Pestic. Phytomed. (Belgrade), 27(1), 2012, 77–81
DOI: 10.2298/PIF1201077G

UDC: 632.951.1:632.981.1
Scientific paper

Development of Water Based Pesticide System

Slavica Gašić, Dragica Brkić, Ljiljana Radivojević and Anđelka Tomašević

Institute of Pesticides and Environmental Protection, Banatska 31b, 11080 Belgrade, Serbia (slavica.gasic@pesting.org.rs)

Received: February 20, 2012
Accepted: February 24, 2012

SUMMARY

It is well known that emulsifiable concentrates (EC), besides good properties have problem with a high solvent content thus are not environmental friendly and can cause problems for users. The interest in developing oil-in-water emulsions (EW) instead emulsifiable concentrates is increasing due to toxicological problems with solvents. Oil-in-water emulsions can reduce phytotoxicity, ecotoxicity and dermal toxicity, have a higher flash point than EC and are safer in transport and storage; also EW are more compatible with water based SC formulations for blends of active ingredients. Plant protection often includes the use of some pyretroides as active ingredients, for example Cypermethrin, alone or combined with Chlorpyrifos. It is a very old product which is formulated as EC formulation. In this study oil-in-water emulsion (EW) was developed with the same active ingredients. The EW formulation was tested and the results show that it was stable and therefore could be used in plant protection.

Keywords: Emulsions; Pesticides; Formulations; Oils; Water; Emulsifiers

INTRODUCTION

Importance of pesticide use in increasing agricultural production is well established, however, they can cause damage to the environment and sometimes to users. Recently the pesticide industry has made a good progress in terms of development and production of low risk environmental friendly pesticide formulations, although pesticides are still mainly available in conventional formulations such as dustable powders, wettable powders, emulsifiable concentrates, solutions, etc. Such conventional formulations could cause problems related to environmental protection, leaving residues in ecosystem, food, final products, etc. Hence, there is a growing demand for use of environmental friendly water based formulations as oil-in-water emulsions, aqueous suspension concentrates, aqueous capsule suspensions and so on instead of conventional pesticide formulations. These formulations are tended not only to replace toxic, non degradable ingredients from formulations, but also to increase the efficacy of products through a proper choice and a balance of all components in the formulation (Gašić and Orešković, 2006; Knowles, 2006).

Emulsifiable concentrate (EC) conventionally contain one or more active ingredients, one or more emulsifiers and a water-immiscible solvent. Typical solvents

used in conventional EC formulations are aromatic hydrocarbons. They have very low solubility in water and a high capability of dissolving a wide range of active ingredients. However, the solvents used in the conventional EC formulations could damage the environment or may cause toxicity problems. Oil-in-water emulsions (EW) consist of an active ingredient dissolved in a water-immiscible solvent, which is dispersed as fine oil-phase droplets in water in the presence of surfactants. However, they still contain the solvent but in lower amount than EC formulations. This type of formulation is important in agriculture as a mean of formulating oil based systems in a more environmentally convenient form than the conventional emulsifiable concentrate (EC). Such EW formulations tend to have lower skin and eye toxicity compared to corresponding EC products as well as higher flash point. Also EW formulations are safer in transport and storage and they are more compatible with water based SC formulations for blends of active ingredients (Mulquem, 2003).

Plant protection is often includes the use of pyretroides as active ingredients, for example Cypermethrin, alone or combined with Chlorpyrifos. It is a very old product which is formulated as EC formulation. The objective of this study was to develop oil-in-water formulation containing Cypermethrin (20 g/l) and Chlorpyrifos (200 g/l).

MATERIAL AND METHODS

Cypermethrin technical material (92% min.) originated from "Tagros Chemicals, India Ltd." Egmore, Chennai, India and Chlorpyrifos (97% min.) originated from "Nanjing Essence Fine-Chemical Co., Ltd." Nanjing, P.R. China. All reagents and a solvent were purchased from commercial sources and used without additional purification. The emulsifiers (Ajinomoto OmniChem, Belgium and Rhodia, Italy) and the solvent (Imperial oil Ltd.) were of commercial quality and were not additionally purified.

The content of active ingredients in technical materials and formulations, was detected by gas and liquid chromatographic methods (GC; HPLC) using DANI GC 1000 DPC and Milton Ray CM 4000 (AOAC 1998, CIPAC 1985).

The oil-in-water emulsion (EW) was obtained by progressively adding oil phase in water phase under stirring. The oil phase was prepared with active ingredients Chlorpyrifos (20%), Cypermethrin (2%), solvent Solvesso 100 (35%), and a mixture of two nonionic emulsifiers (7%), while the water phase was prepared with water, antifoam agent (0.2%) and monopropylenglicol (5%). The oil phase was added in the water phase under high shear mixing. For homogenization Ultraturrax high shear mixer (T25, speed 8000 rpm/min, duration 10 minutes) was used. Formulation prepared in this way contained 200 g/l of Chlopyrifos and 20 g/l of Cypermethrin. After formulating, the accelerated storage tests (storage stability) were carried out according to CIPAC methods MT 39 and MT 46. The storage (stability) test (0°C) was performed during one week/one month and the storage test (54°C) during two weeks/three months. After each stability test the same characteristics were assessed according to standard CIPAC methods: pH MT 75, density MT 3, persistent foam MT 47.2, emulsion stability and re-emulsification MT 36.1 (CIPAC, 1995).

Particle size distribution was measured by CILAS 1064, and visual aspects of formulations were checked using Axioskop 40 (Carl Zeiss, 63x Canon camera). Before visual aspect was checked, the samples were diluted with distillated water.

RESULTS AND DISCUSSION

The results are presented in Tables 1-3 and Figures 1-2.

Controling the stability and aging of an emulsion is important because of application perspectives. The stability of a product at low and high temperature is one of the technical indices of product quolity. The major factors which affect the stability of formulation are concentration and the balance of the hydrophilicity and lipopholicity of added surfactants. The stability of oil-in-water emulsions can be predicted by measuring some physical parameters before and after accelerated tests. Storage at 0°C and 54°C has been used to control physical and chemical stability. It has been generaly accepted that two weeks at 54°C represent 2 years in normal conditions. There is no evidence which indicate that a product has a satisfactory shelf life (of at least 2 years) in the different temperature zones. The test thus provides a useful guide for performance after storage in warm or continental temperature climates. However, it is not quite sure that the a product which passes these tests will be satisfactory in field conditions.

Oil-in-water emulsions unlike emulsifiable concentrates in the undiluted state are only stable in kinetic

sense. This is because this system is inherently thermodinamically unstable and can only be formed non-spontaneously. Emulsions are metastable systems and can be kineticaly stabilized with emulsifiers. We prepered an oil-in-water (EW) emulsion with two active ingredients which were first disolved in the solvent and than emulsified in water. We decided to prolong stability tests and checked shelf live stability by measuring a number of physical parameters before and after storage test to be sure that the formulation had satisfactory stability (Gašić and Orešković, 2008; Gašić and Brkić, 2011).

Table 1. Physical and chemical properties of fresh EW formulation

Aspect	Milky liquid	
Content of Active Ingredients:		
Cypermethrin	21.2 g/l	
Chlorpyrifos	205.7 g/l	
Density	1.0223 g/cm^3	
pH (1% in Distilled Water)	5.7	
Foam Persistence	4.0 cm^3	
Particle Size Distribution (Mean Diameter)	1.65 μm	
Stability of Emulsion Reemusification	0.5h	0/0
	1h	0/0
	2h	0/0
	24h	1/0
	REE	0/0

Table 2. Physical and chemical properties of EW formulation after stability test at 0^{0}C

Test period	7 days	30 days
Content of Active Ingredients:		
Cypermethrin	–	21.2 g/l
Chlorpyrifos	–	205.7 g/l
Density	1.0230 g/cm^3	1.0234 g/cm^3
pH (1% in Distilled Water)	6.0	6.0
Foam Persistence	6.0 cm^3	6.0 cm^3
Particle Size Distribution (Mean Diameter)	1.49 μm	1.56 μm
Stability of Emulsion Reemusification 0.5h	0/0	0/0
1h	0/0	0/0
2h	0/0	0/0
24h	1.5/0	0/0
REE	0/0	0/0

Table 3. Physical and chemical properties of EW formulation after stability test at 54^{0}C

Test period	14 days	90 days
Content of Active Ingredients:		
Cypermethrin	20.8 g/l	22.0 g/l
Chlorpyrifos	207.3 g/l	210.0 g/l
Density	1.0247 g/cm^3	1.0255 g/cm^3
pH (1% in Distilled Water)	5.6	5.4
Foam Persistence	4.0 cm^3	3.0 cm^3
Particle Size Distribution (Mean Diameter)	1.53 μm	1.48 μm
Stability of Emulsion Reemusification 0.5h	0/0	0/0
1h	0/0	0/0
2h	0/0	0/0
24h	0/0	1.5/0
REE	0/0	0/0

Based on the obtained results it can be councluded that the particle size distribution varied from 1.48 μm to 1.65 μm. The variation of density was 1.0223-1.0255 g/cm^3. pH value ranged from 4.6-6.0 and according to Pesticide manual (Tomlin, 2009) under this pH values both active ingredients are stable. The persistence of foam ranged from 0-6 cm^3. The stability of emulsion and reemulsification were good. The visual aspect of water diluted EW formulation showed very fine drops of internal (oil) phase in water (Figure 2) which was in accordance with narrow range of particle size distribution (Figure 1). The content of active substances did not change by more than 5% for Chlorpyrifos compared to the content before stability test and for Cypermethrin not more than 5% after two weeks and 7% after three months. However these diferences are considered to be aceptable (Anonymous, 2010).

After all tests were terminated, we councluded that there were differences between the values of controling parameters but the changes, even after storage tests in extrem temperature regions in prolonged period of time, were not significant and the formulation had satisfactory stability. The developed EW formulation still contains solvent (to dissolve active ingredients that form internal phase), but in lower amount compared to the corresponding EC formulations. This indicates that from the environmental point of view this formulation is a better solution. By replecing the tradicional EC formulations with

EW formulations of pesticides, the use of organic solvents harmful to the environment can be significantly reduced with satisfactory pesticide effectivenes, so good environmental and economical effects could be expected. The next step should be the application of prepared EW formulation altogether with EC formulation with the same active ingredients in order to check its effectivness.

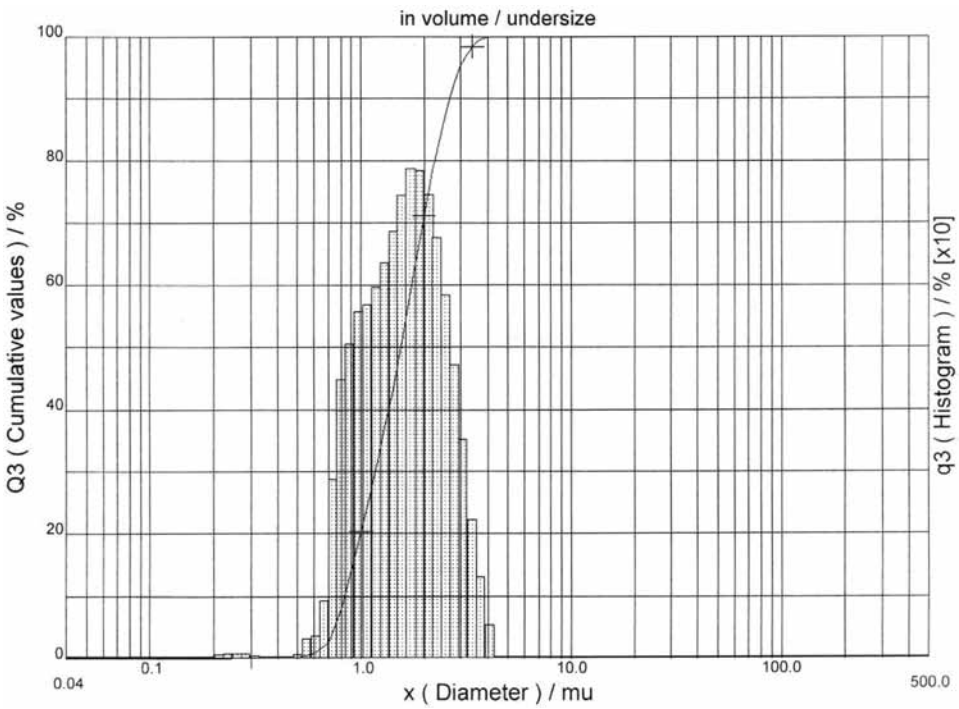

Figure 1. Particle size distribution in EW formulation

Figure 2. Aspect of water diluted EW formulation

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education and Science of the Republic of Serbia for financial support (Projects No. III 46008 and TR 31043).

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Razvoj preparata pesticida na vodenoj osnovi

REZIME

Poznato je da koncentrati za emulzije (EC) osim dobrih osobina koje nesporno imaju mogu da ispolje negativan uticaj na životnu sredinu i korisnika, pošto u svom sastavu imaju visok procenat rastvarača. Interesovanje za razvoj emulzija ulje u vodi (EW) kao moguće zamene za koncentrate za emulzije (EC), je nastalo upravo zbog problema koji mogu da nastanu usled negativnog uticaja organskih rastvarača prisutnih u velikoj meri. Primenom emulzija ulja u vodi (EW) može da se smanjiti fitotoksičnost, da se suzbije nepovoljno dejstvo na životnu sredinu i korisnika (npr. eliminisanjem dermalne toksičnosti), zatim EW formulacije imaju višu tačku paljenja u poređenju sa EC formulacijama te su bezbednije za transport i skladištenje, a imaju i dodatnu prednost da su pogodnije za zajedničku primenu sa koncentratima za suspenzije (SC), kada je to potrebno. Kada se radi o zaštiti bilja onda može da se zapazi da se vrlo često koriste aktivne materije iz grupe piretroida, na primer cipermetrin koji se primenjuje sam ili u kombinaciji sa drugim aktivnim materijama kao što je recimo hlorpirifos. Kombinacija upravo ove dve aktivne materije je zastupljena u proizvodu koji se već dugo nalazi na tržištu i koji je uglavnom formulisan kao koncentrat za emulziju. U ovom istraživanju je učinjen pokušaj da se razvije formulacija emulzije ulja u vodi (EW) sa istim aktivnim materijama. Razvijena formulacija je ispitana i rezultati su pokazali da je dovoljno stabilna i da bi mogla da se primeni u zaštiti bilja.

Ključne reči: Emulzije; pesticidi; formulacije; ulje; voda; emulgatori