Synergistic Effect of Sylgard 309® with Prepared and Commercial Formulations of Malathion and Chlorpyrifos against *Tribolium Castaneum* (Coleoptera: Tenebrionidae)

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ABSTRACT

The physical properties, toxicity and potency of the prepared and commercial formulations of malathion and chlorpyrifos in addition to their synergistic effect with Sylgard 309® against the red flour beetle *Tribolium castaneum* (Coleoptera: Tenebrionidae) were investigated. The mixture of the technical chlorpyrifos or malathion dissolved in xylene with the either emulsifiers (Calcicum or Sodium Dodecylbenzene Sulfonate [Ca DBS or Na DBS]) as ionic liquids succeeded in inducing emulsion stability in two successful prepared formulations for each insecticide as well as Triton-X100. The prepared formulation passed the cold/stability tests. The toxicity of the all tested formulations was evaluated against *T. castaneum*. The prepared formulations were matching those locally sold commercial formulations of malathion and chlorpyrifos which have been produced by Egyptian chemical and insecticides companies. The prepared formulations of either malathion or chlorpyrifos that containing the emulsifier Ca DBS were more toxic than those containing Na DBS. All the tested formulations of chlorpyrifos were more efficient toxic than those of malathion. The toxicity index, relative potency and potency were calculated based on 24 and 48 hrs bioassay to compare the prepared formulations with the commercial ones. Chlorpyrifos formulations were more synergized than malathion formulations by Sylgard 309® (as a synergist) and therefore, the use of such synergist will reduce the costs of application, insecticidal rate, and thus reduces both the environmental stress and the resistance pressure.

INTRODUCTION

Malathion is a pesticide that is used to kill insects on agricultural crops, stored products and others. Chlorpyrifos is an organophosphate insecticide, acaricide, nematicide and a less persistent termiticide **(Horwood, 2007).** Pesticide emulsion-concentrate formulations are complex mixtures of chemicals, often consisting of the active ingredient, a surfactant, a petroleum fraction (inert components) and adjuvants **(Schwope *et al.*, 1992).** The formulation gives the product its unique physi

cal form and specific characteristics, enabling it to fill a market niche. The choice of pesticides for the control of storage pests is very limited because of the strict requirements imposed for the safe use of synthetic insecticides on or near food. The continuous use of chemical pesticides for the control of insect pests has resulted in serious problems such as insecticide resistance in pests **(Pacheco *et al.*, 1990; Sartori *et al.*, 1990)**.

Pesticide synergism is one of the several techniques that can be used to control pesticide resistance **(Hammock & Soderland, 1986; Kemp and Caseley, 1991; Busvine, 1980).**The introduction of synergists in pest control could be great benefit both economically and ecologically **(Metcalf, 1992).**

Research on adjuvant and formulation technology for agrochemicals has advanced rapidly in recent years. Part of the progress is due to the increased efforts by the agrochemical manufacturers to renew older products when patent protection expires and companies have fewer new actives to add to or replace older products. Sylgard 309® is a nonionic adjuvant (surfactant) (in which the molecular head is hydrophilic, without having any ionic components) and specifically designed to enhance the efficacy of pesticides. Sylgard 309® is not toxic to mammals and was found to synergize pymetrozine against insects **(Acheampong and Stark, 2004)**. Also, Sylgard 309® was found to enhance herbicides **(Roggenbuck *et al.*, 1993 & 1994)**. The addition of an effective and safe synergistic agent will lead to reduce the insecticide rate, and thus reduces both the environmental stress and the resistance pressure.

The present investigation will focuses on formulating chlopyrifos-ethyl and malathion to be used as successful preparations for controlling certain insect-pests. The evaluation of the toxicity of the prepared formulations compared to the commercial ones of chlorpyrifos and malathion against the red flour beetle *Tribolium castaneum* (Coleoptera: Tenebrionidae) was considered. The synergistic effect with Sylgard 309® was also determined.

MATERIALS AND METHODS

Insecticides Used

1.Malathion 95% Technical grade

Chemical name: diethyl (dimethoxythiophosphorylthio)succinate; *S*-1,2-bis(ethoxycarbonyl)ethyl *O,O*-dimethyl phosphorodithioate

2.Chlorpyrifos (Chlorpyrifos -ethyl) 96% Technical grade

Chemical name: *O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphoro- thioate

Formulating the selected pesticides

1. Solvent and emulsifiers

Xylene was used for formulating the E.C. of both malathion and chlorprifos. Two formulations for each insecticide were prepared using two different emulsifiers. These emulsifiers were calcium dodecy benzene sulfonate 57% in butanol and sodium dodecy benzene sulfonate 57% in butanol (anionic liquids). Triton-X100 (as a non anionic liquid) was also added to each formulation.

2. The preparation of Formulations

Different combinations of each technical insecticide with the solvent and each of the used emulsifiers+ Triton-X100 were prepared and tested to select the most stable and successful formulations through a series of physical and chemical tests .

The standard commercial formulations

Two commercial EC formulations for each of the selected insecticides were used to be compared with the prepared formulations. The commercial formulations of malathion were Malatox® (produced by El-Helb company for Pesticides & Chemicals) and Malason® (produced by Kafr El-Zayat Company for Pesticides & Chemicals). The commercial formulations of chlorpyrifos were Octafos® (El-Nasr Company for Intermediate Chemicals) and Chlorpyrifos-KZ® (Kafr El-Zayat Company for Pesticides & Chemicals).

Physico-chemical properties of standard (commercial) and prepared formulations

In a laboratory study, the physico-chemical properties of these standard (commercial formulations) and prepared formulations for the two selected organophosphorous compounds (malathion and chlopyrifos) were investigated for stability tests.

Free acidity (as % H2 SO_4) and alkalinity (%Na OH) were determined according to the method of **WHO specification (1973).** Emulsion stability tests (cold and heat stability) were also done according to the method of **WHO Specifications (1973).**Viscosity was measured by the Digital Viscometer_Brookfield, Model: lvdv e230 and the surface tension was measured by a stalagmometer.

The toxicity of the standard and prepared formulations

The toxicity of the standard commercial and prepared formulations of both organophosphorous insecticides were evaluated against the red flour beetle *Tribolium casatneum* (Herbst) (Coleoptera: Tenebrionidae).

1. Insect

Susceptible strain of *Tribolium castaneum* was obtained from an established laboratory culture, Faculty of Agric. (Saba Basha), Alex. Univ., Alexandria, Egypt. The insect was reared under the hygrothermic conditions of 25± 2° C and 70± 5% R.H for several generations and the age of the adults that have been used for the test was about 2-3 weeks.

2. Bioassay

A residual film bioassay procedure was used to evaluate the toxicity of the standard and prepared formulations of the tested insecticides. The products were diluted with water to obtain serial concentrations of each to be tested against the insect. Each concentration (1ml) was applied and regularly distributed on filter paper (9cm diameter). Each concentration was replicated 3 times. The papers were left over at room temperature to allow the water to evaporate and became dry. The filter paper was handled carefully and fixed in its place. Ten adult insects were released into the filter paper and maintained in a constant room temperature of 25± 2° C for 48 hours. The mortality was recorded after 24 and 48 hours. The insects were categorized to alive or dead (brittle and showing no movement over a 5 min observation period).

The data were analyzed by the aid of a computer. The correction of mortality percentages, if there were any control mortality was done through a computer program "Probit" using **Abbott's formula (1925).** Probit (mortality)/log conc. regression equations, LC_{50} and LC_{95}'s and associated fiducial limits were calculated by the method described by **Finney (1971).**

Synergistic effect of the tested formulations with Sylgard 309®

The synergistic effect of the tested formulations of chlorpyrifos and malathion with "Sylgard 309®" was evaluated against *T. castaneum*). Sylgard 309® is a registered trademark of Dow Agro Sciences. Different concentrations of each of the tested formulations were prepared as a final volume of 100ml containing 0.25 ml of "Sylgard 309®" (0.25%) . one ml of each the prepared concentrations with Sylgard 309® was applied to a 9cm diameter filter paper. The bioassay was done as that previously mentioned. The synergistic ratio was calculated as follows:

$$\text{Synergistic ratio} = \frac{\text{LC50 for insecticide alone}}{\text{LC50 for insecticide + synergist}}$$

If the synergistic ratio> 1 (synergism), =1 (addition) and< 1= antagonism

The potency of each prepared formulation was determined by the method of **Finney (1978)** as compared with the standard formulation of each of the tested insecticides.

RESULTS AND DISCUSSION

1. Formulation of Chlorpyrifos-ethyl and malathion emulsifiable concentrates

Although there have been a move toward an integrated pest management approach, the use of chemical management remains a cornerstone of pest management. The primary objectives of formulation technology are to optimize the biological activity of the pesticide, and to give a product which is safe and convenient for use. However, because of the wide variety of pesticide active ingredients which are available, many different types of formulations have been developed depending mainly on the physico-chemical properties of the active ingredients. It is more economical to reduce the applied amounts of pesticides than to decompose the non-bioactive amounts if ever possible. An important way to achieve this aim is the design of formulations which combine an optimum of bioactivity with a minimum amount of pesticides.

1.1. Chlorpyrifos formulations

1.1.1 Physical properties

Several attempts were made for formulating chlorpyrifos EC 48%. The prepared formulations and the commercial ones were tested for their

emulsion stability, acidity, alkalinity (according to **WHO specifications, 1973**), in addition to viscosity and surface tension. The type of chlorpyrifos (commercial and prepared) formulations and their physical properties are presented in Table1. Two successful preparations were compared with two commercial formulations.

The mixture of the technical chlorpyrifos with the either emulsifiers (Calcicum or Sodium Dodecylbenzene Sulfonate [Ca DBS or Na DBS]) as ionic liquids succeeded in inducing emulsion stability in both of the prepared formulation. TritonX-100 was found to enhance the stability of the prepared formulations. In this respect, **Mata-Sandoval *et al.* (2001)** reported that TritonX-100 as a heterogeneous nonionic octylphenol ethoxylate surfactant can be added to increase the apparent water solubility of hydrophobic organic compounds.

The prepared formulations will be referred as F1 (with **Ca DBS)** and F2 (with **Na DBS)**. Regarding the all detected physical properties, it is noticed that F1 is more or less similar to Octafos® and F2 to Chlorpyrifos-KZ®. Free acidity calculated as H_2SO_4% for the all prepared and commercial formulation was found to be ranged from 0.018 (F2) to 0.023 (F1).

The viscosity range was 6.31 - 7.35 CP and the range of the surface tension was 27.1-29.7 Dyne/cm at 24°C. The prepared formulation F2 had the higher viscosity and surface tension, while the commercial compound Octafos® had the lower ones. The emulsion stability test proved that the creaming (separation in ml) of the all tested chlorpyrifos formulations was less than the maximum separation (2ml either after 0.5 or 2.0 hours) that have been recommended by **FAO specifications (2004)**.

1.1.2. Cold/ heat Stability

Reformulating certain insecticides such as chlorpyrifos and malathion to meet specific regulations or increasing their effectiveness to replace successful pesticide product (formulation) with another one of equivalent performance can be usually accepted. Table 2 shows cold/ heat stabilities of the all prepared (F1 and F2) and the commercial emulsifiable concentrate (E.C) formulations of chlorpyrifos 48%.

1.2. Malathion formulations

1.2.1 Physical properties

The physical properties of the prepared malathion formulations compared to the commercial formulations are shown in Table 3.

The determined Free acidity as H_2SO_4% for the all prepared and commercial formulations of malathion was found to be ranged from 0.12 (F1) to 0.19 (Malatox®), with the exception of Malason-KZ® which have been found to have less acidity of 0.017% (as H_2SO_4) (the acceptable acidity of a malathion concentrate should not be greater than 0.5%). It is noticed that the surface tension of the prepared and commercial formulations of chlorpyrifos (with a range of 27.1- 29.7 Dyne/cm) were less than those of malathion (with a range of 38.1- 41.1 Dyne/cm).

According to **WHO Specification (1973)**, any separation, including creaming at the top and bottom of 100 ml of emulsion should not exceed 2 ml. The commercial formulations were found to have a little more stability as they were prepared as emulsions in either soft and/or hard water.

Table 1: Physical properties of two prepared chlorpyrifos E.C Formulations (F1&F2) compared to the commercial formulations

Formulations	Emulsion stability test (ml separation)				Acidity $\%H_2SO_4$	Viscosity (cP=mPa·s)	Surface tension Dyne/cm at 24°C
	Hard water		Soft water				
	1/2h	2h	1/2h	2h			
(F1) Chlorpyrifos 48% + Ca DBS 4.8% + Triton 4.8%	0.75	1.00	0.50	0.75	0.023	6.35	27.5
(F2) Chlorpyrifos 48% + Na DBS 4.8% + Triton 4.0%	0.75	1.20	0.50	0.75	0.018	7.35	29.7
Octafos®	0.00	0.00	0.00	0.00	0.021	6.31	27.1
Chlorpyrifos-KZ®	0.25	0.50	0.00	0.25	0.019	7.20	28.3

Acidity for Xylene = 0.0, Ca DBS= 0.46 ($\%H_2SO_4$) and alkalinity for Na DBS = 1.39, TritonX-100 = 0.051 (% Na OH). * F1 = Formulation 1 and F2 = Formulation 2

Table2: Cold/ heat stability for chlorpyrifos formulations (E C 48%)

Formulations	Cold stability (ml separation)				Heat stability (ml separation)			
	Hard water		Soft water		Hard water		Soft water	
	1/2h	2h	1/2h	2h	2h	2h	2h	2h
(F1) Chlorpyrifos 48% + Cadbs 4.8% + Triton 4.8%	1.00	1.25	0.75	1.00	0.50	0.75	0.00	0.25
(F2) Chlorpyrifos 48% + Na DBS 4.8% + Triton 4.0%	1.25	1.50	0.75	1.25	0.75	1.25	0.50	0.75
Octafos®	0.50	0.75	0.25	0.50	0.00	0.00	0.00	0.00
Chlorpyrifos-KZ®	0.75	1.00	0.00	0.25	0.25	0.50	0.00	0.25

Table 3: Physical properties of two prepared malathion formulations compared to the commercial formulations

Formulations	Emulsion stability test (ml separation)				Acidity $\%H_2SO_4$	Viscosity (cP=mPa's)	Surface tension Dyne/cm at 24°C
	Hard water		Soft water				
	1/2h	2h	1/2h	2h			
(F1) Malathion 57% + Ca DBS 4.4% + Triton 4.0%	0.75	1.25	0.50	1.00	0.12	11.00	40.1
(F2) Malathion 57% + Na DBS 5.0% + Triton 4.8%	1.00	1.50	1.00	1.25	0.16	10.00	38.5
Malatox®	0.25	0.75	0.00	0.25	0.19	9.82	38.1
Malason-KZ®	0.25	0.25	0.00	0.25	0.017	9.50	38.9

Acidity for Xylene = 0.0%, Ca DBS = 0.46% H_2SO_4,
alkalinity for Na DBS = 1.39%, TritonX-100 = 0.051% NaOH

1.2.2 Cold/ heat stability

All the prepared and commercial formulations were satisfactory and fulfilled the specified requirements (Table 4). They passed successfully the cold and heat effect giving a separationrange of 0.25-1.25ml and that was less than the maximum acceptable limits (4ml) (FAO Specification ,2004).

2. Toxicity of the tested formulations

The prepared EC formulations of malathion (F1&F2) and chlorpyrifos (F1&F2) and two corresponding commercial formulations of each insecticide were tested against the rust-red flour beetle *Tribolium castaneum*. Results of response of *T. castaneum* to the different tested EC formulations of malathion and chlorpyrifos after a 24 hrs bioassay are given in Table 5.

Table 4: Cold/ heat stability for emulsifiable concentrate (E.C) formulations of malathion 57%

Formulations	Cold stability (ml separation)				Heat stability			
	Hard water		Soft water		Hard water		Soft water	
	1/2h	2h	1/2h	2h	2h	2h	2h	2h
(F1) Malathion 57% + Ca DBS 4.4% + Triton 4.0%	1.00	1.25	0.50	o.75	0.75	1.25	0.50	1.00
(F2) Malathion 57% + Na DBS 5.0% + Triton 4.8%	1.25	1.5	0.75	1.00	1.00	1.50	1.00	1.25
Malatox®	0.50	0.75	0.25	0.50	0.25	0.75	00	0.25
Malason-KZ®	0.50	1.00	0.25	0.50	0.25	0.25	00	0.25

Generally, it was found that all the tested formulations of chlorpyrifos were more and highly toxic than those of malathion. Regarding the formulations of malathion, the commercial formulation Malatox® was found to be more toxic against *T. castaneum* adults compared with the other malathion formulations showing the lower LC_{50} value of 38644.11 ppm followed by F1 (3936.26 ppm). The least efficient tested formulation was F2 giving a high value of LC_{50} of 42888.17 ppm. Nevertheless, the prepared

formulations were matching those locally sold commercial formulations which have been produced by Egyptian chemical and insecticides companies.

Regarding the response of *T. castaneum* adults exposed to impregnated filter papers with different tested concentrations of each of the tested chlorpyrifos formulations, the results of mortality after a 24 hrs bioassay revealed that there were no obvious differences between the effectiveness of the formulations F1, Octafos® and Chlorpyrifos-KZ® giving more or less the same LC_{50}s as a value of about 21 ppm. Meanwhile, it was found that F2 showed the highest LC_{50}value of 24.89 ppm; and therefore it was considered to be the least effective one. Herein, those prepared formulations of either malathion or chlorpyrifos that containing the emulsifier Ca DBS were more toxic than those containing Na DBS. **Pereira *et al.* (2009)** stated that the toxicity of a chemical can be affected by the formulation.

The included results in Table 6 show the response of *T. castaneum* to the different tested formulation of malathion and chlopyrifos after a 48 hrs bioassay. These results confirmed the detected results of the toxicity of these tested formulations obtained after an exposure period of 24 hrs. The calculated LC_{50} for the 48 hrs bioassay were decreased and less than those obtained after a 24 hrs bioassay. On the other word, the tested formulations of chlorpyrifos were more efficient and toxic than those of malathion. Also, those prepared formulations of either malathion or chlopyrifos that contain Ca DBS were more toxic than the prepared formulation containing Na DBS.

Malatox® (LC_{50} = 31333.83 ppm) was the most efficient formulation compared with the other formulations of malathion, while Ocatfos® was the best (LC_{50} = 11.83 ppm) compared with the other formulation of chlorpyrifos. The superior toxic efficiency against *T. castaneum* based on LC_{50} values was achieved by Ocatfos® either after the exposure period of 24 or 48 hrs.

3. Potency of the tested formulations

For more comparison between the prepared and selected commercial formulations (purchased from the local market) of malathion and/or chlorpyrifos, the toxicity index, the relative potency and the

mathematical potency suggested by **Finney (1978)** were calculated. Tables 7& 8 showed that the calculated toxicity index and relative potency values assure the results of toxicity of both the prepared and commercial formulations of malathion and chlorpyrifos when they were tested against *T. castaneum* adults after either 24 or 48 hrs, respectively. Concerning malathion formulations, there were no difference between the commercial Malatox® formulation and the F1 prepared formulation (containing Ca DBS). F2 was found to have the lower values of toxicity index and the relative potency but still not far away from the other tested prepared or commercial formulations.

Regarding chlorpyrifos formulations, it was found that the potency of F1 was more or less similar to that of the commercial formulation Ocatfos® which was the most effective formulation tested against *T. castaneum* giving the higher toxicity index (100) and relative potency (1) values since these values of the other tested formulations were less than 100 and 1, respectively.

The potency of the prepared EC formulations (*F*) compared to the commercial ones (*com*) of either malathion or chlorpyrifos as calculated according to **Finney (1978)** is shown in Tables 7 & 8 (24 & 48 hrs bioassay, respectively). The horizontal distance between the Ld-p line of a formulated preparation and the Ld-p line of a commercial one (***M***) is considered to be a preliminary indication of potency. ***M*** calculated as

$$M = (\bar{X}_{com} - \bar{X}_{F}) - (\bar{y}_{com} - \bar{y}_{F})/\text{slope}_{F}$$

If ***M*** value is negative, it means that the Ld-p line of the prepared formulation (F1 or F2) moves downwards to the right side giving a high value of LC_{50} (less toxic and less potent) and vise versa. ***M*** value will lead to the real value of potency (***R***) and this value (***R***= 20 antilog [***M***]) might be more than 20 and in this case it expresses that the prepared formulation is more toxic (potent) than the commercial one which has been considered as standard for comparison. Moreover, the potency of the prepared formulation compared with the commercial one can be measured as $\acute{R}$ = 1antilog ***M***. Herein, $\acute{R}$ value would be < 1, (the formulated preparation will be less potent), $\acute{R}$ = 1 (equal toxicity) and $\acute{R}$> 1 (the formulated preparation will be less potent than the commercial one compared with).

Table 7 shows the potency (***R*** and ***Ŕ***) values calculated from a 24 hrs bioassay. It could be seen that the calculated ***R*** value for F1 of malathion is more than 20 (20.65) and ***Ŕ*** > 1 (1.03) when it was compared with Malason-KZ® and therefore this prepared formulation is more toxic and potent than that commercial one. It is the only case found with higher ***R*** (more than 20); and therefore F1 on the other hand is less toxic than the other commercial formulation (Malatox®) and F2 is less toxic or potent than both tested commercial formulations.

It was also found that F1 formulation of chlopyrifos was as effective as Chlorpyrifos-KZ® giving a value of ***R*** reached 20.00 (***Ŕ*** = 1). Both prepared formulations of chlorpyrifos (F1 & F2) were less toxic than Octafos®, while F2 (***R***= 17.97) was less toxic than Chlorpyrifos-KZ®.

For the 48 hrs bioassay (Table 8), the data revealed and assured that F1 of malathion was more toxic than Malason® (***R*** = 20.64) and F1 of chlorpyrifos was more toxic than Chlorpyrifos-KZ® (***R*** = 23.56) and these prepared F1 formulations of both insecticides containing Ca DBS and that might support the use of Ca DBS for preparing effective formulations.

4. Synergistic effect of Sylgard 309® with the all tested formulations

Sylgard 309® as a synergist was used at a rate of 0.25% diluted in water that has been used for preparation of the serial dilutions (concentrations) of tested formulations (prepared and commercial). The term synergism is confined to those cases in which Sylgard 309® was considered to be inactive or negligibly active when used alone but its mixture with an insecticide formulation is more toxic. It can be seen from the data represented in Table 9 that the LC_{50} values of the mixture of 0.25% Sylgard 309® and the all tested EC formulations compared with the formulations alone are showing cases of synergism. It is also noticed that the synergistic ratio of the all chlorpyrifos formulations were high than those of malathion. More synergistic effect was occurred when Sylgard 309® was added to chlorpyrifos formulations.

The data shown in Table 10 (48 hrs bioassay) assured the same mode of action of both Sylgard 309® and the tested formulations of either malathion or chlorpyrifos pronouncing synergism. Chlorpyrifos formulations were also more synergized with Sylgard 309® than malathion formulations.

It is found that adding Sylgard 309® to either formulation of malathion and chlorpyrifos reduced their LC_{50}s and the fiducial limits became more narrow due to its synergistic effect.

Rinehold and Jenkins (2006) reported that some coadjuvants such as organosilicone that are compatible with insecticides improve the effectiveness of insecticide applications. Thus, it is possible to decrease the use of insecticides, which will minimize the losses by evaporation and drift. At the same time, it allows for a better penetration of the active ingredient through the insect cuticle and the plant structures. Therefore, **Araya and delaCerda (2008)** used siliconate adjuvants to improve the sprayed insecticides coverage and penetration to control *Psaudococcus. viburni* in grapevines. Moreover, they could also improve the efficiency of insecticides and considerably reducing the costs of control.

It could be concluded that the special effect of Sylgard 309® with the tested formulations will permit more economical control of insects. The dose or the rate of insecticide application will be reduced and therefore reduces the environment pollution and might reduce the incidence of insect's resistance.

Table 5: Response of a laboratory strain of *T. castaneum* to different EC formulations of malathion and chlorpyrifos (24 hours bioassay)

Formulation	LC_{50} (ppm)	Fiducial limits Lower- Upper	LC_{95} (ppm)	Fiducial limits Lower- Upper	Slope ± SE	P
Malathion						
F1	39362.26	36056.88 - 42971.10	82930.57	65696.5 - 104696.9	5.08 ±0.47	0.07
F2	42888.17	38868.10 – 47326.00	93897.73	71378.5 - 123538.2	4.83 ±0.48	0.02
Malatox®	38644.11	35300.53 - 42304.83	84489.47	66281.5 - 107712.4	4.84 ±0.42	0.24
Malason-KZ®	40617.63	37067.61- 44508.26	87090.31	67920.0 - 111684.7	4.97 ±0.47	0.07
Chlorpyrifos						
F 1	21.60	18.35 - 25.40	77.53	59.39-101.63	2.96 ±0.11	0.01
F2	24.89	21.34 - 29.02	86.40	65.79-113.88	3.04 ±0.12	0.04
Octafos®	21.11	17.95 - 24.81	73.83	57.02-95.61	3.03 ±0.11	0.02
Chlorpyrifos KZ®	21.81	18.48 - 25.71	81.40	61.67-107.92	2.88 ±0.10	0.06

Table 6: Response of a laboratory strain of *T. castaneum* to different EC formulations of malathion and chlorpyrifos (48 hours bioassay)

Formulation	LC_{50} (ppm)	Fiducial limits Lower- Upper	LC_{95} (ppm)	Fiducial limits Lower- Upper	Slope ± SE	P
Malathion						
F1	32458.44	29911.26 - 35222.39	66005.2	55069.6 - 79119.0	5.34 ±0.42	0.04
F2	35092.85	32159.98 - 38293.85	76362.3	61403.6 - 94975.7	4.87 ±0.39	0.09
Malatox®	31333.83	28915.82 - 33953.82	62076.7	52458.0 - 73464.4	5.54 ±0.44	0.01
Malason-KZ®	33350.66	30703.34 - 36226.14	68896.7	56945.0 - 83364.2	5.22 ±0.42	0.03
Chlorpyrifos						
F1	12.30	10.10_14.95	45.13	34.87-58.74	2.91 ±0.10	0.09
F2	13.79	11.28-16.83	56.86	43.09-75.49	2.67 ±0.10	0.25
Octafos®	11.83	9.75-13.31	40.73	31.70-52.62	3.06 ±0.12	0.07
Chlorpyrifos-KZ®	13.52	11.11-16.41	52.15	40.03-68.33	2.81 ±9.59	0.12

Table 7: Comparison between the efficiencies of the different evaluated EC formulations of malathion and chlorpyrifos against a susceptible strain of *T. castaneum* (24 hours bioassay)

Formulation	LC_{50} (ppm)	Log (dose)/ N.E.D. response	Toxicity Index	Relative Potency	Potency[a] of prepared formulations Compared with standards (commercials)			
					Malatox®		Malason- KZ®	
Malathion					*M* (Fiducial limits) (M_l ~ M_u)*	*R*** (*Ŕ*)***	*M* (Fiducial limits) (M_l ~ M_u)	*R* (*Ŕ*)
F1	39362.26	Y=-23.35+5.08x	98.18	1.1	- 0.063307 (-0.014 ~ -0.113)*	17.29 (0.86)	+ 0.01378 (0.128 ~ -0.100)	20.65 (1.03)
F2	42888.17	Y=-22.39+4.83x	90.10	1	-0.09211 (-0.039 ~ -0.145)	16.18 (0.81)	-0.01207 (0.041~ -0.065)	19.45 (0.97)
Malatox®	38644.11	Y=-22.21+4.84x	100	1.11				
Malason KZ®	40617.63	Y=-22.89+4.97x	95.14	1.06				
Chlorpyrifos					Octafos®		Chlorpyrifos- KZ®	
F1	21.60	y = -3.95+2.96x	97.73	1.15	- 0.037027 (0.057 ~ -0.131)	18.36 (0.92)	+ 0.000 (0.093 ~ -0.093)	20.00 (1.00)
F2	24.89	y = -4.25+3.04x	84.81	1	- 0.082763 (0.008 ~ -0.174)	16.53 (1.83)	- 0.04645 (0.043 ~ -0.136)	17.97 (0.89)
Octafos®	21.11	y = -4.01+3.03x	100	1.18				
Chlorpyrifos-KZ®	21.81	y = -3.85+2.88x	96.79	1.14				

a calculated according to Finney (1978), * (M_{Lower} ~ M_{Upper}), **R= 20 antilog *M* and * ** *Ŕ*= 1 antilog *M*

Table 8: Comparison between the efficiency of the different evaluated EC formulations of malathion and chlorpyrifos against a susceptible strain of *T. castaneum* (48 hours bioassay)

Formulation	LC_{50} (ppm)	Log (dose)/ N.E.D. response	Toxicity Index	Relative Potency	Potency[a] of prepared formulations Compared with standards (commercials)			
		Malathion			Malatox®		Malason- KZ®	
					M (Fiducial limits) ($M_l \sim M_u$)*	R^{**} ($\acute{R}$)***	*M* (Fiducial limits) ($M_l \sim M_u$)	*R* ($\acute{R}$)
F1	32458.44	y =-24.07+5.34x	96.54	1.08	- 0.011273 (0.036 ~ -0.058)*	19.49# (0.97)	+ 0.013745 (-0.060 ~ -0.032)	20.64 (1.03)
F2	35092.85	y =-22.14+4.87x	89.29	1.00	-0.050 (0.001 ~ -0.101)	17.83 (0.89)	-0.02643 (0.023 ~ -0.076)	18.82 (0.94)
Malatox®	31333.83	y =-24.91+5.54x	100	1.09				
Malason- KZ®	33350.66	y =-23.61+5.22x	93.95	1.05				
		Chlorpyrifos			Octafos®		Chlorpyrifos- KZ®	
F1	12.30	y =-3.18+2.91x	96.18	1.12	- 0.04309 (0.047 ~ -0.133)	18.11 (0.91)	+ 0.07120 (0.171 ~ -0.028)	23.56 (1.18)
F2	13.79	y =-3.05+2.67x	85.79	1.00	- 0.17348 (-0.072 ~ -0.275)	13.41 (0.67)	- 0.03633 (0.070 ~ -0.142)	18.40 (0.92)
Octafos®	11.83	y =-3.29+3.06x	100	1.17				
Chlorpyrifos®-KZ	13.52	y =-3.17+2.81x	87.50	1.02				

a calculated according to Finney (1978), * ($M_{Lower} \sim M_{Upper}$), **R = 20 antilog M and *** $\acute{R}$ = 1 antilog M

Table 9: Synergistic effect of the prepared EC formulations of malathion and chlorpyrifos with Sylgard 309® (a synergist) against *T. castaneum* after a 24 hours bioassay

Formulation	LC_{50} (ppm)	Fiducial limits Lower- Upper	Synergistic Ratio	Status of Synergism
		Malathion		
F1	39362.26	36056.88 - 42971.10	1.12	S*
F1 +S	35277.82	32295.24 - 38535.97		
F2	42888.17	38868.10 - 47352. 00	1.21	S
F2 +S	35395.28	32556.51 - 38481.65		
		Chlorpyrifos		
F1	21.60	18.35 - 25.40	2.34	S
F1 +S	9.25	7.65 - 11.16		
F2	24.89	21.34 - 29.02	2.20	S
F 2 +S	11.33	9.40 - 13.62		

*S= Synergism

Table 10: Synergistic effect of the prepared EC formulations of malathion and chlorpyrifos with Sylgard 309® against susceptible strain of *T. castaneum* after a 48 hours bioassay

Formulation	LC_{50} (ppm)	Fiducial limits Lower- Upper	Synergistic Ratio	Status of Synergism
		Malathion		
F1	32458.44	29911.26 - 35222.39	1.14	S*
F1 +S	28408.81	25896.39 - 31164.53		
F 2	35092.85	32159.98 - 38293.27	1.19	S
F2 +S	29442.78	26968.25 - 32144.01		
		Chlorpyrifos		
F1	12.30	10.10 - 14.95	2.12	S
F1 +S	5.81	4.47 - 7.50		
F2	13.79	11.28 - 16.83	2.02	S
F2 +S	6.84	5.42 - 8.59		

*S= Synergism

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الملخص العربي

الفعل التنشيطي لمركب السيلجارد 309 مع التجهيزات المحضرة والمصنعة للملاثيون والكلوربيريفوس ضد حشرة خنفساء الدقيق الحمراء

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تم تقييم الخواص الطبيعية وكفاءة تجهيزات محضرة وتجارية لمركبي الملاثيون والكلوربيريفوس وكذلك الفعل التنشيطي لهذه التجهيزات جميعاً مع مركب السيلجارد 309 (خليط سايكوني عضوي غير أنيوني ذو نشاط سطحي) ضد خنفساء الدقيق الحمراء. وقد تم إذابة المادة الفعالة من كل مبيد في الزيلين مع إضافة إحدي عوامل الآستحلاب المستخدمة (كالسيوم أو صوديوم دوديسيل بنزين سلفونات) وكذلك ترايتون اكس 100 لزيادة ثبات التجهيزة المحضرة. هذا وقد إجتازت تجهيزتين ناجحتين من كل مبيد وذلك من عدة تجهيزات مجربة الإختبارات الخاصة بالثبات في الظروف الباردة أو الحرارة العالية.

وقد تم تقييم التجهيزات الناجحة والتجهيزات المصنعة التجارية (التي استخدمت للمقارنة) ضد حشرة خنفساء الدقيق الحمراء في تقييم حيوي لمدة 24 و 48 ساعة حيث وجد تطابق في السمية بين التجهيزات المحضرة والتجارية. وقد وجد أن تلك التجهيزات المحضرة والتي يدخل في تكوينها عامل الإستحلاب كالسيوم دوديسيل بنزين سلفونات كانت أكثر سمية من تلك التي تحتوي علي الصوديوم دوديسيل بنزين سلفونات. وقد أظهرت النتائج أن كل تجهيزات مبيد الكلوربيريفوس كانت أكثر سمية من تجهيزات الملاثيون ضد الحشرة المختبرة.

ولمقارنة التجهيزات المحضرة مع التجهيزات التجارية فقد تم حساب كل من الكفاءة النسبية ودليل السمية. وبإستخدام مركب السيلجارد 309 (0,25%) أدي إلي تنشيط كل التجهيزات المستخدمة مع حدوث زيادة في تنشيط مركب الكلوربيريفوس بصورة أكبر من الملاثيون. وعلي هذا فإن استخدام هذا المنشط سوف يؤدي إلي تقليل الجرعة أو معدل التطبيق وبالتالي تقليل التكاليف وخفض الضرر علي البيئة وربما يؤدي ذلك أيضاً إلي تأخير ظاهرة المقاومة.