil
	6	24 hr	Nil	Nil	Nil					
	7	25 days	Nil	Nil	Nil					
Synergized carbaryl EC	0-1	2 hr	Nil	Nil	Nil	10	7 hr	Nil	Nil	Nil
	3	6 hr	Nil	Nil	Nil	6	24 hr	Nil	Nil	Nil
	7	24 hr	Nil	Nil	Nil		55 hr	Nil	Nil	Slight
		48 hr	Nil	Nil	Slight		11 days	Nil	Nil	Slight
		25 days	Nil	Nil	Slight (no further increase)					(no further increase)

c) Acidity, flash point and general description.

Particular	Acidity(%) as H ₂ SO ₄ (w/w)		Flash point (°C)	Description
	Pre-heat storage	Post-heat storage		
Carbaryl EC	0.056	0.064	49.5	Clear stable liquid, deep yellow colour free from extraneous impurities
Synergized carbaryl EC	0.056	0.070	51.0	Clear stable liquid, brown colour free from extraneous impurities

^{a)} C.L.: creamed layer at top, O.L.: free oil separation layer, S.S.: solid settled, F.L.: froth layer at top. The values after the heat stability test were the same as before the test except a change in 2 hr creamed layer value from <1.0 to nil.

^{b)} O.M.: oily matter, Turb.: turbidity, S.S.: solid separation.

potato (*Solanum tuberosum*) in which case the emulsions from the synergized EC severely damaged about 43% of the treated leaves. Cotton (*Gossypium hirsutum*) was in addition sprayed with 0.2 and 0.5% carbaryl emulsions. Whereas 0.2% emulsions caused no phytotoxicity, the 0.5% concentrations from both the concentrates were phytotoxic. Increasing synergist concentration in the emulsions increased phytotoxic effect. The solvent and surfactant had no effect. The 0.2% carbaryl emulsions from the synergized EC were phytotoxic against okra (*Hibiscus esculentus*) too.

3. Synergization by Isobornyl Thiocyanacetate

The factors of synergism by using isobornyl

thiocyanacetate as a carbaryl synergist are reported in Table 2. Whereas the preliminary screening of isobornyl thiocyanacetate as a carbaryl synergist (carbaryl : synergist, 1 : 5) by applying acetone solutions on filter papers revealed a factor of 31.4, the same in the 1 : 1 synergized EC by the direct spray technique was 2.5. A higher factor by the filter paper impregnation technique was expected because no fixative oil as prescribed in³⁾ was used. This screening had a limited objective of confirming the synergistic ability of isobornyl thiocyanacetate before its incorporation into the EC. The factor obtained by testing the concentrates by the direct spray technique provided an index for the probable potential of the synergist in the final formulation.

Table 2 Synergisation of carbaryl by isobornyl thiocynoacetate against *Tribolium castaneum* Herbst.

Particular	Heterogeneity	Regression equation	Log (LC ₅₀ ×) ± SE	LC ₅₀ (% carbaryl)	Fiducial limits	Factor of synergism
A. Filter paper impregnation method						
Carbaryl alone	$\chi^2_{(4)} = 4.777$	$Y = 1.523x + 2.317$	$\times 10^1$ 1.7610 ± 0.1411	5.7680	4.1680–7.9820	—
Carbaryl + isobornyl thiocynoacetate (1+5)	$\chi^2_{(3)} = 0.846$	$Y = 5.755x - 2.272$	$\times 10^2$ 1.2630 ± 0.0550	0.1832	0.1614–0.2080	31.4
B. Potter's direct spray technique						
Carbaryl EC	$\chi^2_{(5)} = 0.698$	$Y = 2.737x - 0.606$	$\times 10^3$ 2.0482 ± 0.0686	0.1117	0.0954–0.1308	—
Synergized carbaryl EC	$\chi^2_{(5)} = 4.223$	$Y = 2.939x + 0.149$	$\times 10^3$ 1.6505 ± 0.0647	0.0447	0.0385–0.0519	2.5

4. Comparison with the Commercial Carbaryl Water Dispersible Powder

The data in Table 3 reveal that for the same bioefficacy by Potter's direct spray technique, 1 unit of carbaryl from its WDP, 0.368 unit from EC and 0.219 unit from the synergized EC were required. It implied that as compared to the use of a WDP, only about 1/3 to 1/5 of carbaryl from these concentrates was required, resulting in a considerable economy in the use of this insecticide on one hand and a pollution free environment on the other. This finding has been verified on a field scale against cotton.

It may be mentioned that the reason for the differences in the LC₅₀ values of carbaryl emulsions in Tables 2 and 3 by the Potter's direct spray technique was that these bioassay experiments were conducted under ambient conditions during two different seasons of the year—namely summer (Table 2, Temp. ~35°C, R.H. ~40%) and rainy summer (Table 3, Temp. ~35°C, R.H. ~95%). The environment influenced the actual volume of the spray reaching petri-dishes.

5. Field Evaluation against Cotton

5.1 Bollworms control

Data in Table 4 reveal that all the treatments were effective in controlling cotton bollworms. Fenvalerate was most effective followed by the synergized carbaryl EC, carbaryl WDP and carbaryl EC respectively. Fenvalerate, carbaryl-synergized EC and WDP were statistically at par at 5% level. These were better than carbaryl EC.

It is apparent that both the carbaryl emulsifiable concentrates, despite their lower rate of application, were effective in controlling bollworms. Performance of the 0.05% synergized EC matched with 0.02% fenvalerate and 0.2% carbaryl WDP treatments. Carbaryl EC, though not as effective as these three treatments, gave a significant control of bollworms; the differences being significant even at 1% CD level. A slightly higher dose of carbaryl from this EC may be required for a parallel performance.

5.2 Seed cotton yield

Concomitant with the reduced bollworm damage, the yield increased in all the treatments. Highest yield was with fenvalerate,

Table 3 Comparative performance of the emulsifiable concentrates with the commercial carbaryl water dispersible powder.

Particular	WDP	EC	Synergized EC
Heterogeneity	$\chi^2_{(5)}=5.617$	$\chi^2_{(5)}=2.301$	$\chi^2_{(4)}=4.035$
Regression equation	$Y=0.839x+2.633$	$Y=0.922x+3.721$	$Y=1.975x+0.732$
Log (LC ₅₀ ×) ^{a)} ± SE	2.8210 ± 0.3116	1.3872 ± 0.3822	2.1610 ± 0.1098
LC ₅₀ (% carbaryl)	0.0662	0.0244	0.0145
Fiducial limits	0.0323–0.1357	0.0101–0.0588	0.0113–0.0187
Relative carbaryl units	1.000	0.368	0.219

^{a)} × 10³ for EC, × 10⁴ for synergized EC and WDP.

Table 4 Relative efficacy of carbaryl and fenvalerate formulations against cotton bollworm complex.

Treatment	Bollworm infestation (%) observations				Seed cotton yield (kg/ha)
	I	II	III	IV	
Carbaryl EC	14.97	19.61	21.45	27.26	907.0
Synergised carbaryl EC	12.76	16.46	19.15	22.37	1169.1
Carbaryl WDP	13.73	18.91	20.03	21.33	1135.8
Fenvalerate EC	9.59	13.11	16.37	21.12	1267.5
Control	22.08	23.99	28.47	37.69	691.3
Sem ±	1.56	1.14	0.67	1.41	52.43
CD (5%)	5.10	3.71	2.19	4.59	161.54
CD (1%)	7.41	3.79	3.19	6.58	226.48

As to I, II, III, and IV, the treatment was commenced from 11th August, 1980 at 10 days interval, and the observations were done 10 days after the treatment.

Table 5 Residues of carbaryl and fenvalerate on cotton (*Gossypium hirsutum*).

Spray	Days	Residues in leaves (ppm)			
		Carbaryl EC	Synergised carbaryl EC	Carbaryl WDP	Fenvalerate EC
I ^{a)}	0	4.60	6.87	15.24	7.28
	10	1.92	1.86	1.64	1.22
II	0	8.42	6.22	16.80	6.32
	10	1.70	0.68	0.55	1.32
III	0	3.24	3.27	17.10	8.26
	10	0.23	0.78	0.77	1.22
IV	0	4.50	6.00	27.20	6.80
	10	0.62	0.96	6.62	1.40
V	0	6.68	6.54	31.40	7.34
	10	0.72	0.81	4.32	1.44
Lint at harvest		ND ^{b)}	ND	0.164	0.085
Seed at harvest		ND	ND	0.147	0.037

^{a)} Spray I was done on 11th August, 1980. Sprays II, III, IV and V followed at 10 days interval each.^{b)} ND: less than 0.01 ppm.

followed by synergized carbaryl EC, carbaryl WDP and carbaryl EC. The former three treatments were statistically at par and were better than carbaryl EC.

5.3 Insecticide residue

The deposits of different sprays were generally in the order of their sprayed concentrations (Table 5). The rate of insecticide dissipation by using different carbaryl formulations appeared to be the same; in 10 days, 58.2–96.7% of the applied insecticide being lost.

Fenvalerate deposits, despite its lower rate of application, were either comparable to or higher than those from carbaryl EC formulations. It could be ascribed to some inherent property of fenvalerate or to the nature of the formulation auxiliaries. The dissipation rate of fenvalerate was similar to carbaryl.

As is apparent from Table 5, at harvest no detectable residues (<0.01 ppm) of carbaryl existed from either of two emulsifiable concentrates in both lint as well as seed. The WDP left 0.164 and 0.147 ppm and fenvalerate 0.085 and 0.037 ppm residues in lint and seed respectively. The carbaryl emulsifiable concentrates as such, appeared better than both the carbaryl WDP as well as fenvalerate.

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REFERENCES

- 1) B. S. Parmar & Shiv Dutta: Patent application submitted on August 5, 1981 to Indian Council of Agricultural Research for patenting.
- 2) I. S. I.: Methods of tests for pesticides and their formulations, IS: 6940 (1973)
- 3) F. A. O.: *FAO Plant Prot. Bull.* **18**, 107 (1970)
- 4) C. Potter: *Ann. Appl. Biol.* **28**, 142 (1941)
- 5) D. K. Sarkar & B. S. Parmar: *Agric. Biol. Chem.* **43**, 2291 (1979)
- 6) D. J. Finney: "Probit Analysis," 3rd Ed., Cambridge Univ. Press, p. 318, 1971
- 7) P. R. Chadwick: *Pyrethrum Post* **7**, 25 (1963)
- 8) W. R. Benson & J. M. Finnochiro: *J. Assoc. Off. Agric. Chem.* **48**, 696 (1965)
- 9) E. R. Holden: *J. Assoc. Off. Anal. Chem.* **5**, 713 (1973)
- 10) H. K. Jain, N. P. Agnihotri & K. P. Srivastava: *J. Entomol. Res.* **3**, 212 (1979)
- 11) H. K. Jain, N. P. Agnihotri & K. P. Srivastava: *J. Entomol. Res.* **4**, 161 (1980)
- 12) C.I.P.A.C.: "CIPAC Handbook," Vol. I, pp. 910, 930 (1970)

要 約

Isobornyl thiocynoacetate によるカルバリル乳剤の殺虫効果の改良

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Isobornyl thiocynoacetate を共力剤としてカルバリル乳剤の改良を試みたところ、両者 1:1 の組成で殺虫効果において 2.5 倍の共力効果が得られた。この共力剤を加えた乳剤は、バレイシヨおよびオクラに対して薬害を生じた。圃場試験の結果は、この改良剤の有効成分で 0.05% の乳濁液が市販の水和剤の 0.2% (成分) 懸濁液および 0.02% フェンバレート乳濁液に相当する殺虫効果と収量増のあることを示している。また、収穫時においてカルバリル水和剤およびフェンバレート乳剤散布区で各薬剤の残留が認められるのに、カルバリル乳剤では検知できなかった (<0.01 ppm)。