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DEVELOPMENT OF HERBICIDE FORMULATIONS BASED ON QUIZALOFOP-P-ETHYL

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ABSTRACT

Pesticides are formulated in many different ways. Quizalofop-P-ethyl is selective post emergence herbicide which can be found on the market formulated as emulsifiable concentrate (EC) and suspension concentrate (SC). The objective of this investigation was to develop two types of formulations: emulsifiable concentrate (EC) and went a step forward and developed oil in water (EW) formulation. Oil in water (EW) is a kind of pesticide formulation which contains water instead of almost all organic solvents. EW recently replaces EC as a new excellent environmentally-friendly pesticide formulation. We started investigation with development of EC formulation (50 g a.s./L) and after that developed EW formulation with the same concentration of active ingredient. The results obtained by testing developed formulations according to FAO and WHO recommendations shown that they had necessary stability to be applied in plant protection.

Key words: herbicide, emulsifiable concentrate (EC), emulsion oil in water (EW)

INTRODUCTION

The active ingredient in an herbicide formulation is the chemical that controls the target weed. The herbicide product is usually made up of active ingredients mixed with inert to allow dilution, application, and stability. The mixture of active and inert ingredients (solvents, emulsifiers, adjuvant etc.) is called a formulation. A single active ingredient often is sold in several different kinds of formulation. The formulation can have a major impact on the effectiveness of a product, including how well it mixes and performs in various environmental conditions and what influence has on users and environment. The primary purpose of formulation is to optimize the biological activity of the pesticide, and to give a product which is safe and convenient for use (Knowles, 2005).

Quizalofop-p-Ethyl, [Ethyl (2R)-2-[4-(6-chloroquinoxalin-2yloxy) phenoxy] propionate] is selective post emergence herbicide which control annual perennial grass weeds and can be used in different crops. This active ingredient can be found on the market formulated as emulsifiable concentrate (EC) and suspension concentrate (SC) (MacBean, 2012). The presence of organic solvents in EC formulations can lead to safety hazards in use and to a negative impact on the environment generally. Recently the solvents which are used in EC formulations have come under toxicological and subsequently regulatory pressure. As a results some of the most common solvents are no longer available. On the other side oil in water (EW) is a kind of pesticide formulation with appearance of milky white liquid which is formed by dispersing liquid pesticide or disolved solid pesticide mixed with inert in water. Since the formulation contains water instead of almost all organic solvents, EW recently replaces EC as a new excellent environmentally-friendly pesticide formulation (Mulqueen, 2003; Knowles, 2008).

The objective of this study was to investigate the possibility of developing formulations such as EC and EW starting from Quizalofop- P-Ethyl as active ingredient in concentration of 50 g/L.

MATERIALS AND METHODS

Quizalofop-P-Ethhyl technical material (95% min.) was originate from Sinochem Ningbo, P.R China. All reagents and solvents were purchased from commercial sources and used without further purification. Emulsifiers which were used were of commercial quality (Ajinomoto OmniChem, Belgium and Rhodia, Milano, Italy) and were used without further purification.

The content of active ingredient Quizalofop-P-Ethyl was determined by high performance liquid chromatography (*HPLC*) using ultraviolet detection (UV) (Helwett Packard HP 1050 liquid chromatorgraph).

Particle size distribution was measured by CILAS 1064 liquid and visual aspect of formulations checked by Axioskop 40 (Carl Zeiss, 63x Canon camera).

The pH was controlled by CIPAC method MT 75; Density CIPAC method MT 3; Persistent foaming CIPAC MT 47.2; Storage stability CIPAC MT 39.3 and MT 46.3 (Dobrat, Martin, 1995).

EW formulations are unstable systems, therefore special attention was focused to stability tests and that measurement were prolonged to ensure that developed EW formulation is stable enough to be used in plant protection.

Emulsifiable concentrate (EC) of Quizalofop-P-Ethyl was prepared by mixing solvent (Solvesso 100), emulsifiers (6%) and active material (5%). For homogenization magnetic stirrer was used.

Emulsion oil in water (EW) of Quizalofop-P-Ethyl was obtained by progressively adding oil phase in water phase under stirring. Oil phase was prepared with active material (5%), esterified rape seed oil (10%), Solvesso 100 (40%) and mixture of emulsifiers (8%), while water phase was prepared with water, antifoam agent (0.2%) and monopropylenglicol (5%) as antifreeze. Oil phase was adding into water phase under high shear mixing. For homogenization Ultra turrax mixer (speed 8000 o/min, duration 15 minutes) was used.

RESULTS AND DISCUSION

The objective of this investigation was development stable formulations of emulsifiable concentrate and oil in water emulsion with Quizalofop-p-Ethyl as active ingredient. Emulsifiable concentrate represent oil solution of active ingredient altogether with emulsifiers. This type of formulation is generally applicable for active ingredients which are soluble in organic solvents such as herbicide Quizalofop-p-Ethyl. This is an old type of formulation and its development is relatively simple. EC formulations are designed to be added to water and to be applied after emulsification (Mollet, Grubenmann, 2001). Emulsifers are adding to the formulations to ensure good emulsification after dilution with water. In investigation we started for initial screening of suitable solvent for the technical material and proper emulsifiers based on knowledge of active ingredient and emulsifiers. After selection of solvent and emulsifiers the right balance between them was found by experimentation which aim was development of stable emulsion to provide the desired results later during application. The samples were stored at controlled temperatures in order to evaluate their stability over the time. Among different samples which were prepared it was found the best solution on the basis of stability and physico-chemical properties. The results of chosen formulation are given in the Table 1. The obtained results indicated that the formulation remained stable after stability test; content of active ingredient was changed from 46.3 g/L (5.16%) to 46.7 g/l (5.20%), density 0.8963-0.8977 g/cm^3, pH 4.8-5.0 (stable region for this active ingredient), persistent foaming 20-22 cm^3 (which is not going be a problem for application) and stability after 0.5h and 2h were good and reemulsification was complete.

Table 1. Physical and chemical properties of fresh EC formulation and after stability tests

Time	fresh formulation		after 7 days		after 14 days	
Temperature	room temperature		0^{0}C		54^{0}C	
Content of Quizalopf-P-Ethyl	46.3 g/l		46.4 g/l		46.7 g/l	
Density	0.8973 g/cm^3		0.8963 g/cm^3		0.8977 g/cm^3	
pH (1% in distilled water)	5.0		4.8		5.0	
Persistent foaming	22 cm^3		20 cm^3		20 cm^3	
Stability of emulsion and reemulsification	0.5h	0/0	0.5h	0/0	0.5h	0/0
	1h	0/0	1h	0/0	1h	0/0
	2h	0/0	2h	0/0	2h	0/0
	24h	1/0	24h	2/0	24h	2/0
	REE	0/0	REE	0/0	REE	0/0

The difficulty in preparing oil in water formulation is that the formulation belongs to thermodynamically unstable system. Actually oil in water formulation composed of two phases: dispersed oil phase with active ingredient and a continuous water phase. The active ingredients for this type of formulation must be liquid (or dissolved solids in organic solvent) and oil phase must have a low water solubility. The proper choice of oil and emulsifiers is very important to avoid different kind of stability problems such as flocculation and coalescence which are the major routes of emulsion degradation. Suitable solvent should be immiscible or at least with low solubility, in water and oil solution should be stable to crystallization at different temperatures during storage. We prepared the formulation by dissolving the active ingredients (Quizalofop-P-Ethyl) in oil phase (solvesso 100) and the oil solution is than emulsified into water phase. Suitable emulsifiers for this type of formulations are those which form and stabilize oil-water emulsions. Emulsifier by forming electric double layer on the surface of the dispersed phase and steric hindrance effect of interfacial film keep stability of emulsion (Tadros, 2005). For stabilization we used nonionic blended emulsifiers as they have good performance and have wide range of application. In this study, the optimum emulsifiers content were determined through a series of tests. EW requires high-strength shearing, stirring and homogenization to prepare technical material (active ingredient) into 0.5-1.5 μm droplets, and make it disperse in aqueous solution and maintain the state of stable storage (Gašić et al., 2006; 2012). For homogenization we used Ultra turrax mixer which is strong enough to serve a purpose. The particle size distribution was controlled by observation with optical microscope (Figure 1) and by light scattering as it is critical for the stability of emulsion. A narrow particle size distribution is necessary to achieve as it will ensure better stability than a wide particle size distribution (Zhang, 2014). In particular, the storage stability of formulation should meet the guidelines of the Manual on development and use of FAO and WHO specification for pesticides (Anonymous, 2010). In accordance with this manual the content of active ingredient in the formulation is not allowed to decline by more than 10% when formulation stored at room temperature over a period of two years. The shelf life of oil in water formulation can be predicted by the measurement of the active ingredient content and a series of physical parameters before and after storage tests. Storage at temperature of 0^0C (seven days) and 54^0C (14 days) is used to control physical and chemical stability. To test the storage stability samples of the formulation under development are stored for a specific time in tightly sealed glass vessels at the different temperature indicated in each case (Tables 3 and 4). Special attention was focused on particle size distribution as the most important parameter for this type of formulation (Table 5). The samples are subsequently examined and compared with the value of fresh prepared formulation at the beginning of the storage (Table 2). As the method designed to predict shelf life might be inadequate to ensure a robust product in storage we prolonged stability test to make sure that we will have stable formulations.

Table 2. Physical and chemical properties of fresh EW formulation

Aspect	Milky liquid	
Content of active material Quizalopf-P-Ethyl:	51.0 g/l	
Density	0.9486 g/cm^3	
pH (1% in distilled water)	5.5	
Persistent foaming	5 cm^3	
Particle size Distribution (Mean diameter)	1.04 μm	
Stability of emulsion and reemulsification	0.5h	0/0
	1h	0/0
	2h	0.5/0
	24h	2/0
	REE	0/0

Table 3. Physical and chemical properties of EW formulation after stability test at 0°C

Test period	7 days		30 days
Content of active material Quizalopf-P-Ethyl:	49.5		48.3 g/l
Density	0.9537 g/cm^3		0.9507 g/cm^3
pH (1% in distilled water)	5.5		5.8
Persistent foaming	1 cm^3		0 cm^3
Particle size Distribution (Mean diameter)	0.99 μm		0.98 μm
Stability of emulsion and reemulsification	0.5h	0/0	1/0
	1h	0/0	1/0
	2h	1/0	1/0
	24h	2/0	1.5/0
	REE	0/0	1/0

Table 4. Physical and chemical properties of EW formulation after stability test at 54°C

Test period	14 days	90 days
Content of active material Quizalopf-P-Ethyl:	49.5	48.4 g/l
Density	0.9535 g/cm^3	0.9535 g/cm^3
pH (1% in distilled water)	5.4	4.9
Persistent foaming	5 cm^3	6 cm^3
Particle size Distribution (Mean diameter)	0.80 μm	0.90 μm
Stability of emulsion and reemulsification	0.5h 0/0	0/0
	1h 0/0	0/0
	2h 0/0	1/0
	24h 1/0	2/0.1
	REE 0/0	0/0.1

The results showed that particle size distribution varied from 0.80 μm to 1.04 μm which means that even after prolonged stability tests particle size distribution remind fine which indicated that emulsion will be stable. Variation of density was 0.9486 g/cm^3 to 0.9537 g/cm^3; pH value varied from 4.9 to 5.8 and at these pH values the active ingredient is stable, as it stable in neutral and acidic media (MacBean, 2012) Persistent foam varied from 0 cm^3 to 6.0 cm^3. Visual aspect of aqueous diluted EW formulation showed very fine droplets (Figure 1). The content of active ingredient varied from 48.3 g/l (5.08% to) to 51.0 g/l (5.34%) and this differences are considered to be acceptable (Anonymous, 2010). Stability of emulsion was good after 30 minutes and one hour and reemulsification complete.

It can be concluded that two different types of formulations were prepared using Quizalofop-P-Ethyl as the active material. First developed emulsifiable concentrate (EC) is common way of commercially formulation of this active ingredient, but oil in water (EW) emulsion represent new formulation solution for this herbicide. Emulsion oil in water as water base system has various advantages over EC formulation (e.g. safety aspect) which meet recent demands of regulatory authorities and the pesticide industry.

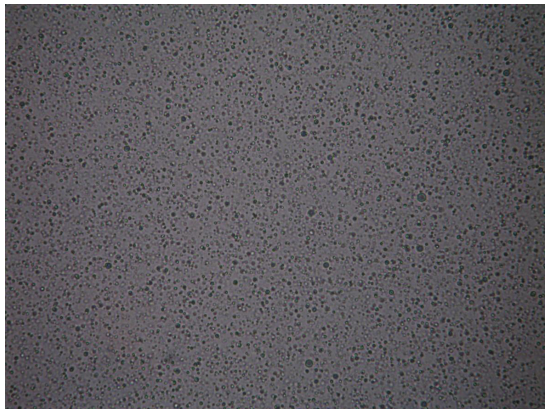

Fig.1. Aspect of aqueous dilute oil in water (EW) formulation of Quizalofop-P-Ethyl

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Table 5. Particle size distribution after prolonged stability tests for EW formulation

	Diametar at 10% (μm)	Diametar at 50% (μm)	Diametar at 90% (μm)	Mean Diametar (μm)
fresh formulation	0.72	0.97	1.47	1.04
stability test - 7 days at 0±2 ^{0}C	0.67	0.93	1.42	0.99
stability test - 30 days at 0±2 ^{0}C	0.64	0.92	1.42	0.98
stability test - 14 days at 54±2 ^{0}C	0.45	0.76	1.21	0.80
stability test - 90 days at 54±2 ^{0}C	0.53	0.85	1.34	0.90

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