EFFECT OF COMMERCIAL PACKAGES ON PHYSICO-CHEMICAL PROPERTIES OF SOME PESTICIDES IN WETTABLE POWDER FORMULATION UNDER TROPICAL STORAGE CONDITIONS

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ABSTRACT

Four pesticides in wettable-powder formulations were supplied in their commercial packages from their manufactured company to evaluate the interaction effect between physico-chemical properties of these pesticides and their packages under tropical storage conditions (54±1°C) for three days compared with WHO and CIPAC storage, in glass container.

The tested pesticides were : Metalaxyl + copper chloride 50 %, Benalaxyl + copper oxychloride 46 %, Dimethomorph + copper oxychloride 46 %, and Iminocataidin + trisbesulate 40 %; whereas the raw material of the tested packages were polyethylene (po), polyethylene inside aluminum (al/po), polyethylene inside paper (pa/po), and aluminum inside paper (pa/al).

The studied physico-chemical properties were % foam, % suspensibility, wettability, and free acidity or alkalinity for tested pesticides, whereas conductivity, pH, surface tension and salinity were studied for spray solution of the same tested pesticides.

The obtained results clearly show that, all tested package caused bad effect for suspensibility % in both hard and soft water except (pa/po) package with Dimethomorph + copper oxychloride in hard water. So, they failed in suspensibility test at package storage since the suspensibility percentage of these pesticides were less than 60 %, although they passed in this test at WHO glass storage. On the other hand, the effect of tested packages on foam % of tested pesticides was between no effect or improvement effect upwards of that stored in glass container, whereas aluminum package increased free alkalinity of tested pesticides when it combined with paper or polyethylene package.

Except of (po) package in case of Iminocataidin + trisbesulate, all tested packages showed slight improvement in wettability/second as comparing with glass container.

On the other hand, all tested packages showed bad effect against one or more property of physico-chemical properties of tested pesticides spray solutions such as pH, conductivity and surface tension. pH value of spray solution of tested pesticides affected as resulting to storage in tested packages in three forms : a) increasing in pH without any effect on conductivity as shown in case of Iminocataidin + trisbesulate with (po) package. b) increasing in pH values in hard and soft water and conductivity in soft water only as shown with Benalaxyl + copper chloride with (pa/al) packages. and c) decreasing in pH values in hard and soft water and conductivity in soft water of Dimethomorph + copper oxychloride with (pa/po) package.

(pa/po) and (pa/al) packages caused increase in surface tension of tested pesticides spray solution in hard and soft water with the first package and hard water only with the second.

From above results, it could be concluded that, there are relationship between raw materials of packages that used in packing of wettable powder formulations under Egyptian pesticides market conditions and physico-chemical properties of this formulation. On the other hand, the test of suspensibility at WHO

glass container is unsuitable, although the same pesticide passed this test at WHO glass container but failed in this test at commercial package, therefore this test and other tests should be carried out practically in the useful raw material package used for packing pesticides.

INTRODUCTION

During the past few years leglisative, environmental safety and commercial pressures have caused a significant change in the way that manufactures of crop protection chemicals regard product. Packaging is now regarded as major part of total delivery system approach to developing and marketing agrochemical products. Formulation package are considered as a single entity with almost equal importance.

A useful metaphor for packaging is "a bridge between the formulated active ingredient and application method". Together, the formulation, package and application method constitute a "delivery system" which preserve the efficacy of an active ingredient and translate to the target pest. The packaging portion of that system must integrate with formulation, it protects as well as integrate with application method it supplies (Gleish, 1996).

The formulation and packaging concept for product depends on many factors. physico-chemical properties of an active ingredient such as physical state, the chemical stability and solubility in water and organic solvents determine technically and commercially feasible types of formulations for which appropriate packaging has to defined. Other important factors influencing the design of formulations packagings include the toxicological properties of active ingredient and, of course user's needs (Frei and Schmid, 1996).

Several crude materials were used to package solid formulation such as polyethylene monolayer back, rigid plastic container, fexible laminate material incorporating aluminum foil (polyester or polyamide), aluminum foil and paper.

According to the WHO (1973 & 1979), WHO/FAO Meeting (2002), the successful wettable powder must have good wettability (not exceed than 1 min.), % suspensibility (not less than 60 %), foam (not exceed than 2 %), free acidity or alkalinity (not exceed than 0.3 %).

On the other hand, retention of spray solution then pesticidal efficiency depends on these properties of spray solution of pesticides, such as decreasing in pH value with increasing its conductivity (Tawfik and El-Sisi, 1987); also, by decreasing surface tension of spray solution (Osipow, 1964).

The physical and chemical stability of pesticides formulations depended on many factors such as storage conditions and type of package (Farag *et al*., 1993).

The current study aims to evaluate the interaction effect between package type and solid formulations under tropical storage conditions (54±1°C) for three days.

MATERIALS AND METHODS

Different types of commercial packages contained four solid pesticides in wettable powder formulation were supplied from their produced

companies to evaluate their effect on physico-chemical properties of these pesticides and their spray solution under tropical conditions at (54±1°C) for three days compared with glass container.

Information about tested pesticides and types of packages were illustrated in Table (1).

Table (1). Tested pesticides corresponded with their packages.

Pesticides tested			Type of formulation	Type of Package	Produced company
Trade name	**Common name**	**Chemical name**			
Milor-Cu	Metalaxyl 50% + copper chloride 59 %	a) Methyl-N-(methoxy acetyl)-N-(2, 6-xylyl-DL-alaninate b) Dicopper chloride trihydroxide	50 % WP	Polyethylene bag in aluminum bag (al/po)	Rotam Agrochemical, Egypt
Galben copper	Benalaxyl 11% + Copper oxychloride 58.8 %	a) Methyl-N-phenyl acetyl-N-2, 6 xylyl-DL-alaninate. b) Dicopper chloride hydroxide	46 % WP	Aluminum in paper box (pa/al)	ISAGRO SPA, Italy
Acrobat copper	Dimethomorph + Copper oxychloride	a) (E-Z)-4-(4-chlorophenyl)-3-(3,4- dimethoxy phenyl) acryloyl) morpholine. b) Dicopper chloride trihydroxide.	46 % WP	Polyethylene bag in paper box (pa/po)	BASF Limited, Egypt
Bellkute	Iminocataidin + trisbesulate	1, 1-iminodi (octa methylene) diguaidinmtris (alkyl benzene sulfonate).	40 % WP	Polyethylene bag (po)	NM Agro., Egypt

Heat stability test at (54±1°C) for three days was carried out according to method described with WHO (1979) on tested pesticides in glass container and different commercial packages. Physico-chemical properties such as foam (%) that was determined according to WHO (1979), while the rest properties were determined according to CIPAC methods : CIPAC MT31 for determination of free acidity or alkalinity, CIPAC MT15.1 for determination of suspensibility, CIPAC MT53.3 for determination of wettability. The following properties were determined for spray solution of the tested pesticides : pH value using Schott Great pH-meter and surface-tension using Du Nouy tension-meter where dyne/cm is the unit of surface-tension measurement. Conductivity and salinity was measured using conduct-meter YS1 model 335-C-T meter (mMHOs is the unit of electrical conductivity measurement).

RESULTS

Data in Table (2) shows the effect of polyethylene packages alone or combined with paper or aluminum packages, also aluminum package in paper package on tested pesticides in wettable powder formulation compared with WHO glass container under tropical storage conditions. The obtained

data indicated that, except (pa/po) package with Dimethomorph + copper oxychloride in hard water, all tested package failed in suspensibility test of tested pesticides formulation in both hard and soft water. The suspensibility % of these pesticides were less than 60 % compared with their success in their test when they stored in WHO glass container.
(according to WHO and CIPAC specification, suspensibility % of WP formulation should be > 60).

Table (2). Effect of different commercial packages on physico-chemical properties of tested pesticides in WP formulation under tropical storage conditions.

Common name	Type of package	Conditions of storage	Physico-chemical properties					
			% Foam		% Suspensibility		Wetta-bility/ second	Alkalinity % as NaOH
			Hard water	Soft water	Hard water	Soft water		
Iminocataidin + trisbesulate	Polyethylene bag (po)	Before storage	30	27	94.8	91.5	12.0	0.16
		In glass container	25	30	85.4	82.5	35.0	0.32
		In commercial package	20	25	19.9	16.5	36.5	0.32
Dimethomorph + copper oxychloride	Polyethylene bag in paper bag (pa/po)	Before storage	3	0.0	67.6	67.9	53.2	0.72
		In glass container	9	15	79.4	79.0	38.5	0.40
		In commercial package	9	8	60.3	34.7	36.0	0.08
Metalaxyl + copper chloride	Polyethylene bag in aluminum bag (al/po)	Before storage	12	33	96.3	97.4	22.7	0.48
		In glass container	23	19	86.1	87.3	40.5	0.24
		In commercial package	8	19	13.6	16.3	32.0	0.88
Benalaxyl + copper chloride	Aluminum bag in paper box (pa/al)	Before storage	13	35	87.6	87.99	22.7	0.40
		In glass container	17	30	78.8	78.5	106.0	0.40
		In commercial package	15	17	23.9	24.8	93.0	0.64

Storage of Iminocataidin + trisbesulate in (po) package and Benalaxyl + copper chloride in (pa/al) package improvement foam with hard and soft water (decrease % foam) as comparing with glass container, whereas storage Metalaxyl + copper chloride in (al/po) package improved foam formation in hard water only. On contrary, the improvement of foam was noticed only in soft water with Dimethomorph + copper chloride that stored in (pa/po) package.

Except Iminocataidin + trisbesulate with (po) package, all tested package showed slight improvement in wettability/second as compared with glass container. This improvement is not compatable with WHO specification in case of Benalaxyl + copper chloride, that wetted in 93 seconds when stored in (pa/al) package.

Free alkalinity increased upwards of glass container when aluminum package was used as outer or inner package in case of Metalaxyl + copper chloride and Benalaxyl + copper chloride, whereas it decreased with

Dimethomorph + copper oxychloride that storage in (pa/po) package. From previous results, it could be discussed that, free alkalinity increased upwards of glass container in case of storage in outer or inner aluminum packages.

Data presented in Table (3) shows the effect of commercial package types on physico-chemical properties for spray solution after storage under tropical storage conditions compared with glass container.

Table (3). Effect of different commercial packages on physico-chemical properties of spray solution of tested pesticides in WP formulation under tropical storage conditions.

Common name	Type of package	Conditions of storage	Conductivity ms/m		pH		Surface tension dyne/cm		Salinity	
			Hard water	Soft water	Hard water	Soft water	Hard water	Soft water	Hard water	Soft water
Iminocataidin + trisbesulate	Polyethylene bag (po)	Before storage	900	190	7.35	7.37	57.6	64.0	1.0	1.0
		In glass container	900	190	7.25	7.32	64.0	57.6	1.0	0.5
		In commercial package	900	190	7.40	7.39	57.6	57.6	1.0	0.5
Dimethomorph + copper oxychloride	Polyethylene bag in paper bag (pa/po)	Before storage	900	120	7.85	8.10	54.8	52.3	1.0	0.1
		In glass container	900	210	7.91	8.39	54.8	54.9	0.9	0.1
		In commercial package	900	120	7.65	7.62	60.6	60.6	1.0	0.1
Metalaxyl + copper chloride	Polyethylene bag in aluminum bag (al/po)	Before storage	1100	220	7.12	7.26	52.4	52.4	1.0	0.1
		In glass container	1000	200	7.21	7.23	52.4	54.8	1.0	0.1
		In commercial package	1000	200	8.79	9.22	52.4	54.8	1.0	0.1
Benalaxyl + copper chloride	Aluminum bag in paper box (pa/al)	Before storage	1000	220	7.33	7.49	39.7	41.1	1.0	0.1
		In glass container	1200	330	7.38	7.55	41.1	42.7	1.0	0.2
		In commercial package	1200	350	7.40	7.60	42.7	42.7	1.0	0.2

ms/m : millisiemens/meter

Generally, all tested packages showed bad effect against one or more of physico-chemical properties of tested pesticides spray solutions as follow :

1- pH values and conductivity :

As known, retention and effectiveness of pesticides spray solutions increased with decreasing in pH values and with increasing its conductivity. Spray solution of tested pesticides affected as resulting to storage in tested package in three forms : a) increasing in pH values in hard and soft water without any effect on conductivity as found in case of Iminocataidin + trisbesulate with (po) package and Metalaxyl + copper chloride with (al/po) package. b) increasing in pH values in hard and soft water and conductivity in soft water only as show with Benalaxyl + copper chloride in (pa/al) packages. and c) decreasing in pH values of soft and hard water and conductivity in soft water of Dimethomorph + copper oxychloride with (pa/po) package.

2- Surface tension :

Decreasing in surface tension of spray solution, cause improving in

wettability and spreading on the treated surface then increasing deposit and activity of pesticides (Fahmy *et al.*, 1991).

(pa/po) packages caused increase in spray solution surface tension of Dimethomorph + copper oxychloride in hard and soft water, whereas the same indication was noticed in hard water only in case of Benalaxyl + copper chloride with (pa/al) package.

DISCUSSION

The effect of interaction between different types of commercial packages and physico-chemical properties of tested pesticides in wettable powder formulation and their spray solution was studied under tropical storage conditions (54±1°C) for three days as comparing with WHO glass container.

The obtained results clearly show that, all tested packages caused bad effect against suspensibility of tested pesticides formulation in both hard and soft water compared with their success at WHO glass container.

The above results may be due to the bad effect of raw material packages on dispersing agents within tested formulations. Hodgoson (1987) indicated that, the suspensions is thermodynamically unstable this in view of high surface area created in their by large surface free energy. The system tends to reduce this energy by number of breakdown process. So, the particles will be aggregated. This aggregation is usually prevented by use suspending agent or dispersing agent.

The effect of tested packages on foam formation of tested pesticides was between no effect or improvement effect upwards of glass container. There are relationship between this indication and packages raw material types and water types (hard and soft). According to El-Sisi (1985), the suspension should not have more than 2 % foam when applied at field. The improvement foam (decrease % foam) may be due to the rule of tested package that optimizing the effectiveness of antifoam agents in tested formulation. As known, antifoam agent was used to eliminate air entrapment in formulation (Ruckenstein *et al.*, 1989).

Aluminum packages in combined with paper or polyethylene packages increased free alkalinity of tested pesticides, from our previous results it could be concluded that, there are relationship between aluminum packages and increasing of free alkalinity of tested pesticides.

Except (po) package, all tested packages showed slight improvement in wettability/second as compared with glass container. The above indication may be due to the effect of tested packages on wetting agent in tested formulation. Knowles (1998) indicated that, the wetting agent lowered interfacial tension between the solid particles and water and ensure the powder wets and mixes with water.

Generally, all tested packages showed bad effect against one or more property of physico-chemical properties of tested pesticides spray solutions such as pH values, conductivity and surface tension. As known, the effectiveness of pesticides spray solutions conjugating with decrease in pH values with increase in its conductivity. Spray solution of tested pesticides

affected as resulting to storage in tested packages in three forms : a) increase in pH without any effect on conductivity, b) increase in pH and conductivity, and c) decrease in pH values and conductivity. This indication may be due to the effect of tested package on ion changes between tested pesticides (soluble materials) and water. El-Attal *et al*. (1984) reported that the increase of electric conductivity of insecticide spray solution would lead to deionization of insecticide and increase its deposit and penetrate in the treated plant surfaces.

(pa/po) and (pa/al) packages caused increase in surface tension of tested pesticides spray solution in hard and soft water with the first package and in hard water only with the second. From the previous results it could be conclude that, there are a relationship between paper package when it was as outer package and increase of surface tension. The increase in surface tension may be due to the effect of raw material packages on wetting and dispersing agent in tested pesticides agent.

CONCLUSION

From above results, it could be concluded that, there are relationship between raw materials of packages that used in packing of wettable powder formulations under Egyptian pesticides market conditions and physico-chemical properties of this formulation. On the other hand, thetest of suspensibility at WHO glass container is unsuitable because the same pesticide passed this test at WHO container but failed in this test at commercial package, therefore, this test and other tests should be carried out practically in the useful raw material package used for packing pesticides.

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تـأثير العبــوات التجاريـة علـى الصـفات الطبيعيـة والكيميائيـة لـبعض المبيـدات التـى على صورة مستحضرات قابلة للبلل تحت ظروف التخزين الحار

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تم جمع أربع مبيدات فى صورة مساحيق قابلة للبلل داخل عبواتها التجارية من الشركات المنتجة لها .. لتقييم التأثير المتداخل بين هذه المبيدات وعبواتها على الصفات الطبيعية والكيميائية لهذه المبيدات تحت ظروف التخزين الحار على درجة حرارة (54±1°م) لمدة 72 ساعة ومقارنتها بتخزين منظمة الصحة العالمية (داخل حاويات زجاجية) تحت نفس الظروف. المبيدات التى تمت دراستها كانت : ميتاكسيل + كوبر كلوريد 50 %، بينالاكسيل + كوبر أوكسى كلوريد 46 %، داى ميثومورف + كوبر أوكسى كلوريد 46 %، أمينوكاتاايدين + ترای سبسيولات 40 %. بينما كانت المواد الخام للعبوات تحت الدراسة هى مادة البولى إيثيلين (po)، البولى إيثيلين داخل رقائق الألومنيوم (al/po)، البولى إيثيلين داخل الورق (pa/po)، الألومنيوم داخل الورق (pa/al). كانت الصفات الطبيعية والكيميائية التى تمت دراستها فى حالة المبيدات هى : النسبة المئوية للرغاوى، النسبة المئوية للتعلق، القابلية للبلل، الحموضة أوالقلوية الحرة؛ بينما قدر التوصيل الكهربى، درجة الـ (pH)، التوتر السطحى، الملوحة فى حالة محاليل الرش للمبيدات المختبرة. وقد أوضحت النتائج المتحصل عليها الآتى :

- كل العبوات المختبرة سببت تأثيراً سيئا على النسبة المئوية للتعلق فى الماء اليسر والعسر للمبيدات المختبرة وأن كل المبيدات فيما عدا مبيد الداى ميثومورف + كوبر أوكسى كلوريد مع الماء اليسر المخزن فى عبوة الـ (pa/po) فشلت فى إختبار التعلق، حيث كانت النسبة المئوية للتعلق مع هذه المبيدات أقل من 60 %.
- كذلك إنحصر تأثير هذه العبوات على النسبة المئوية للرغاوى مابين عدم التأثير وتقليل تكوين الرغاوى، وقد

توقف هذا المؤثر على نوع المادة الخام للعبوة وكذلك نوع الماء المستخدم (عسر أو يسر).

- لوحظ زيادة القلوية الحرة فى حالة المبيدات المخزنة فى عبوتين أحدهما الألومنيوم والأخرى فى البولى إيثيلين أو الورق وذلك بالمقارنة بنفس المبيدات عند تخزينها فى حاويات زجاجية.
- تحسنت القابلية للبلل للمبيدات تحت الدراسة تحسناً ضئيلاً مع كل العبوات فيما عدا عبوة البولى إيثيلين (po) مع مبيد الأمينوكاتايدين + تراى سبسيولات.
- أظهرت العبوات المختبرة تأثيرا سيئاً ضد واحدة أو أكثر من الصفات الطبيعية-الكيميائية لمحاليل الرش للمبيدات المختبرة حيث تأثرت درجة الـ pH والتوصيل الكهربى لهذه المحاليل فى ثلاث صور : (أ) زيادة درجة الـ pH دون ظهور أى تأثير على الكهربية، كما لوحظ فى حالة مبيد أمينوكاتايدين + تراى سبسيولات مع عبوة (po). (ب) زيادة درجة الـ pH فى الماء العسر واليسر والكهربية فى الماء اليسر فقط، كما لوحظ مع بيتالاكسيل + كوبر كلوريد مع عبوة (pa/al). (جـ) نقص درجة الـ pH فى الماء العسر واليسر والكهربية فى الماء اليسر كما لوحظ فى مبيد داى ميثومورف + الكوبر أوكسى كلوريد مع عبوة (pa/po).
- أظهرت عبوتى (pa/po) و (pa/al) تأثيراً سيئاً على التوتر السطحى لمحاليل الرش للمبيدات المختبرة فى الماء اليسر والعسر فى حالة العبوة الأولى والماء العسر مع العبوة الثانية.

من ذلك يتضح أن هناك علاقة مابين المواد الخام للعبوات المستخدمة فى تعبئة مساحيق المبيدات القابلة للبلل تحت ظروف السوق المصرية وبين الصفات الطبيعية – الكيميائية لهذه المستحضرات. وأن التخزين فى العبوات الزجاجية كأسلوب لتقييم هذه المبيدات طبقاً لتوصيات منظمة الصحة العالمية غير مناسب حيث نجحت المبيدات المختبرة طبقاً لهذا التخزين فى إختبار ثبات التعلق، بينما فشلت نفس المبيدات فى هذا الإختبار عندما خزنت فى عبواتها التجارية. وبالنسبة لبقية الصفات فإن هذه العلاقة تتراوح مابين تحسين بعض هذه الصفات وإتلاف البعض الآخر فتكون المحصلة عدم صلاحية هذه المبيدات للتطبيق الحقلى، ولذلك فإن هذه العلاقة تحتاج لمزيد من الدراسة لتحديد أنسب العبوات التى تتناسب مع كل مستحضر على حدة.