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IMPROVEMENT THE PHYSICO-CHEMICAL PROPERTIES AND EFFICIENCY OF SOME INSECTICIDES FORMULATION BY USING ADJUVANTS AGAINST COTTON LEAFWORM *Spodoptera littoralis* (BOISD.)

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ABSTRACT

The effect of different groups of chemical additives: surfactants (polyethylene glycol 600 dilaurate, polyethylene glycol 600 monolaurate and Sisi 6), sticking agents (Glue and Arabic gum), thickening agents (poly acryl amid and hydroxy methyl celelluse) and acidifying agents (citric acid, oxalic acid, sulphonic acid and tartaric acid) on physico-chemical properties, efficiency and persistence of Curacron and Superalpha were studied against 4th instar larvae of the cotton leafworm *S. littoralis* (Boisd.). The surface tension and pH value of insecticides decreased whereas the viscosity and conductivity increased as a result of mixing with the adjuvants. Such change in physical properties of insecticides led to increase in their retention and insecticidal efficiency. Generally the effect of tested additives on physico-chemical properties of Curacron and superalpha was as follow: Sulphonic acid gave the highest decrease in surface tension. Polyacryl amid and hydroxyl methyl celelluse (HMC) recorded the highest increase in viscosity. Oxalic acid gave highest increase in electrical conductivity and lowest decrease in pH value of tested insecticides. Sisi 6 increased effectiveness of 3/4 recommended rate of Curacron to be higher than full recommended rate against *S. littoralis* (Boisd.), but polyacryl amid increased the persistence of Super alpha to be higher than 3/4 recommended rate but less than complete rate.

INTRODUCTION

The use of certain additives in pesticide formulations would improve their field performance and increase the bioactivity with consequent decrease in their rates of application, then reducing plant protection costs, thereby, approaching close to the principle of integrated pest management (IPM) by reducing the hazards to the environment. Many authors proved the relation between additives and the physical properties of pesticidal spray solutions as they affected both the retention and pesticidal efficiency. Adjuvants change the physico-chemical properties of spray solution to be more effective, stable and protect it from degradation factors. Adjuvants are mixed with pesticides for many purposes such as reducing drift and increasing deposit in addition to increase the adherence and improve wetting and spreading on the treated surface (Chapman and Mason 1993). Wang *et al.* (2002) mentioned that the penetration was positively correlated with both the concentration of adjuvant (mineral oil, higher aliphatic acid and non ionic surfactant) and the time after application in a given range of treatment. Sticker Adjuvants enhance

adhesion of pesticide sprays to plant surfaces and increase their resistance to rain (Gaskin and Steele 2009).

The aim of the present work is to study the effect of additives in increasing the residual activity and reduce the dosage rate of tested insecticides to at least the lower limit of recommended concentration against the cotton leafworm, *Spodoptera littoralis* (Boisd.)

MATERIALS AND METHODS

I-Tested Insecticides:

A- Curacron 72% EC (Profenofos) 750 ml/ feddan (1 feddan = 4200m^2) as Organophosphorus insecticide.

B- Superalpha 10% EC (alpha-cypermethrin) 250 ml / feddan as Synthetic pyrethroid insecticide.

II- Adjuvants:

A- Surfactants

1- Non ionic surfactant

a- Polyethylene glycol 600 dilaurate (PEG 600DL) produced by the national Co. for Starch, Yeast and Detergents, Alexandria

b- Polyethylene glycol 600 monolaurate (PEG 600ML) produced by the national Co. for Starch, Yeast and Detergents, Alexandria.

2- Anionic surfactant:

Sisi 6 Local surfactant produced by Central Agricultural pesticides laboratory, Ministry of Agriculture,Dokki

B- Sticking agents

1- Glue (granules),it is animal alboprotein supplied by El-Sabaa Company.

2- Arabic gum, it is a plant polyscarried supplied by El-Gomhoriya Company for chemicals, Egypt.

C- Thickening agent

1- Poly acryl amid

2- HMC (Hydroxy methyl celelluse)

They supplied by El-Gomhoriya Company for chemicals, Egypt.

D- Acidifying agents

1- Citric Acid

2- Oxalic Acid

3- Sulphonic Acid

4- Tartaric

They supplied by El-Gomhoriya Company for chemicals, Egypt.

III- Physical properties determination:

Physical compatibility between the used insecticides and additives was studied by the determination of emulsion stability for curacron and superalpha according to WHO (1979) specification (visually methode).

The physico-chemical properties of pesticide solution alone or mixed with additive were determined according to CIPAC Hand Book (2003) as the following: pH value using Schott Gerate pH-meter CG 818.Viscosity using Ostwald viscometer where m poise is the unit of viscosity measurement and surface tension using Du Nouy tensiometer where dyne/cm is the unit of

surface tension measurement. Conductivity was measured using the conductmeter YSI model 33S-C-T meter (m MHOS is the unit of electrical conductivity measurement).

IV- Evaluation of insecticidal efficacy:

Field experiments were conducted according to Ministry of Agriculture protocol semi-field at Elbaramoon district, Dakahlia Governorate during season 2009. A hand sprayer equipment with one nozzle was used for spraying (spray volume was 200 liter/feddan). With the purpose of evaluate the initial as well as the residual efficacy of the insecticides with complete and 3/4 the recommended rate and their combinations with different adjuvants at 3/4 recommended rate against 4th instars larvae of the cotton leafworm *S. littoralis* (Boisd.). Samples of three leaves were collected at random from each of treated and untreated plants. The collected leaves were instantly transferred to the laboratory (Plant Protection Research Institute, Mansoura branch) and introduced to the starved 4th instar larvae in glass jars covered with muslin cloth, each jar contained ten larvae replicate and four replicates for each treatment. Samples were taken immediately after one hour of spraying (zero time) and then after 3, 6, 9 and 12 days from application to evaluate the residual performances in cotton field during the period from 10th till 22nd August, 2009. The larvae were exposed to the treated leaves, and then mortality percentages were recorded after 24 hr post-treatment. The obtained data were corrected by Abbott's formula (1925).

RESULTS

I- Physico-chemical properties of some certain additives in water:

Data in Table (1) clearly indicated that, all tested adjuvant affected on the physico-chemical properties of water that will be used for dilution of insecticides when they added at rate 0.5% for all soluble additives except polyacryl amid at 0.25% and HMC at 0.1%. Sulphonic acid showed the highest decreasing in surface tension followed by Sisi 6, ML600, HMC, glue and DL600 where as no changes were found with citric acid. On contrast the others additives increased the surface tension of water. Polyacryl amid and HMC gave highest increase in viscosity but the others caused slightly increase except Oxalic acid and Tartaric acid that showed slightly decrease. All chemical additives increased the electrical conductivity except DL600 and ML600.Oxalic acid gave highest increase in electrical conductivity followed by sulphonic acid, Tartaric acid and Citric acid. All adjuvants decreased the pH value where Oxalic acid recorded highest decrease followed by sulphonic acid, Tartaric acid and Citric acid.

II- Effect of adjuvant on physico-chemical properties of spray solution of tested insecticides:

According to emulsion stability test, there are a physical compatibility were found between tested insecticides and Adjuvants. Data in Table (2) showed that the physico-chemical properties of Curacron spray solution alone and its combination with compatible additives. The results indicated that all tested additive materials decreased the surface tension of Curacron

spray solution except Arabic gum. Sulphonic acid gave the highest decrease in surface tension followed by Sisi6 and ML600. Polyacryl amid and HMC recorded the highest increase in Viscosity while the other compatible materials have no change in viscosity except glue and Arabic gum that recorded a slight increase. All the compatible materials showed high increase in the electrical conductivity except DL600 and ML600 where Oxalic acid gave the highest increase in electrical conductivity followed by Sulphonic acid, Citric acid and Tartaric acid. Oxalic acid gave the highest decrease in pH value followed by Sulphonic acid, Tartaric acid, Citric acid and ML600, while the other compatible materials increased the pH value.

Table (1): Physico-chemical properties of certain additives in water

Tested materials	Concentration %	Surface tension Dyne/cm	Viscosity mps	Conductivity µMHOS	pH
Citric acid	0.5	72.0	11.3	1400	2.37
Sulphonic acid	0.5	30.4	10.9	4200	2.10
Oxalic acid	0.5	76.0	9.6	8000	1.94
Tartaric acid	0.5	76.0	9.2	1800	2.19
DL 600	0.5	68.4	10.0	335	6.40
ML 600	0.5	38.0	10.4	305	5.78
Sisi6	0.5	31.1	10.9	432	6.64
Glue	0.5	68.4	12.2	490	6.35
Arabic gum	0.5	76.0	11.3	430	6.83
Polyacryl amid	0.1	80.5	56.5	400	6.52
HMC	0.25	54.7	45.7	500	6.54
Water	----	72.0	10.0	350	7.00

HMC. Hydroxy methyl cellus

Table (2): Physico-chemical properties of spray solution of curacron alone and its tank mix with additives

Treatment	Surface tension Dyne/cm	Viscosity mps	Conductivity µMHOS	pH
Curacron	34.2	10.4	360	6.14
+Citric acid	32.6	10.4	1450	2.21
+Sulphonic acid	24.9	10.4	4000	1.96
+Oxalic acid	33.4	10.4	9000	1.83
+Tartaric acid	33.8	10.4	1400	2.08
+DL 600	31.1	10.4	360	6.24
+ML 600	30.4	10.4	350	5.78
+Sisi6	29.1	10.0	435	6.32
+Glue	30.4	10.9	500	6.32
+Arabic gum	35.1	10.9	420	6.39
+Pol acryl amid	33.4	43.5	450	6.36
+HMC	33.4	43.5	500	6.18
H_2O	72.0	10.0	320	7.00

HMC. Hydroxy methyl cellus

Data in Table (3) showed that the physico-chemical properties of Superalpha spray solution alone and its combination with compatible additives. The results indicated that all tested additive materials decreased the surface tension of superalpha spray solution. Sulphonic acid gave the highest decrease in surface tension followed by Sisi6, ML600 and DL600. Polyacryl amid and HMC recorded the highest increase in Viscosity while the

other compatible materials have slightly increase except Sisi6, DL600 and Tartaric acid. Oxalic acid gave the highest decrease in pH value followed by Sulphonic acid; Tartaric acid and Citric acid while the other compatible materials gave slightly decrease in pH value except HMC, Arabic gum and Sisi6 which increased the pH value.

Table (3): Physico-chemical properties of spray solution of superalpha alone and its tank mix with additives

Treatment	Surface tension Dyne/cm	Viscosity mps	Conductivity µMHOS	pH
Superalpha	40.2	9.6	380	6.47
+Citric acid	36.0	10.0	1400	2.20
+Sulphonic acid	23.6	10.4	4400	1.96
+Oxalic acid	38.0	10.4	10000	1.80
+Tartaric acid	35.1	9.6	1850	2.07
+DL 600	32.6	9.1	375	6.35
+ML 600	31.8	11.3	330	5.77
+Sisi6	25.3	9.6	480	6.53
+Glue	36.9	10.4	500	6.32
+Arabic gum	35.1	10.9	438	6.53
+Polyacryl amid	39.1	43.5	420	6.35
+HMC	36.9	43.5	600	6.75
H2O	72.0	10.0	320	7.00

HMC. Hydroxy methyl cellus

III- Toxicity of tested insecticides alone and its mixtures with the tested chemical additives on the cotton leafworm

Data presented in Table (4) cleared that; most additives improved the insecticidal action of the 3/4 recommended rate against 4th instar larvae of the cotton leafworm *S. littoralis* (Boisd.). Using Curacron in complete and 3/4 of the recommended rate of application gave 100% initial larval mortality, while the addition of adjuvants to Curacron using 3/4 of the recommended rate of the application gave the same initial larval mortality of Curacron alone at 3/4 recommended rate except Sulphonic acid, DL600 and Glue which gave 97.5% of initial larval mortality of Curacron alone at the same rate. According to the mean residual effect and mean general effect, it was noticed that all the Adjuvants increased the percentage of larval mortality than that obtained with Curacron at 3/4 of the rate (synergistic effect) except Sulphonic acid, ML600, Glue, HMC and Polyacryl amid (antagonistic effect). Sisi 6 gave the highest average residual effect when it combined with Curacron followed by DL600, Tartaric acid, Oxalic acid, Citric acid and Arabic gum. The percentage of larval mortality of these mixtures was similar to complete rate.

Data presented in Table (5) cleared that; all the additives improved the insecticidal action of the 3/4 recommended rate against 4th instar larvae of the cotton leafworm *S. littoralis* (Boisd.). Using Superalpha in complete and 3/4 of the recommended rate gave 85% and 72.5% initial larval mortality respectively, while the addition of adjuvants to Superalpha using 3/4 of the recommended rate of the application increased the percentage of mortality to 82.5%, 80%, 77.5%, and 75% for glue, HMC, DL600 and Arabic gum respectively. According to the mean of the residual effect and mean of the

general effect, it was noticed that all the adjuvants increased the percentage of larval mortality than that obtained with Superalpha at 3/4 of the rate except in case of combination with ML600. On the other hand Polyacryl amid and oxalic acid gave the highest residual effect when it combined with Superalpha that was near to complete rate effect followed by citric acid, tartaric acid, Sisi6, HMC, Arabic gum, Glue, Sulphonic acid and DL600.

Table (4): Toxicity of Curacron alone and its tank mixed with chemical additives against 4th instars larvae of cotton leafworm.

Treatments	Rate of application	Corrected % Mortality after Treatment (days)						General mean of % Mortality
		IK	Residual effect				Mean of % Residual effect	
			3	6	9	12		
Alone								
Curacron	**1F**	100.00	97.43	82.05	44.73	34.21	64.61	71.68
Curacron	**3/4F**	100.00	97.43	69.23	39.47	28.95	58.77	67.01
Mixed								
Curacron +Citric acid	**3/4F+0.5%**	100.00	100.00	94.87	34.21	18.42	61.87	69.50
+Sulphonic acid	**3/4F+0.5%**	97.50	84.62	71.80	7.90	5.26	42.40	53.42
+Oxalic acid	**3/4F+0.5%**	100.00	97.44	89.74	39.47	28.95	63.89	71.12
+Tartaric acid	**3/4F+0.5%**	100.00	94.87	84.61	47.36	39.47	66.58	73.26
+DL 600	**3/4F+0.5%**	97.50	97.44	94.87	57.90	21.05	67.82	73.75
+ML 600	**3/4F+0.5%**	100.00	87.17	87.17	26.31	23.68	56.08	64.86
+Sisi 6	**3/4F+0.5%**	100.00	100.00	97.43	78.94	15.79	73.04	78.43
+Glue	**3/4F+0.5%**	97.50	97.43	87.17	5.26	2.63	28.90	42.61
+Arabic gum	**3/4F+0.5%**	100.00	100.00	89.74	44.73	7.90	60.59	68.47
+Poly acryl amid	**3/4F+0.1%**	100.00	84.61	79.49	39.47	2.63	51.55	61.23
+HMC	**3/4F+0.25%**	100.00	92.30	30.76	15.78	13.15	37.99	50.39

F: Field dilution rate **IK: Initial Kill after one hour from application**

Table (5): Toxicity of Superalpha alone and its tank mixed with chemical additives against 4th instars larvae of cotton leafworm.

Treatments	Rate of application	Corrected % Mortality after Treatment (days)						General mean of% Mortality
		IK	Residual effect				Mean of % Residual effect	
			3	6	9	12		
Alone								
Superalpha	**1F**	85.00	53.85	52.50	5.13	2.50	28.49	39.79
Superalpha	**3/4F**	72.50	30.77	22.50	0.00	0.00	13.92	25.15
Mixed								
Superalpha+Citric acid	**3/4F+0.5%**	67.50	41.02	32.50	5.12	0.00	19.66	29.23
+Sulphonic acid	**3/4F+0.5%**	47.50	33.33	20.00	7.69	2.50	15.88	22.26
+Oxalic acid	**3/4F+0.5%**	57.50	51.28	30.00	7.50	5.12	23.47	30.28
+Tartaric acid	**3/4F+0.5%**	55.00	41.02	30.00	5.12	0.00	19.03	26.22
+DL 600	**3/4F+0.5%**	77.50	35.89	22.50	5.12	0.00	15.87	28.20
+ML 600	**3/4F+0.5%**	65.00	10.25	7.69	2.50	0.00	5.11	17.09
+Sisi 6	**3/4F+0.5%**	50.00	48.71	17.50	7.69	0.00	18.47	24.78
+Glue	**3/4F+0.5%**	82.50	30.76	27.50	7.50	7.50	17.72	30.67
+Arabic gum	**3/4F+0.5%**	75.00	35.89	30.00	5.12	2.50	18.37	29.70
+Poly acryl amid	**3/4F+0.1%**	70.00	58.97	52.50	2.56	0.00	28.51	36.81
+HMC	**3/4F+0.25%**	80.00	38.46	30.00	5.12	0.00	18.39	30.71

F: Field dilution rate **IK: Initial Kill after one hour from application**

DISCUSSION

The data showed that adjuvants increased toxicity of candidate insecticides and decreased the rate of field application; this is due to the ability of adjuvants to change the physico-chemical properties of spray solution. Such as decreasing pH value with increasing conductivity, decreasing surface tension and increasing viscosity. The decrease in surface tension of insecticide spray solution give a prediction that adjuvants will increase wettability, spreading and depositing of insecticide spray solution on treated surface plant with increasing of insecticidal efficiency (Furmidge 1962). EL-Attal *et al.* (1984) reported that the increase of electrical conductivity of insecticide spray solution would lead to deionization of insecticide and increase its deposit and penetrate in the treated plant surface, then cause increase in insecticidal efficiency. On the other hand the increase of viscosity of spray solution would increase the deposited on the treated plant leaves, then reduce the drift and increase the efficiency of insecticides (Bode *et al.* 1976). Reducing the pH value of spray solution might increase the attraction between sprayed solution and treated plants then increasing the insecticidal efficiency (Tawfic and EL-Sisi 1987). Similar results were reported by several investigations, i.e. Abdalla *et al.* (1989), EL-Metwally *et al.* (1989), El- Fateh Radwan *et al.* (1994) and Hussein (2002).

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تحسين الخواص الطبيعيه والكيميائيه والكفاءة الاباديه لبعض مستحضرات المبيدات باستخدام بعض الإضافات على دودة ورق القطن

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***المعمل المركزى للمبيدات - مركز البحوث الزراعيه – الدقى – الجيزة**

****معهد بحوث وقايه النباتات - - مركز البحوث الزراعيه – الدقى – الجيزة**

*****كليه العلوم – جامعه بنها**

أجرى هذا البحث بهدف دراسة تأثير عدد من الاضافات الكيميائيه التابعه لمجاميع مختلفه وهى : مواد معدلة للحموضة (حمض الستريك – حمض السلفونيك – حمض الاوكساليك – حمض الطرطريك) ومواد ذات نشاط سطحى (بولى اثيلين جليكول ٦٠٠ ثنائى ليورات – بولى اثيلين جليكول ٦٠٠ آحادى ليورات – سيسي ٦) ومواد لاصقة (الغراء – الصمغ العربى) ومواد مغلظة (هيدروكسيد ميثيل سليلوز – بولى اكرايل اميد) على الفاعليه الاباديه لكل من مبيدى الكوراكرون وسوبر ألفا. أوضحت النتائج أن كل الاضافات المختبرة أظهرت توافق طبيعى عند الخلط فى التانك بتركيز ٠.٥% لكل الاضافات عدا بولى اكرايل اميد بتركيز ٠.١ % وهيدروكسى مثيل سليلوز بتركيز ٠.٢٥% . أدى اضافه كل من حمض الطرطريك و بولى اثيلين جليكول ٦٠٠ داى ليورات والسيسى ٦ بتركيز ٠.٥% الى مبيد الكوراكرون بمعدل٤/٣ الجرعة الموصى بها الى تحسين التاثير السام مقارنة بالجرعه الكامله. على الجانب الاخر وجد أن اضافه حمض السلفونيك و الغراء و بولى أكرايل أميد وهيدروكسى مثيل سليلوز أدى الى خفض التاثير السام مقارنه بالمبيد بمفرده عند معدل٤/٣ الجرعة الموصى بها. أما فى حاله سوبر ألفا نجد أن كل الاضافات أدت الى تحسين التأثير السام بدرجة تفوق ٤/٣ المعدل الموصى به عدا حمض السلفونيك و السيسى ٦ اللذان أديا الى خفض التاثير السام.

قام بتحكيم البحث

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