Improving the properties of emulsifiable formulation of pesticides in relation to efficacy against insect pests

iii. Adjuvants enhancing efficacy of cypermethrin and fenitrothion against the Egyptian cotton leafworm, *Spodoptera littoralis*

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Abstract: Non-ionic polyoxyethylene glycol (PEG) 600 di-laurate surfactant, wetting agent; octylphenol ethoxylate (Extravon®) and vegetable oil; Codacide oil were assayed to determine their physical properties alone and/or in combination with two insecticides; cypermethrin (25% EC) and fenitrothion (50% EC) at their half-recommend field rate in Egypt. Efficacy of the admixed insecticides with the evaluated adjuvants has been examined against the 4th instar larvae of Egyptian cotton leafworm, *Spodoptera littoralis*. The obtained results showed that the PEG 600 di-laurate reduced the surface tension for cypermethrin and fenitrothion from 68.62 and 56.7 dyne/cm to 36.14 and 36.7 dyne/cm, respectively, in comparison with Extravon® and Codacide oil. Also, the evaluated adjuvants gave acceptable properties towards the emulsion stability, foaming and emulsification; after 0.5 hr. of mixing PEG 600 di-laurate ranked the most efficient adjuvant for improving the emulsifiable concentrate of the insecticides. It was noticed that the addition of the evaluated adjuvants significantly increased the residual toxicity of the formulated insecticides. It could be also concluded that PEG 600 di-laurate in combination with the tested insecticides at their half recommended field rate gave a good potential for controlling the Egyptian cotton leafworm more than Extravon® and Codacide oil.

Keywords: *Spodoptera littoralis*, Adjuvants, Emulsifiable, cypermethrin, fenitrothion

1. Introduction

The pesticides formulation technology is highly dependent upon the toxic active ingredient, inert substances and adjuvants. Adjuvants are designed to perform specific functions, including buffering, dispersing, emulsifying, spreading, sticking, and wetting properties **(Foy and Pritchard, 1996, Knowles, 2012)**. They are used with pesticides sprays to aid the penetration of the active compound through the waxy layer on plant surfaces and insect exoskeletons by reducing the surface tension **(Schönherr and Baur, 1994, Wang and Liu, 2007)**. Generally, the adjuvants can improve the properties of pesticide applications leading to the enhancement of their effectiveness and biological activity against unwanted insect pests **(Larson, 1997; Cowles *et al.*, 2000; Liu and Stansly, 2000; Lacey *et al.*, 2006)**.

Research on adjuvants and formulation technology of agrochemicals has recently advanced and resulted a large number of adjuvants and pesticide products in the market worldwide. Choosing the best adjuvants is usually difficult. Accordingly, growers must choose from thousands of commercial products and are confused by product descriptions with unfamiliar ingredients and functions in order to select the appropriate pesticide product **(Zollinger, 2000)**. The type of pesticide formulation and in some cases the choice of product of the same formulation type, can markedly affect the results obtained in practical use.

The objectives of the current study aimed to evaluate the influence of some adjuvants including a non-ionic surfactant and wetting agents on the properties of emulsifiable concentrates of two certain insecticide compounds, cypermethrin and fenitrothion selected from two different chemical classes of pesticides, using the spray tank in the field. Also, the efficacy of the insecticide-adjuvant mixtures against the Egyptian cotton leafworm, *Spodoptera littoralis* was inspected and determined under laboratory conditions.

2. Materials and Methods

2.1. Adjuvants

2.1.1. Polyoxyethylene glycol (PEG) 600 di-laurateis, used as a non-ionic surfactant; purchased from the Egyptian Co. for Starch, Yeast and Detergent, Alexandria, Egypt.
2.1.2. Octylphenol ethoxylate (Extravon®), used as a wetting agent; purchased from Syngenta international AG Co., Basel, Switzerland.
2.1.3. Codacide oil, used as vegetable oil adjuvants; purchased from Microcide Limited, Shepherds Grove, Stanton, Bury St Edmunds, Suffolk IP31 2AR, UK.

2.2. Pesticides

2.2.1.Cypermethrin (25% EC), as Sparkile®; a commercial contact pyrethroid insecticide obtained from EL-Help

Pesticides and Chemicals Co., Egypt. The recommended use rate is 600 cm^3/feddan as foliar application.

2.2.2. Fenitrothion (50% EC), as Sumithion®; an organophosphorus insecticide obtained from Summitomo Co., Japan. The recommended use rate is 1.0 L/feddan as foliar application.

2.3. Physical properties of adjuvants alone and in combination with the insecticides

2.3.1. Hydrophilic-lipophilic Balance (HLB) was determined using the method described by **Griffin (1954)**.

2.3.2. Surface tension value (dyne cm-1) was determined using Traube Stalgamometer method **(Phares, 1965)**.

2.3.3. Emulsion stability test of each pesticide alone or/ and admixed with each of the evaluated adjuvants was determined according to **Sherman (1968)**.

2.4. Experiments

2.4.1. Insect rearing

The Egyptian cotton leafworm, *Spodoptera littoralis* was reared on castor-bean leaves for three generations under the prevailing hygro-thermic laboratory conditions of 25±1 °C; 65-70% RH, and a 16:8 L/D cycle until moths emergence. The 4th instars larva was employed in the experiment.

2.4.2. Treatments

The cotton plants were field sprayed by cypermethrin or fenitrothion formulations alone and/or mixed with each tested adjuvant. Both of the insecticides were tested at their recommended (R) and/or half-recommended (0.5 R) rate. Evaluation of the efficacy of the tested insecticides alone and/or mixed with each of the evaluated adjuvants was run by feeding 4th instars larvae of the cotton leafworm on the treated cotton leaves. In order to evaluate the residual efficacy of the tested insecticides alone and/ or admixed with each adjuvant, the leaves were picked and offered to the raised larvae after 3, 6 and 9 days from spraying. The treatments were tricely replicated; with ten 4th instars larvae for each replicate. The mortality percentages were estimated after 48 hrs. and corrected according to the **Abbott formula (1925)**.

2.4.3. Statistical analysis

The obtained results were statistically analyzed according to **(Steel and Torrie, 1980)** and values ± SE were separated by the least significant difference (L.S.D) at 0.05 probability level.

3. Results and Discussion:

3.1. Physical properties of the insecticides-adjuvants combinations

The emulsifiable concentrate formulations EC of the insecticides are usually diluted with water to be sprayed on plants. Because the surface tension of water is high; 72.8 dyne cm-1, it is important to reduce this value to improve some properties of the pesticides such as emulsification, wetting and spreading properties on the plant surface to enhance their residual effect against different pests.

The exhibited results in Table (1) show that the extracted surface tension values are clearly decreased with increasing the adjuvants concentration where it lowered to a ranging value between (60.7 & 44.8), (37.11 & 32.14) and (56.06 & 37.0) dyne cm-1 with Codacide oil, Extravon, and PEG 600 di-laurate, respectively. On the other hand, the foaming value post 1/2 hr. of mixing was low and not exceeded value of about 5.0 ml indicating that the least value is obtained with polyoxyethylene glycol PEG 600 di-laurate and Codacide oil where the values of foaming amounted to (1.8 – 4.7 ml) and (1.2 – 3.6 ml), respectively. These findings are acceptable according to WHO specifications. Moreover, the HLB values of evaluated adjuvants, with exception of Codacide oil, show that these substances are fruitful to obtain good emulsion of pesticides in water (O/W type emulsion). The Hydrophilic-Lipophilic Balance (HLB) value increased up to more than "10" with both PEG 600 di-laurate and Extravon substances. This indicates that the two adjuvants can give milky stable emulsion (O/W type) without shaking. This explanation is fully agreed with **Griffin (1954)** and **Krogh *et al.* (2003)**. Generally, the evaluated adjuvants are promising for lowering the interfacial tension of water by adding materials as a tank-mixed adjuvant.

The demonstrated results in Table (2) clearly elucidate the estimated physical properties of cypermethrin (Sparkile® 25% EC) alone and in combination with the tested adjuvants. The calculated surface tension values of insecticide were 62.5 and 68.62 dyne cm^{-1} at recommended (R) and 1/2 recommended rates (1/2R), respectively. It was also revealed that the surface tension values of the half-recommended rate of cypermethrin were decreased when mixed with 0.5% PEG 600 di-laurate, 0.25% Extravon, and 0.5% Codacide oil as 36.14, 40.60 and 49.30 dyne cm^{-1}, respectively. On the other hand, the extracted foaming values ranged between 3.0 and 5.0 ml. These results indicated that PEG 600 di-laurate is the most efficient adjuvant to decrease the value of surface tension. Generally, treatments were passed the stability of the emulsion.

Also, for fenitrothion insecticide, the data included in Table (3) indicate that the surface tension values of 0.5 recommended rate of fenitrothion (Sumithion® 50% EC) was highly decreased when mixed with PEG 600 dilaurate (0.2%), followed by Extravon (0.25%) and Codacide oil (0.5%), where the obtained values were 36.7, 40.5, and 40.7 dyne cm-1, respectively. Compared for the calculated surface tension values of (54.3 and 56.7) dyne cm-1 for the recommended and half-recommended rates of the insecticides, respectively. Moreover, the fenitrothion insecticide-adjuvant mixtures passed the emulsion stability tests without desirable properties (oily or creamy separation). The foaming values were 7.0 and 3.0 ml with the recommended and half recommended rates of this insecticide, respectively. Whereas, the foaming values were 2.5, 4.5 and 6.5 ml when the half recommended rates of fenitrothion was mixed individually with PEG 600 di-laurate, Extravon and Codacide oil, respectively. Our results are in agreement with **Thacker and Young**

Table (1): Physical properties of inspected adjuvants in their aqueous dilutions

Adjuvants	Concentration (%)	Surface tension "Y" (dyne/cm)	Surface activity (Y0 – Y)	Foams (mL) post 1/2 hr. of mixing	HLB
Codacide oil	0.25	60.70	12.10	1.2 – 3.6	5-6
	0.50	52.55	20.25		
	1.00	44.81	26.99		
Extravon®	0.25	37.11	35.69	1.5 – 2.8	11
	0.50	35.48	37.32		
	1.00	32.14	40.66		
Polyoxyethylene glycol (PEG) 600 di-laurate	0.25	56.06	16.74	1.8 – 4.7	11-13
	0.50	48.37	24.43		
	1.00	37.00	35.80		

Surface activity =(Y0) surface tension of water (72.8 dyne/Cm at 25°C) – (Y) surface tension of an adjuvant; HLB = Hydrophilic – Lipophilic Balance; **R** and **1/2R**: Recommended and half-recommended rates of field application under Egyptian conditions; Each value is the average of three replicates ± SE..

Table (2): The estimated physical properties of cypermethrin (25% EC) alone and in combination with tested adjuvants

Insecticides and adjuvants	Adjuvants concentration (%)	Surface tension (dyne/cm)	Emulsion properties	
			Stability post 1/2 hr. of mixing	Foams ml post 1/2 hr. of mixing
cypermethrin (R)*	0.0	62.50	No creamy or oily sedimentation	5
cypermethrin (1/2R)*	0.0	68.62	No creamy or oily sedimentation	3
cypermethrin (1/2R) + Codacide oil	0.5	49.30	0.5 ml creamy separation	3.0
cypermethrin (1/2R) + Extravon	0.25	40.60	No creamy or oily sedimentation	4.5
cypermethrin (1/2R) + PEG 600 di-laurate	0.5	36.14	No creamy or oily sedimentation	3-5

R and **1/2R**: Recommended and half-recommended rates of field application under Egyptian conditions; Each value is the average of three replicates ± SE.

Table (3): The measured physical properties of fenitrothion (50% EC) alone and in combination with some adjuvants

Insecticides and adjuvants	Adjuvant concentration (%)	Surface tension (dyne/cm)	Emulsion properties	
			Stability post 1/2 hr. of mixing	Foams ml post 1/2 hr. of mixing
fenitrothion (R)*	0.0	54.3	No creamy or oily sedimentation	7.0
fenitrothion (1/2R)*	0.0	56.7	No creamy or oily sedimentation	3.0
fenitrothion (1/2R) + Codacide oil	0.5	40.7	1.0 ml oily separation	6.5
fenitrothion (1/2R) + Extravon	0.25	40.5	No creamy or oily sedimentation	4.5
fenitrothion (1/2R) + PEG 600 di-laurate	0.5	36.7	No creamy or oily sedimentation	2.5

Table (4): Residual toxicity of cypermethrin (25% EC) treatment at two rates of application upon the Egyptian cotton leafworm *Spodoptera littoralis* larvae

cypermethrin-adjuvant	Mortality (%)			Mean
	3 days	6 days	9 days	
Recommended Rate (R)	100.0±0.0	92.0±0.0	84.0±2.1	92.0^{a}
Half-Recommended rate (1/2R)	92.0±0.75	80.0±1.2	69.7±1.7	80.6^{b}
1/2R + Codacide oil	100.0±0.0	95.5±0.5	80.8±1.2	91.7^{a}
1/2R + Extravon®	96.0±1.5	94.5±1.8	79.8±0.7	90.1^{a}
1/2R + PEG 600 di-laurate	100.0±0.0	97.5±1.1	74.5±1.8	90.7^{a}

$LSD_{0.05}$ = 3.11

Table (5): Residual toxicity of fenitrothion treatment at two rates of application upon the Egyptian cotton leaf worm *Spodoptera littoralis* larvae

fenitrothion – adjuvant	Mortality (%)			Mean
	3 days	6 days	9 days	
Recommended Rate (R)	92.2±2.6	72.5±0.8	60.0±3.5	75.2[a]
Half-Recommended rate (1/2R)	81.6±2.1	65.0±1.5	53.7±2.7	66.8[c]
1/2R + Codacide oil	85.5±2.2	70.7±1.8	5.38±1.9	71.5[b]
1/2R + Extravon®	87.2±1.1	71.2±2.1	62.4±2.2	73.6[ab]
1/2R + PEG 600 di-laurate	90.6±0.8	71.1±1.5	93.5±1.9	75.3[a]

$LSD_{0.05}$ = 3.21

(1999) who found that adjuvants enhance the insecticides efficacy through improving their physical properties.

3.2. Residual toxicity of the insecticides alone and/or mixed with three evaluated adjuvants against the 4th instar larvae of Egyptian cotton leaf worm, *Spodotera littoralis*

The presented data in Tables (4 and 5) show the residual toxicity of both insecticides: cypermethrin and fenitrothion either alone and/or mixed with three different adjuvants (Codacide oil, Extravon and PEG 600 di-laurate) against the 4th instar larvae of the cotton leafworm. The cotton plants were individually sprayed with each of the selected insecticides at two rates of application [recommended (R) and 0.5 Recommended (0.5R)]. Moreover, the tested adjuvants were mixed individually with the 0.5R of each insecticide in order to determine the effect of the adjuvant on the residual toxicity of insecticide against the target pest. The sprayed leaves were offered to larvae throughout different consequent intervals of 3, 6 and 9 days. The deduced general means of larval mortality after 3, 6 and 9 days of spraying proved the potent residual efficacy of cypermethrin and fenitrothion alone and/or mixed with adjuvants. The data in table (4) indicated that when cypermethrin tested at the recommended rate (R) it gave the highest larval mortality of 92.0% after 9 days of application compared to its 0.5 recommended rate (0.5R), either applied alone or mixed with adjuvants. Interestingly, the larval mortalities have increased significantly when 0.5R of cypermethrin was mixed with each of the used adjuvants compared to its tested (0.5R) alone. In this concern the means of larval mortalities were 90.7, 90.1 and 90.7% when 0.5R of cypermethrin was mixed with Codacide oil, Extravon and PEG 600 di-laurate, respectively, versus 80.6% larval mortality when 0.5R of cypermethrin was tested alone. In some concept, the residual toxicity of fenitrothion has also been evaluated alone and/or mixed with each of the tested adjuvants. As shown in table (5) the general means of larval mortality percentages values after 9 days of the application with fenitrothion, ranged between 75.3 – 71.5% when mixed with the tested adjuvants. However, the 0.5 recommended rate of the fenitrothion alone gave a lowest mortality value (66.8%) against the tested larvae. The above obtained results also revealed that the evaluated adjuvants had enhanced the residual efficacy of both insecticides against the Egyptian cotton leafworm. These findings are in agreement with **Hatem *et al.* (2009)** who stated that mixing organophosphorus, pyrethroid and carbamate pesticides with inorganic and organic acids had shown some useful synergistic effects on the 4thinstar larvae of *Spodoptera littorals*. **El-shahaat *et.al.* (2010)** reported that the emulsifiable concentrates, related to certain pesticides may be efficient against cotton bollworm when tank mixed with surfactants, which improved the absorption and adhesion of these pesticides on the sprayed plants. Also, **Liu and Stansly (2000)** showed that the surfactants and botanical oils revealed a good potential for controlling the nymphs of silver leaf white fly *Bemisia argentifolii* on collards and tomato plants. Despite, the role and importance of the surfactants had been previously investigated by many investigators **(Stevens *et al.*, 1988, Stevens *et al.*, 1993, Schönherr *et al.*, 1999 and Wu *et al.*, 2010)**, but many questions are still need to be answered in particular about determination of the most suitable adjuvant which should be added to the insecticide formulation to provide an effective pest control agent with no effect on crop health.

So far, our results indicated that PEG 600 di-laurate is the most suitable surfactant for both tested insecticides which decrease the surface tension values for cypermethrin and fenitrothion when used at 0.5R from 68.62 and 56.7 dyne cm^{-1} to 36.14 and 36.7 dyne cm^{-1}, respectively. These findings may be attributed to the fact that the emulsifiers and other adjuvants can decrease the surface tension or increase the surface activity of the pesticides dilution under field application and therefore increase the residual efficacy **(Imai *et al.*, 1994)**. This influence could improve the treated plant surface **(Knowles, 1998; Knowles, 2012)**.

Finally, it could be concluded that adjuvants may be important to reduce the surface tension value of water (72.8 dyne cm-1) to a suitable value for improving the wettability and spreading of the diluted pesticides on plant surfaces which lead to enhance the efficacy of insecticides.

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الملخص العربى

تهدف الدراسة إلى تقييم فعالية المبيدات الحشرية السيبرمثرين، والفينيتروثيون منفردة ومختلطة مع المواد المساعدة (بولى أوكسي إثيلين جلايكول600 داي لوريت، إكسترافون و زيت كوداسيد) ضد يرقات الطور الرابع من دودة القطن المصرية التى تربت على ورق الخروع معملياً، وأظهرت النتائج التي تم الحصول عليها أن بولى أوكسي إثيلين جلايكول600 داي لوريت كان قادرا على الحد من التوتر السطحي لمركب السيبرمثرين و فينيتروثيون من 68.62 و 56.7 داين / سم إلى 36.14 و 36.7 داين / سم، على التوالي، بالمقارنة مع إكسترافون وزيت كوداسيد. أيضا، أعطيت المواد المساعدة خصائص مقبولة نحو الاستقرار للمستحلب و رغوة واستحلاب بعد 0.5 ساعة. من خلط بولى أوكسي إثيلين جلايكول600 داي لوريت حيث كان المساعد الأكثر فعالية لتحسين تركيز مستحلب المبيدات الحشرية المختبرة. وقد لوحظ أن إضافة المواد المساعدة التى تم تقييمها زادت بشكل ملحوظ من سمية متبقية المبيدات الحشرية المختبرة. ويمكن القول بأن بولى أوكسي إثيلين جلايكول 600 دي لوريت مخلوطاً مع نصف الجرعة الحقلية الموصى بها من المبيدات الحشرية المختبرة أعطت نتائج جيدة للسيطرة على دودة ورق القطن أكثر من إكسترافون، وزيت كوداسيد.