Correlating the Insecticidal Potency and Resistance Levels to the Physico-chemical Properties for Three Different Methomyl Formulations

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Abstract: Many Methomyl formulations are widely used in the field of pest control especially to fight cotton leaf worm *Spodoptera Littorals* (Boisd) in many crops in Egypt. In the current study the insecticidal efficiency and its correlation with some physicochemical properties and types of formulations for three Methomyl formulations were studied. The three different Methomyl formulations used are Neomyl 90% SP, Neomyl 20% SL and Lanate 25% WP. For the first time some physical properties as compressibility factor (C.F) and Hausner index (H.I) that control flow ability of solid formulations, were evaluated under different storage conditions. Resistance levels of cotton leaf worm against the studied three Methomyl formulations were also assayed.

Keywords: Methomyl, insecticidal potency, resistance levels, physico-chemical properties and formulation.

1.Introduction

In many countries, cotton (*Gossypium spp.*) is one of the most important fiber producing plants. Its plant not only provides fiber for the textile industry, but also plays a role in the feeding and oil industries. Cotton crop is often damaged by various insect pests as trips, cotton aphids, plant bugs, stink bugs, bollworm and spider mites causing significant yield losses **(Bacheler, 2012)**. Cotton leaf worm, *Spodoptera littoralis* (Boisd.) is known as one of the most destructive agricultural lepidopterous pests, attacking numerous economically important crops and vegetables especially cotton plant **(El-Guindy *et al*, 1989;Abdallah 1991;Abo-Elghar *et al.*, 2005; Mahmoud, 2013; Yousef *et al*, 2013)** The overlapping of crops that serve as hosts of this insect throughout the annual cropping cycle encourages high population densities. Cotton leaf worm control program is based mainly on the using of synthetic insecticides, that their intensive use causes many environmental and resistance problems **(Rashwan, 1991;.El-Barmawy,1992)**.

Carbamates are among the most extensively used insecticides comprising the third major group of synthetic insecticides being utilized worldwide for agriculture and frequently have been used because of their relatively short life in the environment and fast action on the target pest **(Kaur,2006)**..Methomyl is acarbamate oxime insecticide and was introduced in the global market in 1966 as a broad spectrum of insecticide, where it is used in Egypt in different forms of formulations to control cotton leaf worm and other pests. One of the most important requirements for compressible physical properties of the powdered formulations is their good ability to flow. It is typically determined by some powder properties such as density, tapped density and the angle of repose. There are some common techniques used to establish the potential flow ability of powdered formulations. The good flow ability is critical to guarantee rapid and uniform die filling during final product formation **(Maarschalk,1998; Zhang,2003;Prescott and Barnum, 2000; Abdullah and Geldart,1999; Schüssele and Bauer-Brandl 2003)**.

The aim of the current study is to evaluate the physicochemical properties and the insecticidal activity of three different commercial Methomyl formulations used to fight the cotton leaf worm and correlate the relation between their insecticidal activities and both formulation types and the physical properties of such formulations. In this study the flow ability of two Methomyl powdered formulations was assayed under different storage conditions and its relation with the insecticidal activity was studied for the first time.

2.Materials and Methods

2.1.Insects

2.1.1.Susceptible strain:

Susceptible strain (S-strain) of cotton leaf worm, *S. littoralis* was obtained from pest Rearing Department in the Central Agricultural Pesticides Laboratory, and maintained without exposure to any insecticide since 1980 where they were reared on the fresh castor bean leaves. The culture was reared under laboratory conditions (25± 2° C and 65 ± 5% R.H).

2.1.2.Field strains:

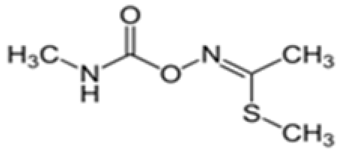
Field strainsof the cotton leaf worm, *S. littoralis,* which used as experimental insect were collected from cotton field in Sharkia Governorate during early cotton season of 2014-2015. All the egg masses were collected pre-spray season, then transferred to the laboratory and kept until hatching at 25 ± 2° C and 65 ± 5% R.H). The larvae were kept in 1 liter glass jars covered with muslin and reared on fresh leaves of castor bean until they reached the 4^{th} larval instar. The experimental insects in the present insecticidal investigation were obtained from this laboratory strain and were divided into three groups.

2.2.Insecticide

The insecticide used in the present workis Methomyl and their formulations were collected from the local

Egyptian market. These formulations are Neomyl 90% SP and Neomyl 20% SL, from the production of Kafr El-Zayat Co., for pesticide and chemicals. The third one is Lannate 25% WP from local company Du-pont Egypt that is manufactured by Du pont DE Nemours USA. All the three tested formulations have Methomyl as an active gradient.

Methomyl chemical structure is shown as follows:



2.3.Bioassay procedure

The effects of the above formulations on 4th instars larvae of *S. Littoralis* were determined using the leaf dipping technique. For each chemical, five serial concentrations (in ppm) were prepared in distilled water and fresh castor bean leaves were dipped in each concentration for ten seconds then left to dry. The treated leaves were transferred to petri dishes and ten larvae were placed in each one the nit was covered. Five replicates were prepared for each concentration. Mortalities were recorded 24 hours after insecticides treatment. Mortality data were corrected using Abbott' s formula **(Abbott, 1925)** and subjected to statistical analysis by the method of **(Finney,1952)** . The rates of resistance were expressed as resistance ratio (R.R) at the LC_{50} level of the field strains as compared with the laboratory strain which has been reared under laboratory conditions for more than 3 generations without exposure to any insecticides **(Busvine, 1957)**. Resistance ratio (R.R) = LC_{50}value of the field strain / LC_{50}value of the laboratory strain.

2.4.Physical properties measurements

The physicochemical properties of the three tested formulations were measured initially under normal or laboratory conditions. Cold storage was proceeded at 0°C ± 1 for 7 days in refrigerator. Two samples were used for hot storage conditions, where they were kept in glass bottles in an oven at 54°C ± 2 for 3 and 14 days according to the standard procedure **(Finney,1952)** . The physical properties of Methomyl samples and their spray solutions in soft and hard water were measured separately according to the approved ASTM (American Standards for Testing and Materials) and CIPAC hand book. Methods and devices used in testing process are given in table (1).

Table (1). Apparatus and methods used for measuring the physical properties.

Property	Apparatus name/ model	Methods no/ title
Bulk density	Manually	CIPAC – MT 186
Tap density	Copley densitometer	ASTM – B 527 -06
Acidity or alkalinity	Hanna 901 automatic titrator	CIPAC – MT 191
pH	Jenway pH meter	CIPAC – MT 75.3
Viscosity	Brookfield viscometer DV+II pro.	ASTM-D 2196-15
Surface tension	Force tensiomate sigma 700	ASTM-D 1331-14
Density and specific gravity	Rudolph densitometer 2910	ASTM-D 4052-11
Conductivity and salinity	Thermo ion 115	CIPAC - MT 32

3.Results and Discussion.

3.1.The physicochemical properties of the powdered Methomyl formulations under different storage conditions

Data presented in table (2) show the effect of different storage conditions on the physicochemical properties of the two investigated solid formulations. From the obtained data we can conclude that, there was non significant change in both density and tap density values for both formulations after cold storage and hot storage conditions. After 14 days of hot storage, density value is slightly decreased by 0.02gm/cm^3(3.4%) in case of Neomyl 90% SP and 0.021gm/cm^3(4.4%) in case of Lannate 25% WP. Maximum tap density increases are obtained after 3 days of hot storage in Neomyl 90% SP and 14 days in case of Lannate 25% WP. The recorded increases were found to be 0.023 gm/cm^3 (3.1%) in case of Neomyl 90% SP and 0.027 gm/cm^3(4.1%) in case of Lannate 25% WP. On the other hand, storage conditions and durations slightly change the pH values. After cold storage, PH of Neomyl 90% SP was found to have the highest value of change where it changed from 6.81to 7.31, while Lannate 25% WP behaves differently under all storage conditions.

In addition, the two investigated solid formulations record acidic characters under both types of storage and there are no significant variations in their acidity values with time and conditions of storage. This may be due to the fact that, although there are a slight variations in the pH values, but these variations are around the neutralization point of acid-base titration. Carr's compressibility factor (C.F %) and Hausner ratio (H.R %), are a measuring parameters for the powder of flow ability.

Table (2). The physicochemical properties of powdered Methomyl formulations (Neomyl 90% SP) and (Lannate 25%WP) after storage conditions.

Properties	Neomyl 90 % SP				Lannate 25 % WP			
	initial	Cold storage	Hot storage		initial	Cold storage	Hot storage	
		7 days	3 days	14 days		7 days	3 days	14 days
Density (gm/cm^3)	0.588	0.581	0.581	0.568	0.476	0.467	0.467	0.455
Tap density (gm/cm^3)	0.735	0.735	0.758	0.735	0.658	0.658	0.685	0.667
pH	6.81	7.31	6.88	6.92	6.65	6.35	6.42	6.35
Acidity	0.004	0.002	0.001	0.005	0.006	0.015	0.006	0.009
Hausner Ratio (H.R)	1.25	1.26	1.30	1.29	1.38	1.41	1.47	1.47
Compressibility Factor (C.F)	20.0	20.39	23.26	22.73	27.62	28.97	31.78	31.82

These two factors are measured according to the following equations:-

$C.I = [(\rho_{tap} - \rho_{bulk})/\rho_{tap}]\times 100$

$H.R = [\rho_{tap} / \rho_{bulk}]\times 100$

The data presented in table (2) and illustrated by fig (1) show the flow properties of the two tested solid formulations under the standard storage conditions. Data obtained show that the hot storage has negative effect on the flow ability of Neomyl 90% SP where the recorded C.F and H.R values are 1.25 and 20.0 for the initial sample (unsorted) and 1.30, 1.29, 23.26 and 22.73 for 3 the days and 14 days storage respectively. The cold storage conditions was found to have no significant effect on the flow ability properties, where the recorded C.F value is 20.39 and H.R is 1.26. This is in agreement with the reported researches where it was reported that when Hausner ratio H.R value is ≤ 1.25 and C.F value is ≤ 20.0 this means that the powder is free to flow. When H.R value is>1.25 and C.F value is> 20.0, it reflects the poor flow ability of the powdered formulations, a thing that may affect badly on their biological activity of pesticide in field **(Maarschalk,1998; Zhang,2003;Prescott and Barnum, 2000; Abdullah and Geldart,1999; Schüssele and Bauer-Brandl 2003;Josep *et al,* 2011; Guerin *et al,* 1999; Wu *et al,* 2010)**..

Contrary to what was expected, Lannate 25% WP showed poor flow ability character where its C.F and H.R values were found to be 27.62 and 1.38 respectively before storage. Hot storage exhibited drastic effect on the flow ability of the wet table powdered formulations. The optimum compressibility was found in Lannat 25% WP after hot storage for 14 days where its C.F and H.R values were found to be 31.82 and 1.47 respectively, a think that reflects the bad flow ability of these solid formulations and may affect badly on their field performances.

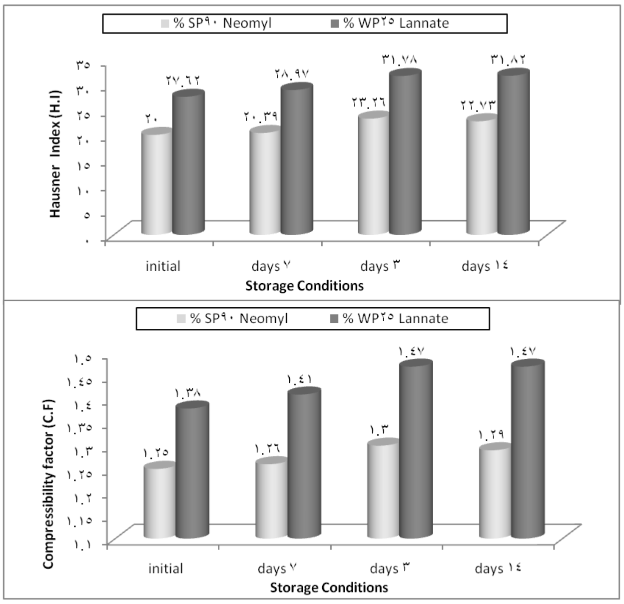


Fig (1): Hausner ratio and compressibility factor of the investigated powdered solid formulations (Neomyl 90% SP and Lannate 25%WP) after storage conditions.

3.2.The physicochemical properties of the liquid Methomyl formulation (Neomyl 20% SL) after different storage conditions

Data presented in table (3) display the physicochemical properties of Neomyl 20% SL formulation after the recommended storage time intervals and conditions

Data obtained clearly show that, there is no reproductive change in the viscosity values after the storage durations, where its values are varied from (2.46 cP) for the initial sample to the highest value (2.66 cP) after 7 days of applying cold storage conditions. In addition, surface tension changes markedly where it records its lowest value (33.20 dyne/cm) in initial sample which does not expose to any storage conditions and its highest value (34.66 dyne/cm) was found to be after 7 days of cold storage.

The obtained data also revealed that, both density and specific gravity possess the highest degree of changein case of the cold storage sample which were (0.971 gm/cm$^{3)}$ and (0.974) as compared with the initial values of (0.956 gm/cm^3) and (0.957) for density and specific

Table (3): The physicochemical properties of the liquid Methomyl formulation (Neomyl 20%SL) after different storage time intervals and conditions.

Properties	Neomyl 20 % SL			
	Initial sample	Cold storage 7 days	Hot storage 3 days	Hot storage 14 days
Viscosity (cP)	2.46	2.66	2.48	2.53
Surface tension (dyne/cm)	33.20	34.66	33.79	33.80
Refractive Index*	ND	ND	ND	ND
Density (gm/cm^3)	0.956	0.971	0.962	0.962
Specific gravity	0.957	0.974	0.964	0.964
pH	6.29	5.53	6.06	5.66
Alkalinity as % of NaOH	0.011	0.005	0.006	0.007

*Tested samples are not transparent enough.

gravity respectively. Hot storage conditions slightly increases the values of density and specific gravity. Also, the maximum depression in the values of both pH and alkalinity is obtained after 7 days of cold storage where it records(5.53) and (0.005)as compared with the initial values of (6.29) and (0.011)for pH and alkalinity on sequence. Hot storage conditions affects slightly on both pH and alkalinity since the two hot storage samples recorded moderate values between initial and cold storage one for both tests.

Generally, cold storage conditions markedly affects the physical properties of Neomyl 20% SL than the hot storage conditions. This effect may be due to the shrinkage property that occurs to the final liquid product at reduced temperature as a result of the molecular interactions between the components of liquid mixture, where some particles inter the intermolecular spaces of matters and spaces between layers of different liquids leading to deviations in values of the measured physical properties(Wu *et al*, 2010; Wang and Zhao, 2005; Anouti *et al,*2010).

3.3.The physicochemical properties of the three Methomyl formulations spray solutions using the recommended doses:

Table (4) display the physicochemical properties of the spray solutions for the three investigated Methomyl formulations in both soft and hard water used for dilution. The data obtained revealed that, viscosity change is limited even with changing the types of formulations and water of dilution. Spray solution of Neomyl 20% SL in soft water possesses the highest value of viscosity (1.99 cp) while Neomyl 90% SP in the same type of water records the lowest value (1.92 cp). Viscosity for spray solutions of Lannate 25 % WP are (1.98 cp) and (1.94 cp) in soft and hard water respectively.

Table (4): The physicochemical properties of the three Methomyl formulations pray solutions in soft water (S.W) and hard water (H.W).

Properties	Neomyl 90% SP		Lannate 25% WP		Neomyl 20% SL	
	S.W	H.W	S.W	H.W	S.W	H.W
Viscosity	1.92	1.96	1.98	1.94	1.99	1.97
Surface tension	65.13	59.13	43.09	54.08	43.04	48.09
pH	6.26	6.47	6.18	6.31	6.05	6.07
Conductivity	66.0	558.0	61.0	557.0	63.0	533.0
Salinity	0.1	0.3	0.1	0.3	0.1	0.3
T.D.S.	36.0	267.0	33.0	256.0	33.0	256.0

On the other hand, surface tension changes remarkably depending on the type of formulation and water of dilution. Surface tension of Neomyl 20% SL was found to be the lowest value, followed by Lannate 25% WP and Neomyl 90% SP. Surface tension of Neomyl 20% SL in soft water is the lowest value (43.03 dyne/cm) while that of Neomyl 90% SP in soft water is the highest value (65.13 dyne/cm). This results may be due to the role of formulation composition where, soluble liquid formulations are characterized by the presence of high concentrations of surface active agents and other additives that may lead to an increase in the viscosity and lowering the surface tension **(Hewitt *et al,* 1997; Hewitt *et al* 2001; Laurier *et al,* 2003;Dan, 1999).** .

From data in table (4) it is clear that, all the tested spray solutions are acidic in their nature and the spray solution's acidity of Neomyl 20% SL is the highest one. This may be due to the using of some additives during the process of manufacturing of Neomyl 20% SL formulation and also may be due to partial hydrolysis of carbamate active ingredient (Tina Smith,2012;Federica, 2009). Data obtained also revealed that, conductivity of the spray solutions in hard water is around ten times than that in soft water. This may be attributed to the large amounts of salts dissolved in hard water. The same trend is found nearly in the values of the total dissolved salts (T.D.S).

3.4.The insecticidal activity of the three tested Methomyl formulations against cotton leaf worm *(spodoptera littoralis)* under laboratory conditions.

Data represented in tables (5-7) and illustrated in fig (2) display the insecticidal activities of the three tested Methomyl formulations against the cotton leaf worm.performance of the main active ingredients. Beside their pesticide activity, surfactants enhance the potency of the active ingredient by allowing for more contacts

Table (5):The insecticidal activity of Lannate 90% SP

Concentration (ppm)	% of mortality
450.0	70.0
225.0	63.0
112.5	60.0
56.2	53.0
28.1	50.0
LC_{50}	30.5
Slope	0.413
Resistance ratio (R.R)	4.15

Table (6): The insecticidal activity of Neomyl 20% SL

Concentration (ppm)	% of mortality
200.0	70.0
100.0	66.0
50.0	63.0
25.0	60.0
12.5	56.0
LC_{50}	3.4
Slope	0.295
Resistance ratio (R.R)	0.47

Table (7): The insecticidal activity of Lannate25% WP

Concentration (ppm)	% of mortality
125.0	56.0
62.5	53.0
31.3	50.0
15.6	40.0
7.8	30.0
LC_{50}	47.6
Slope	0.568
Resistance ratio (R.R)	6.48

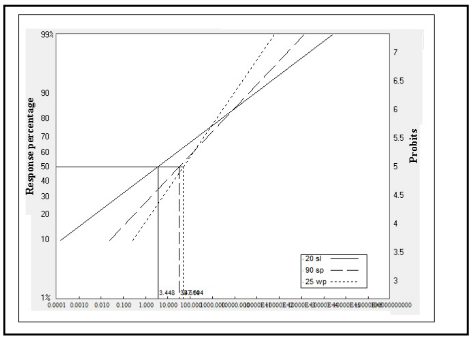


Fig.(2): LDP lines for the three tested Methomylformulations against cotton leaf worm (*spodoptera lettorallis*).

between the spray droplets and the plant surface. They do so by reducing the surface tension of water in the spray solutions to that of an oil or organic solvents, which spread the pesticide more readily on plant surface especially for waxy and oily leaves **(Tong-Xian and Philip, 2000; Radwan, 1982)**.

Data also revealed that the investigated formulations possessed different resistant ratios (R.R) although they have the same active ingredient. According to the values of resistant ratios we can say that cotton leaf worm, *spodoptera littoralis*, is susceptible to Neomyl 20% SL (R.R is 0.47 fold of the susceptible strain), tolerant to solid formulation Neomyl 90% SP (R.R value is 4.15) and highly tolerant to the second solid formulation Lannate 25% WP (R.R value is 6.48). The previous arrangement of the three tested formulations may be due to the difference in their formulation type and the presence of different additives which change the penetration of the active ingredient and are calculated depending on the percentages of the active ingredient in formulations, the reason of variation in LC_{50} values may be due to the type and compositions of the three different formulations. The high activity of the SL formulation may be du to its content to some types of adjuvant that are characterized by their insecticidal activity and/or their ability to enhance the pesticidal performance of the main active ingredients. Beside their pesticidal activity, surfactants enhance the potency of the active ingredient by allowing for more contacts between the spray droplets and the plant surface. They do so by reducing the surface tension of water in the spray solutions to that of an oil or organic solvents, which spread the pesticide more readily on plant surface especially for waxy and oily leaves **Tong-Xian and Philip, 2000; Radwan, 1982)**.

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liorate its effect **(Singab *et al*, 2014; Carlos and Gonzalez ,2010; Belgin *et al* 2015).**

Table (8): The insecticidal activity of Lannate 25% WP after different storage conditions.

Concentration (ppm)	%of Mortality		
	7 days cold storage sample	3days hot storage sample	14 days hot storage sample
125.0	53.6	47.6	44.3
62.5	46.6	42.3	38.9
31.2	39.5	36.9	33.6
15.6	33.2	32.2	28.9
7.8	27.0	27.6	24.3
LC_{50} (ppm)	87.6	170.9	254.2
Slope	0.5892	0.4482	0.4640
Resistance Ratio (R.R)	11.91	23.25	34.58

3.5.The effect of storage conditions on the insecticidal activity of Lannte 25% WP solid formulation.

As we discussed before in table (2), Lannate 25% WP was found to be the highest formulation for Hausner ratio (H.R) and compressibility factor (C.F), that may affect badly on its insecticidal activity especially after storage process. To investigate the impact of storage conditions and durations on the insecticidal activity of Lannate 25% WP, insecticidal activity of the stored and unsorted samples were evaluated and tabulated in table (8). The obtained data clearly show that the activity of such formulation decreases dramatically with increasing the storage durations and conditions. The highest decrease in activity was recorded in the sample that is subjected to the maximum storage duration (14 days). Samples subjected to the hot storage displayed lower activity than that of the cold storage. Comparing the LC_{50} values of the unsorted sample (47.6 ppm) as in table (7) and that after different storage processes reflects the bad effect of this process on the physical properties as well as the biological activity of some pesticides.

Conclusion

Physico-chemical properties and insecticidal activities of three Methomyl formulations were studied before and after applying the standard storage conditions. The three investigated formulations are Neomyl 90% SP, Neomyl 20% SL and Lannate 25% WP. The physical parameters Hausner ratio (H.R) and compressibility factor (C.F), that control the flow ability and potentiality of solid formulations, were studied for the first time. The study revealed that flow ability is a good parameter that may control the activity of solid formulations. Hot storage was found to have a bad effects on the physical properties of solid formulations.

References

Abbot, W.S. (1925). A method of computing the effectiveness of insecticides. J. Econ. Entomol, 18: 265 - 267.

Abdullah, E.C. and Geldart, D; (1999) The use of bulk density measurements as flowability indicators, Powder Technol. 102, 151–165.

Abdallah, M.D;(1991). A general view of the resistance problem of cotton pests in Egypt. Resistant-PestManagement,3: 22-25.

Abo-Elghar, G.E., Zeinab A. E, Adel G. YandHany K; (2005), Monitoring and characterization on insecticide resistance in the cotton leaf worm, *Spodopteralittoralis* (Boisd.) (Lepidoptera, Noctuidae) J. Asia-Pacific Entomol., 8(4): 397-410.

Anonymous, (2002). Manual on Development and Use of FAO and WHO Specifications for Pesticides.1st Edition, pp: 31.

Anouti, M., Vigeant, A., Jacquemin, J., Brigouleix, C. and Lemordant, D;(2010). Volumetric properties, viscosity and refractive index of the protic ionic liquid, pyrrolidinium octanoate, in molecular solvents. J. Chem. Thermodyn. ;42:834–845.

A.S.T.M, (2014). American Society of Testing and Materials. Standard Test Method for Surface and Interfacial Tension of Solution of Surface-Active Agents. D-1331.

A.S.T.M, (2015). American Society of Testing and Materials.. Standard Test Method Standard Test Method for Tap Density of Metal Powders and Compounds B527

A.S.T.M, (2015). American Society of Testing and Materials. Standard Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield type) Viscometer. D-2196.

Belgin, G., T., Taylan, D., Sercan, K., Ersin D. and Vatan, T; (2015). Seasonal dynamics of insecticide resistance, multiple resistance, and morphometric variation in field populations of Culexpipiens. Pesticide Biochemistry and Physiology.

Busvine, J.R; (1957). A critical review of the techniques for testing insecticides. Commonwealth Institute of Entomology, London

Carlos, A., Jose, E. and Gonzalez, Z; (2010). Monitoring resistance of *Helicoverpa armigera* to different insecticides used in cotton in Spain., Crop Protection. 29, 100–10

Dan Hess F; (1999) Surfactants and Additives Proceedings of the California Weed Science Society ,51, 157-172.

Dobrat, W. and A. Martijn; (1995). CIPAC Hand Book, Volumes F. MT 75.3, MT 186 and MT 191

El-Barmawy, Z. El-Shiekh, A. Rashwan, M. and Radwan, H; (1992) Pyrethroids resistance in *Spodop-*

tera littoralis (Boisd) (Lepidoptera: Noctuidae) in lower Egypt. Bull. Ent. Soc. Egypt Econ. Ser. 19: 41-51.

El-Guindy, M.A., Keddis, M.E.,. Abd-Elsattar, M.M and. Ghoneim, Y.F;(1989). Status of resistance in cotton leaf worm *Spodoptera littoralis* (Boisd.) under the present Egyptian cotton pest control programme. Proc. 1st Int.Conf. Econ. Entomol., II: 453-462.

Federica, V. ‹Claudia, S. ‹Alessio, L. ‹Alessandro, F. ‹ Silvia, R. ‹Andrea, D. ‹Andrea, T. ‹Silvano, S.‹ Jason, C. ‹Daniele,P.‹Marco, M. and Giorgio, T; (2009) . Structure property relationships of a class of carbamate based Fatty Acid Amide Hydrolase (FAAH) inhibitors: chemical and biological stability. ChemMedChem.4(9): 1495–1504.

Finney, M.D.J; (1952). Probit Analysis 3rd .Cambridge Univ. Press, London, pp: 333.

Guerin, E., Tchoreloff, P., Leclerc, B., Tanguy, D., Deleui, M. and Couarraze, G; (1999). Rheological characterization of pharmaceutical powders using tap testing, shear cell and mercury porosimeter. International Journal of Pharmaceutics 189, 91±103

Hewitt, A.J., hermansky, C., Valeare, D.L. and Bryant, J.E. (1997). Modeling Atomization and deposition of agricultural sprays. Proc ILASS- Americas, 97, 178-182 , Ottawa- Canda.

Hewitt, A.J., Miller P.C.H., Dexter, R.W., and Bagley, W.E; (2001) the influence of tank mix adjuvant on the formation characteristics and drift potential of agricultural sprays. Proceeding international symposium on adjuvants for agrochemicals, Amsterdam, Netherlands.

Jack S. Bacheler. Managing Insects on Cotton. Chapter11, 2012.

Josep, M., Suñé, N., P.., Manel, R., R, F., Carmen He., Ramon, R., Encarna, G, Montserrat, M. and Josep, R. T; (2011). Optimization of parameters of the SeDeM Diagram Expert System: Hausner index (IH) and relative humidity (%RH) European Journal of Pharmaceutics and Biopharmaceutics 79, 464–472

Kaur, M., Sandhir, R; (2006) Comparative effects of acute and chronic carbofuran exposure on oxidative stress and drug-metabolizing enzymes in liver. Drug. Chem. Toxicol, 29: 415-421.

Laurier, L., Schramm. E., N., Stasiukand, D. and Gerrard, M; (2003). Surfactants and their sapplications. Annu. Rep. Prog. Chem., Sect. C, **99**, 3–48

Maarschalk, K., Bolhuis, G; (1998) Improving properties of materials for direct compactionPart I. Pharm Tech Eur.10(9):30-3.

Mahmoud, H. R; (2013) Biochemical Impacts of Rynaxypyr (Coragen) and Spinetoram (Radiant) on *Spodoptera littoralis* (Boisd.) . Nature and Science, 11(8)

Prescott, J.K. and Barnum, R.A; (2000). On Powder Flowability,*Pharm. Technol.,* Oct 60-84.

Radwanh, H., Mesbah, A., Abdelfattah, S., Abdelmohymen, M. and Hassan, N. (1982). The effect of various adjuvant on the insecticidal activity of diflubenzuron against the cabbage aphid *Brevicorynebrassicae*.Ang. Ent. 94, 420-423

Rashwan, M. El-Barmawy, Z, El-Shiekh and, A. and Radwan, H; (1991) The onset of organophosphates and carbamates resistance among Lower Egypt population of the cotton leaf worm *Spodoptera littoralis* (Boisd). Bull. Ent. Soc. Egypt, Econ. Ser 19: 211-220.

Schüssele, A. and Bauer-Brandl, A; (2003) Note on the measurement of flowability according to the European Pharmacopoeia, Int. J. Pharm. 257, 301–304.

Singab, M., El-Hefny, A., S. and EL-Hadek M., K., M; (2014). Resistance Ratio Assessment to Several Bioinsecticides in Cotton Leaf Worm, *Spodoptera littoralis* at Different Governorates in Egypt. J. Plant Prot. and Path., Mansoura Univ., Vol.5 (5): 605-611.

Tina Smith, (2012). Effects of pH on Pesticides and Growth regulator. On line report.

Tong-Xian, L. and Philip, A. (2000). Insecticidal activity of surfactants and oils against silver leaf whitefly (*Bemisia argentifolii*) nymphs (Homoptera: Aleyrodidae) on collards and tomato. Pest ManagSci 56, 861-866.

Wang J., Zhu, A. and Zhao, Y; (2005). Excess molar volumes and excess logarithm viscosities for binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexaflurophosphate with some organic compounds. J. Solution Chem. 34:585–596.

Wu, T., Su, S., Gung, S., Lin, M., Lin, Y., Lai, C. and Sun, I; (2010). Ionic liquids containing an alkyl sulfate group as potential electrolytes. Electrochim. Acta. ;55:4475–4482.

Yousef, H., Sahier, F.E. and YASMEIN, A.,E ; (2013) Insecticidal Activity of Linoleic Acidagainst *Spodoptera littoralis* (BOISD.) Egypt. J. Agric. Res., 91 (2)

Zhang, Y., Law, Y. and Chakrabarti, S; (2003). Physical properties and compact analysis of commonly used direct compression binders. AAPS Pharm. SciTech. 4(4):E62.