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

I- Evaluation of some adjuvants towards the control of scale insects.

***El-Shahaat, M.S.; *A.S. Abo-Shanab and **Sahar M. Beshr**
*Central Agriculture Pesticides Laboratory, **Plant Protection Research Institute, Agricultural Research Center, Egypt

ABSTRACT

Non-ionic polyoxy ethylene glycol (PEG) surfactants manufactured in Egypt, as well as a foreign wetting agent; ethoxylated octylphenol (Extravon®) were tested alone and in their combinations containing emulsifiable formulation (EC) of Super Masrona mineral oil (95%) in relation to efficacy against two scale insects infesting citrus and olive orchards. The first is citrus wax scale insect (Family: coccidae), *Ceroplastes floridenses* Comst. and the second is an armored scale insect (white olive scale insect) (Fam: Diaspididae), *Leucaspis riccae* (Tag, - Tozz). The obtained results indicated that the PEG oleate and laurate surfactants were fcapableto give stable milky emulsion in water where hydrophilic-lipophilic balance (HLB) values were in the range of (8 - 11). However, HLB values were (11 - 12) and more for PEG 600 non-oleate and extravon, respectively. The evaluated adjuvants highly reduced the surface tension of water (72.8 dyne cm^{-1}) without undesirable effects indicating that these adjuvants are promising to improve the absorption and adhesion of pesticides under field application. On the other hand, the adjuvant lowered the surface tension of super Masrona emulsions that passed the emulsion stability test, except both PEG 600 mono-oleate and extravon where they had foam volumes as 14.0% and 7.0%, respectively.

Super Masrona oil at its ¾ recommended rate mixed with PEG 200 mono-oleate (0.1%) was efficient as the recommended rate of the oil alone against *C. floridenses* in citrus orchard. The same trend was obtained against *L. riccae*, while olive scale insect in olive orchard.

INTRODUCTION

It is well known that the adjuvant had an important role in formulating the agricultural pesticides. Some of these adjuvant include surface-active and wetting agents. They reduce interfacial tension of water of hardly wettable plants, improving the absorption and adhesion of spray-able pesticides. Also, these adjuvant reduce evaporation and drift of pesticides when sprayed on crops and they may increase the efficacy of deposition and plant uptake. On the other side, because the non-ionic surface active agents as emulsifiers are uncharged hydrophilic head group, they will be unaffected by the ions that may be present in the diluting water used in preparing the emulsifiable concentrates of pesticides during spray dilution. These ions can adversely affect on the properties and efficiency of this formulation. Surfactants have been used to enhance the biological performance of the active ingredients by improving capture and penetration of the biological target (Knowles, 1998).

The present study is carried out to evaluate some adjuvants alone and mixed with a petroleum mineral oil; Super Masrona oil, 94 % EC according to their physical properties under laboratory conditions and at field in controlling the two scale insects attacking olive and citrus orchards.

MATERIALS AND METHODS

1) Adjuvant

a) Polyoxyethylene glycol (PEG) laurate or oleate, as a non-ionic surfactant produced by the Egyptian Co. for starch, yeast and detergents.

b) Ethoxylated octylphenol (Extravon) as a wetting agent produced by CIBA-GEIGY Co. (Swistzerland).

2) Pesticides

Super Masrona oil, 95% EC as a petroleum mineral product produced by Misr Co. for petroleum. Its recommended rate in Egypt is 1.5 % as summer spray.

3) Physical properties of the adjuvants alone and in their combinations with the mineral oil

a) Hydrophilic – Lipophilic Balance (HLB): it is determined using 5 ml of each adjuvant with 95 ml water (Griffin; 1954).

b) Surface tension value (dyne cm^{-1}), is determined in series of concentration for each adjuvant by Traub Stalgamometer method (Findley; 1949).

c) Emulsion stability test of the mineral oil alone and in the presence of an adjuvant is carried out according to WHO specifications modified by (Anonymous; 1976).

4) Field trials

Super Masrona oil was sprayed at its recommended rate and three-quarter the recommended rate alone and mixed either with Polyoxyethylene glycol 200 mono-oleate, or Extravon. The rate for the adjuvant in tank mixes is 0.1 % of the final spray volume. The first experiment is done to control the citrus waxy scale insect; *Ceroplastes floridensis* (Comstok) (Family: Coccidae) in citrus orchard in Behiera Governorate on July 2009. On the other hand, the 2nd experiment is carried out in olive orchard at Borg AL-Arab region, Alex., Gov., on July 2009. This experiment was carried out to evaluate the treatments against the olive scale insect; *Leucaspis riccae* (Tozz- Tozz) (Family: Diaspididae). The treatments were distributed via to the complete randomized block design.

The first scale insect (as a soft citrus scale one) was inspected and the % infestation reduction values were calculated according to Henderson and Tilton (1955). The second insect (as an armored scale insect) was exposed to the formula of Stafford and Summers (1963). The obtained results were statistically analyzed according to Steel and Torrie (1980).

RESULTS AND DISCUSSION

The solubility of surfactant in water was considered an approximate guide to their hydrophilic – lipophylic balance (HLB) and their use fullness. According to their study, the HLB values shown in Table (1) indicated that polyoxyethylene glycol (PEG) 200 mono-oleate, 200 di-laurate and 200 mono- laurate surfactants can gave milky dispersion after vigorous agitation when added to water where their HLB values were arranged from 6 to 8. On the other hand, PEG 600 di-oleate, 600 di- laurate substances can give stable milky dispersion where HLB values were in between 9 – 11 range. However, the HLB values for both PEG 600 mono –oleate (11 – 12) and Extravon as wetting agent (more than 12) mean that this adjuvant can give from translucent to clear solutions. These observations indicate that the evaluated adjuvant are promising to improve the O / W emulsion type without undesirable properties at tested concentrations up to 1.0 % in water. These adjuvant highly decreased the surface tension of water (72.8 dyne cm^{-1}) to a range of 45.5 – 31.3 dyne cm^{-1} at 0.1 % concentration without either refused foaming or micelle formation where it is well known that the critical micelle concentration (CMC) is the point maximum surface activity after which the surfactant tends to coagulate in micelle (Osipow, 1964). The ability of the adjuvant to reduce the surface tension of water means that these substances are fruitful to increase the surface activity of the oil / water emulsion, and hence they will improve the absorption, adhesion of pesticides, reduce evaporation and increase deposits of the emulsifiable

concentrate; EC pesticides on the plant surfaces after the field application. These explanations are agreed with that reported by Green Waled (1958), Osipow (1964) and Knowles (1998).

Table (1): Hydrophilic-Lipophilic Balance (HLB), surface tension and surface activity values of some adjuvants in their aqueous dilutions.

Adjuvant	HLB values	Conc. (%)	Surface tension (γ) dyne/cm	Surface activity (γ_o* - γ)
Polyoxyethylene glycol (600 di- Oleate)	9 - 10	0.25	53.67	19.13
		0.50	48.82	23.98
		0.75	46.25	26.55
		1.00	45.53	27.27
Polyoxyethylene glycol . (600 mono- Oleate)	11 - 12	0.25	52.60	20.20
		0.50	49.10	23.70
		0.75	42.40	30.40
		1.00	41.10	31.70
Polyoxyethylene glycol (200 mono- Oleate)	6 – 7	0.25	62.72	10.08
		0.50	41.66	31.14
		0.75	39.15	33.65
		1.00	37.66	35.14
Polyoxyethylene glycol (200 mono- Laurate)	7 – 8	0.25	50.11	22.69
		0.50	45.68	27.12
		0.75	44.85	27.95
		1.00	42.51	30.29
Polyoxyethylene glycol (200 di- Laurate)	6 – 7	0.25	46.80	26.00
		0.50	44.10	28.70
		0.75	39.90	32.90
		1.00	37.20	35.60
Polyoxyethylene glycol (600 di- Laurate)	10 - 11	0.25	58.26	14.54
		0.50	50.57	22.23
		0.75	46.80	26.00
		1.00	39.16	33.64
Polyoxyethylene octylphenol (Extravon)	> 12	0.25	38.12	34.68
		0.50	36.59	36.21
		0.75	35.65	37.15
		1.00	33.25	39.55

(*) = water surface tension value = 72.8 dyne/cm at 25°C

As shown in Table (2), Super Masrona oil, 94 % EC, as petroleum oil, at its recommended rate (1.5%) had a surface tension value of 45.64 dyne cm^{-1}. This value was lowered to a range of (32.5 – 25.25 dyne cm^{-1}) when mixed with the evaluated PEG emulsifiers at 0.5 % concentration while it was 29.96 dyne cm^{-1} with ethoxylated octylphenol (Extravon) at 0.2 %. This wetting agent gave foams as 7.0 % while the highest foam formation (14.0 %) was obtained with PEG 600 mono-oleate. On the other hand, the creamy or oily separation values were in between 1.0 and 1.5 ml in the presence of PEG 600 mono-oleate, 600 di-oleate and 200 di-laurate substances. These values were approximately disappeared post ½ hour of mixing except the value appeared with PEG 600 mono -oleate which was still high (12.0 %). These results are in agreement with obtained by EL-Okda *et al.* (1985, 1988).

Table (3): Some physical properties of Super Masrona mineral oil (95% E.C) at 0.75 recommended rate (1.5%) mixed with some adjuvants.

Tested materials	Adjuvant conc. (%)	Surface tension (γ) dyne/cm	Emulsion properties			
			After mixing		30 min. after mixing	
			Foams (%)	Creamy or oily separation	Foams (%)	Creamy or oily separation
Super Masrona (SM) recommended rate (R) (1.5%)	0.0	45.64	1.0	No separation	1.0	As shown after mixing
Super Masrona (SM) (0.75 R)	0.0	47.11	1.0	No separation	-	
Super Masrona (0.75 R) + Polyoxyethylene glycol (200 mono- Oleate)	0.5	33.84	1.0	1.0 ml creamy separation	0.5	
Super Masrona + Polyoxyethylene glycol (200 mono- Laurate)	0.5	25.61	0.0	No separation	0.0	
Super Masrona + Polyoxyethylene glycol (200 di- Laurate)	0.5	26.08	0.0	1.0 ml oily separation	0.0	
Super Masrona + Polyoxyethylene glycol (600 mono- Oleate)	0.5	32.65	10.0	1.0 ml creamy separation	6.0	
Super Masrona + Polyoxyethylene glycol (600 di- Oleate)	0.5	37.13	2.0	1.5 ml creamy separation	2.0	
Super Masrona + Polyoxyethylene glycol (600 di- Laurate)	0.5	25.65	0.5	1.0 ml oily separation	0.5	
Super Masrona + Ethoxylate octylphenol "Extravon"** (a wetting agent)	0.2	32.46	7.0	No separation	5.0	

**: it was not suitable for using at 0.5% conc.

The physical properties of Super Masrona oil at 0.75 recommended rate mixed with the examined adjuvant are in shown in Table (3). The results show that the mineral oil – adjuvant blends passed the emulsion stability test without adversing influence. The surface tension of Super Masrona was highly decreased to about 37.13–25.65 dyne cm^{-1} indicating that efficient adjuvant is PEG 600 di-laurate, PEG 200 mono-oleate and PEG 200 di-laurate where the surface tension did not exceed about 26.0 dyne cm^{-1}. On the other hand, there was no separation in the prepared emulsion ½ hour after mixing with water.

The field evaluation of Masrona oil treatments on the waxy citrus scale insect; *Ceroplastes floridensis*, in a citrus orchard is shown in Table (4). The infestation reduction percentage effect values were arranged as follow : the recommended rate of the mineral oil mixed with PEG 200 mono-oleate (92.68) ≥ the treatment alone (89.55) ≥ the 0.75 recommended rate of the mixed with the emulsifier (85.09)> the later rate of the oil alone

(77.10). These results indicated that the recommended rate of the EC Masrona oil may be reduced and maintained to be efficient against the controlled pest.

Table (4): Residual toxicity of Super Masrona mineral oil (95% E.C) at two rates mixed with Polyoxyethylene glycol emulsifier to *Ceroplastes floridenses* (Comst.) in citrus orchard.

Weeks after spray	Infestation Reduction (%)			
	Super Masrona (R*)	Super Masrona (R) + Emulsifier** (0.1%)	Super Masrona (0.75 R)	Super Masrona (0.75R) + Emulsifier (0.1 %)
2	94.3 ± 1.6	97.8 ± 0.29	81.1 ± 5.6	90.7 ± 2.6
4	92.5 ± 2.6	94.5 ± 2.90	84.1 ± 2.5	89.6 ± 2.7
6	87.3 ± 6.0	90.9 ± 9.10	76.0 ± 9.1	83.2 ± 1.1
8	84.0 ± 5.9	87.5 ± 3.40	67.2 ± 2.7	80.0 ± 1.8
Mean effect	89.55^{ab}	92.68^{a}	77.10^{c}	85.89^{b}

Values are means of 6 replicates
*: recommended rate (1.5%)
**: Polyoxyethylene glycol 200 mono- Oleate

As indicated in Table (5), the efficacy of Super Masrona treatments at the two evaluated rates were tested against the olive scale insect, *Leucaspis riccae*, in an olive orchard. The obtained results were paralled with those found with 1st scale insect. The lowest infestation reduction % value was related to the 0.75 recommended rate of the mineral oil (86.5) while the remaining treatments were not statistically differed.

Table (5): Residual toxicity of Super Masrona mineral oil (95% E.C) at two rates mixed with Polyoxyethylene glycol emulsifier to *Leucaspis riccae* (Tag,-Tozz) in olive orchard.

Weeks after spray	Infestation Reduction (%)			
	Super Masrona (R*)	Super Masrona (R) + Emulsifier** (0.1%)	Super Masrona (0.75 R)	Super Masrona (0.75R) + Emulsifier (0.1 %)
2	95.6 ± 0.7	99.3 ± 0.7	87.1 ± 3.6	93.0 ± 2.3
4	93.7 ± 4.3	97.9 ± 1.1	88.6 ± 6.2	95.5 ± 3.3
6	98.2 ± 0.9	99.1 ± 0.9	87.8 ± 2.0	96.9 ± 1.8
8	94.9 ± 0.5	96.8 ± 1.5	82.5 ± 2.8	90.7 ± 7.0
Mean effect	95.6^{a}	98.3^{a}	86.5^{c}	93.9^{ab}

Values are means of 6 replicates
*: recommended rate (1.5%)
**: Polyoxyethylene glycol 200 mono- Oleate

It could be concluded that the emulsifiable concentrates of pesticides may be improved to be more efficient against pests using certain non-ionic surfactants because these substances are able to decrease the surface tension of the prepared emulsions without adverse effects. These emulsifers as well as wetting agents can enhance the spreading of the EC formulations on plant surface and they improve the wettability and reducing these formulations under field conditions. This explanation and in agreement with that reported by many investigators (Schwartz and Perry, 1949; Sparr and Brown, 1954; EL-Sebae and EL-Akawi, 1971; EL-Sebae and EL-Okda 1972; EL-Sebae *et al.*, 1976 ; Tadross 1995 and Knowles; 1998).

REFERNCES

Anonymous (1976). Pesticides formulation specifications. CAPL, Agric. Res. Cent., of Agric. (Arabic Information Note).

EL-Okda, M.M., M.S. EL-Shahaat, M.M. Emara, B.M. Abo-Egla and S.M. Morsi (1985). Factors affecting the pesticide formulations. VI. The efficacy of certain local surfactants for formulating emulsifiable mineral oils. Proc. 6th Arab. Pesticides Conf. Tanta Univ., 1:323-333.

EL-Okda, M.M., M.M. Emara, M.S. EL-Shahaat and A.H. Ghaleb (1988). Factors affecting the pesticide formulations. V. Emulsifiable Minneral oil formulations using local ingredients. Alex. Sci. Exch. vol.9, No.3: 347 -367.

EL-Sebae, A.H. and M. EL-Akawi (1971). Studies on the chemical structure and insecticidal activity. 1V. Efficacy of locally spray mineral oils. Alex. J. Agr. Res., 19: 131-138.

EL-Sebae, A.H. and F. A. Haossam EL-Deen, M. Abo-EL-Amayem and A. Marei (1976). Insecticidal efficacy of miscible spray petroleum oils formulated from locally produced Egyptian ingredients. 2nd Arab. Conf. on Pet. Chem. Abo-Daabi: 15-22.

EL-Sebae, A.H. and M.M. EL-Okda (1972). Studies on local formulation of emulsifiable insecticides concentrations. Bull. Ent. Egypt Con. Ser., vol. 1: 67 – 71.

Findley, Y.A. (1949). Practical Physical chemistry. (Longmans Green and Co., London, pp. 335).

Griffin, W.H.C. (1954). Hydrophilic – Lipophilic Balance determination for the non-ionic emulsifiers and their efficacy. J. Soc. Cosmotic Chemist (5): 249 – 251.

Green Waled, H.L. (1958). Determination of HLB character of surface active agents and oil by a water titration. Anal. Chemist, vol (28):1693-1697.

Henderson, C.F. and F.W. Tilton (1955). Tests with acaricides against the brown wheat mite. L. Econ. Ent. 48: 157-161.

Knowles, D.A. (1998). Chemistry and technology of agrochemical formulations. Kluwer Academic Publishers (London).

Osipow, L.I. (1964). Surface chemistry theory and application. Reeinhold Publishing Grop., New York: 473.

Schwartz, A.M. and J.W. Perry (1949). Surface active agents and detergents : Their Chrmistry and Techenology. Vol.1: 549.

Sparr, B.I. and C.V. Brown (1954). Methods of evaluating the emulsifiability of insecticide concentrates. J. Agr. Food Chem., 2:871-873.

Stafford, E. M. and Summers, F. M. (1963). Evaluating control of San Jose scale. Univ. of California, print, Hilgardia. 35: 13-32.

Steel, R.G.D. and J.H. Torri (1980). Primciple and Procedures of statistics. A bio-matrical approach second ed. Mc Graw-Hill Kogahusha, Ltd.

Tadross, T.F. (1995). Surfactant in agrochemical, surfactants series, Marcel Dekker, New york

الملخص العربى

تحسين خواص المركزات القابلة للإستحلاب للمبيدات وعلاقة ذلك بالفاعلية ضد بعض الأفات
1- تقييم بعض المواد الإضافية تجاه مكافحة الحشرات القشرية

محمد سعيد الشحات*، أحمد صالح أبوشنب*، سحر محمد بشر**
*المعمل المركزى للمبيدات، **معهد بحوث وقاية النباتات – مركز البحوث الزراعية – الإسكندرية – مصر

تم إختبار بعض المواد النشطة سطحيا غير الأيونية والمنتجة فى مصر والمنتمية إلى مجموعة بولى أوكسى إيثيلين جليكول (PEG) سواء المرتبطة بحامض الأوليك أو حامض اللوريك وكذ إختبار أحد عوامل التبليل المعروفة تجاريا بـ إكسترافون (إثيوكسيليتيد أوكتايل فينول) فى تخفيفاتها المائية وفى خلائطها مع زيت الرش المعدنى الصيفى المعروف بإسم " سوبر مصرونا 95 % مركز قابل للإستحلاب " وعلاقة ذلك بالفعالية ضد حشرة الموالح الشمعية القشرية وحشرة الزيتون القشرية المدرعة. وقد أظهرت الدراسة النتائج التالية :-

1) عوامل الإستحلاب المنتمية إلى بولى إيثيلين جليكول أولييت أو لوريك لها قيم إتزان هيدروفيلى – ليبوفيلى (HLB) فى المدى من 8 – 11 لجميع المواد المختبرة ماعدا مادة600 مونو –أولييت ومادة إكسترافون حيث أن قيمة HLB (11-12) ، وأكثر من 12 على الترتيب.

2) المواد المختبرة سببت خفضا للتوتر السطحى للماء بدون ظهور أى صفات غير مرغوبة فيما يخص الصفات الفيزيائية مما يوضح أهمية هذه المواد فى تحسين صفات الإلتصاق والإمتصاص على الأسطح النباتية المعاملى تحت الظروف الحقلية.

3) المواد الإضافية تسبب خفضا واضحا للتوتر السطحى لمستحلب زيت سوبر مصرونا مع نجاح المستحلب فى الصفات الخاصة بثبات المستحلب بإستثناء عيب واحد وهو تكوين رغاوى بنسبة 7 % ، 14 % مع مادتى إكسترافون ، 600 مونو –أولييت على الترتيب.

4) زيت سوبر مصرونا بثلاثة أرباع الجرعة الموصى بها مخلوطا مع مادة 200 مونو –أولييت (تركيز 0.1 %) أكثر فعالية ضد حشرة الموالح الشمعية وحشرة الزيتون المحارية متساويا فى ذلك مع الجرعة الموصى بها دون إضافة عامل النشاط السطحى.