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Research Article

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Development of 5% Abamectin EW formulation

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ABSTRACT

In this study, through optimizing the 5% abamectin EW formulation, stable formulation was determined, the optimum formula of 5% abamectin EW were as follows: Abamectin TC 5%, toluene 9%, cyclohexanone 6%, BY-125 7%, NP-10-P 1.34%, thickening agent (xanthan gum) 0.05%, anti freeze agent (ethylene glycol) 5%, defoaming agent 0.1%, distilled water or deionized water was made up of 100%. The product had good cold storage, heat storage and stability with time, was in conformity with the EW quality standard.

Keywords: abamectin, emulsion in water, optimize, formulation

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INTRODUCTION

Emulsion in Water, also known as Concentrate Emulsion, is a liquid preparation of tiny oil droplets dispersed in water [1-3]. The solid TC or liquid TC dissolved in weak- polar solvents as oil phase, with vigorous stirring process, the oil phase dispersed in water by suitable emulsifier, then add preparation antifreeze agent, stabilizer and the e EW formulation is prepared, wherein the aqueous phase is continuous phase, oil phase is dispersed phase [4,5]. In the control of production cost, with water instead of organic solvent, reduces production cost, improves the water emulsion products economic benefits and competitiveness [6]. At present, the EW as a pesticide formulation, has been extensive research and promotion at home and abroad [7].

Abamectin is a macrocyclic lactone derived from the soil bacterium Streptomyces avermitilis that can be sprayed onto the leaf surface or applied to the soil [8]. As biological insecticidal, acaricidal, nematicides, abamectin have stomach toxicity and contact toxicity, it is widely used in agriculture and forestry on controling lepidoptera, diptera, homoptera pests and mites with the characteristics of high efficiency, low toxicity, no pollution, lasting drug efficacy.

Currently, the main formulation of abamectin are EC, granule and low content of water emulsion, Such as 1.8%, 2% abamectin EC and 0.5% abamectin GR and 1.8%, 3% abamectin EW etc. but there are few research works on high concentration of abamectin EW, for the above-mentioned reasons, the formulation of 5% abamectin EW was studied in this paper.

EXTERIMENTAL SECTION

Experimental materials

Pesticide: Abamectin (96%) was provided by Jingbo Agrochemicals Technology Co., Ltd. Solvents: toluene, xylene, acetone, cyclohexanone were Chemically pure. Polyoxyethylene sorbitan ester: Tween-20, Tween-60; polyoxyethylene castor oil ether: By-125, EL-40; phenylethyl phenol polyoxyethylene polyoxypropylene ether: 1601; nonylphenol polyoxyethylene ether phosphate: NP-10-P. antifreezes: ethylene glycol, propylene glycol, urea, ammonium sulfate; thickeners: xanthan gum, carboxymethyl cellulose sodium, polyvinyl alcohol; defoaming agents: n-octyl alcohol, silicone.

Experimental instruments
JA5003N electronic balance (Shanghai precision scientific instruments co., Ltd.); BME shear emulsifying mixer (Jiangsu Qidong Ludao metallurgy Petrochemical Machinery Co.,Ltd.), BT-9300H laser particle size distribution analyzer (Bettersize Instruments LTD.), LC-10AT high performance liquid chromatograph (Shimadzu Corporation), ZK-82 B electrothermal vacuum drying oven (Shanghai Testing Instrument Factory Co., Ltd.). NDJ-1 rotational viscometer (Shanghai Changji Geological Instrument Co., Ltd.).

Preparation method of abamectin EW
5% abamectin EW was prepared with phase inversion method. the weighed abamectin dissolved in appropriate solvent, adding suitable emulsifier, and After mixing evenly as oil phase; at the same time, take water, anti freeze agent, and defoaming agent to mix as an aqueous phase. Under the conditions of shear speed of 2500-3000 r/min, the aqueous phase was slowly poured into the oil phase, the O/W of 5% abamectin EW product was obtained with methods of phase inversion.

Method for determination of water emulsion performances
The EW was stored at controlled temperatures in order to evaluate their stability over the time. The syneresis rate of samples were inspected after storage at 54°C for up to 14 days, and the experimental method of thermal storage stability refers to the national standard GB / T 19136-2003. The emulsion stability of samples were detected after stored at 0°C for up to 14 days, and the experimental method of cold storage stability refer to national standard GB / T 19137 – 2003.

Emulsion stability test
Method for determination of emulsion stability refer to national standard GB / T 1 603--2001. Diluted aqueous pesticide were prepared by mixing the pesticide with Collaborative International Pesticides Analytical Council (CIPAC) standard waters of 342. The diluted aqueous pesticide were then stored at 30°C to evaluate the emulsion stability of the diluted samples over time.

Method of determination particle size of the EW
The particle size of EW was determined by BT-9300H laser particle size distribution analyzer. The particle size of sample of formulation was reflected in D_{50}， D_{90}， D_{10} and span. The formulation of span is as follow:

Span =（D_{90}—D_{10}）/D_{50}

Method of determination the thermal stability of 5% abamectin EW
5% abamectin EW were firstly stored at (54 ± 2) ℃ for 14d, then the decomposition rate of EW samples were determined by high performance liquid chromatography. All samples were measured three times in experiment period and take the mean to eradicate any discrepancies. Chromatographic conditions: the mobile phase: acetonitrile / water =70:30 (V/V), reagent with ultrasonic degassing filter, flow rate: 0.7ml/min, column temperature: 25℃, injection volume: 20 μL, the detection wavelength: 245nm, column: Luna C18 reversed-phase column [9].

RESULTS AND DISCUSSION

The establishment of the solvent system
The dissolving capacity of abamectin in toluene, xylene, acetone, cyclohexanone were determined. The experimental effects were showed that the better compound solvent was toluene and cyclohexanone.

The mass ratio of TC and the compound solvent remained unchanged, stored at 0℃ for 7d, the solution of TC were tested by adjusting the ratio of toluene and cyclohexanone, the results showed that mixed solvents can completely dissolve TC when the solvent composition was 6:4, and the mixed solvent can make preparations to maintain long stability for moderate polarity. At the same time, adding amount of mixed solvents were determined, results showed when the amount of solvents was 13%-16%, raw materials could be dissolved and the viscosity of emulsion was moderate, therefore, the compound solvents of 5% abamectin EW were toluene and cyclohexanone (volume ratio=6:4), and the amount of compound solvents were 13%-16%.

Determination of the emulsifier
The determination of emulsifier is the key of EW formulation. In the EW formulation, The oil phase was emulsified into tiny droplets and dispersed in the aqueous phase by emulsifier to reduce surface and interfacial tension, at the same time, Emulsifier by forming electric double layer on the surface of the dispersed phase and steric hindrance effect of interfacial film to keep stability of emulsion. In this study, the optimum emulsifiers were determined through a series of tests.

(1) Determination of the single emulsifier

Fixed amount of emulsifier was 8%, the emulsifiers such as T-60, T-20, BY-1251601#, 602#, El-40, OP-10 were selected, results as shown in table 1.

As shown in table 1, after cold storage, emulsions containing T-60 or BY-125 had low water separating proportion, when T-20 or El-40 acted as emulsifier, the emulsion appeared few layered. However, when 1601# or 602# acted as emulsifier, water separating proportion was too much, the emulsifier OP-10 had serious oil-water separation phenomenon. Comprehensive analysis of the results, the T-60, BY-125, T-20 and El-40 were selected as the emulsifier to further screening.

Table 1 Screening results of single emulsifier

emulsifier	dispersion properties	emulsifying properties	cold storage stability
T-60	good	better	separate water，7.94%
T-20	good	good	stratification
BY-125	better	good	separate water，8.3%
1601#	good	good	separate water and oil
602#	good	better	separate water ,63.3%
El-40	good	good	stratification
op-10	poor	poor	separate oil，10%

(2) Determination of compound emulsifiers

There are some reports that most of anionic emulsifier can cause water emulsion instability, while the larger molecular weight of phosphate ester emulsifiers can effectively control coalescence and flocculation phenomenon of EW[10]. In this study, took the nonionic emulsifier NP-10-P and the above determined emulsifiers to mix, the mass ratio of two kind of emulsifier was 1:3, the total amount of emulsifiers was 8%. The results are shown in table 2. The results showed that the combination of BY-125 and NP-10-P was in accordance with the requirements after cold storage and hot storage, and was the best emulsifier combination in all combinations.

Table 2 screening results of emulsifiers

emulsifier	Storage	T-60	T-20	EL-40	BY-125
NP-10-P	(0-2)℃	stratification	stratification	precipitation	good
	(54±2)℃	oil separating	oil separating	oil separating	water separating

Table 3 showed that the determination of stability of different combinations of BY-125 and NP-10-P with thermal storage and cold storage. the results showed when the ratio of emulsifier BY-125:NP-10-P was 7:1, the EW has good stability.

Table 3 Optimization of emulsifiers

test sample	the proportion of emulsifier	heat storage (54±2)□	cold storage (0-2)□
A	BY-125:NP-10-P=2:1	oil separating,4.6%	precipitation
B	BY-125:NP-10-P=4:1	oil separating,3.9%	precipitation
C	BY-125:NP-10-P=5:1	water separating, 5.3%	precipitation
D	BY-125:NP-10-P=6:1	water separating, 4.7%	no precipitation
E	BY-125:NP-10-P=7:1	up to standard	no precipitation
F	BY-125:NP-10-P=9:1	no oil and water separating	no precipitation

By optimizing the amount of BY-125 and NP-10-P, we can see from table 4, emulsion water has excellent emulsifying and stability of hot storage when the content of emulsifiers was 8%.

Table 4 determined of the amount of emulsifiers

Test sample	the amount of emulsifiers	emulsifying properties	heat storage (54±2)℃
A	4%	good	oil separating
B	5%	good	oil separating
C	6%	good	oil separating
D	7%	better	up to standard
E	8%	excellent	up to standard
F	9%	better	up to standard

Determination of antifreeze

Experiment showed that the ethylene glycol, propylene glycol and urea had good antifreezing effect, the ethylene glycol can not only act as antifreeze, but also has better auxiliary surface activity function, and the result of the experiment suggested that ethylene glycol as antifreeze was the best with the dosage of 5%.

Determination of thickener

Appropriate amount of thickening agent can improve the storage stability of the EW. In this experiment, 0.05% xanthan gum, polyvinyl alcohol and carboxymethyl cellulose sodium were added, and the observed results are shown in Table 5. The results indicated that xanthan gum as thickener of EW could significantly improve the stability of the emulsion.

Table 5 screening results of thickener

thickener	mass percentages	emulsion stability	dispersibility	heat storage (54±2)℃
xanthan gum	0.05%	up to standard	better	no separating
polyvinyl alcohol	0.05%	up to standard	better	oil separating
CMC	0.05%	up to standard	good	oil separating
CK	0	up to standard	good	water separating

Determination of defoaming agent

In order to eliminate the bubbles in water emulsion process, it is need to add a certain amount of defoaming agent, the test results proved that the compatibility of defoaming agent and water emulsion was good, so organosilicon defoaming agent was chose and the dosage of defoaming agent is 0.1%.

Optimized formulation by orthogonal test

On the base of the preliminary screening of various additives, the proportion and quantity of additives were optimized by orthogonal test. According to experimental purpose, experimental factors are chosen and the level of the factors is decided, experiment factors and levels as shown in table 6.

Table 6 Factor and level of orthogonal test $L_9(3^4)$

Factor	level		
A(By-125)	6.66%	6.86%	7.00%
B(NP-10-P)	1.00%	1.14%	1.34%
C(xanthan gum)	0.03%	0.05%	0.07%

The table 7 showed result of orthogonal test, and the optimized result of formulation was A3B1C2, which were contained xanthan gum 0.05%, NP-10-P 1.34% and By-125 7.00%.

Table 7 Orthogonal test

sample	Blank column	A BY-125/%	B NP-10-P/%	C Xanthan gum /%	Emulsifying properties	Span/μm
Test 1	0	6.66	1.34	0.03	++	4.15
Test 2	0	6.86	1.14	0.05	+	5.41
Test 3	0	7.00	1.00	0.07	+	1.41
Test 4	0	6.66	1.14	0.07	+	6.96
Test 5	0	6.86	1.00	0.03	+	7.39
Test 6	0	7.00	1.34	0.05	+	1.07
Test 7	0	6.66	1.00	0.05	+	4.62
Test 8	0	6.86	1.34	0.07	++	6.41
Test 9	0	7.00	1.14	0.03	+++	0.96
K_1	-	15.73	11.63	12.50	-	-
K_2	-	19.21	13.33	11.10	-	-
K_3	-	3.44	13.42	14.78	-	-
k_1	-	5.24	3.88	4.17	-	-
k_2	-	6.40	4.44	3.70	-	-
k_3	-	1.15	4.47	4.93	-	-
极值 R	-	5.26	0.60	1.23	-	-

Note: '+' is 'good', '++' is better, '+++' is excellent.

The test results of 5% abamectin EW stability

According to the GB/T1603-2001 standard, the stability of 5% abamectin EW was tested. Figure 1shwed that the emulsion dilution of 5% abamectin EW had no precipitation and oil slicks, the stability of dilution meets the requirements of the standard.

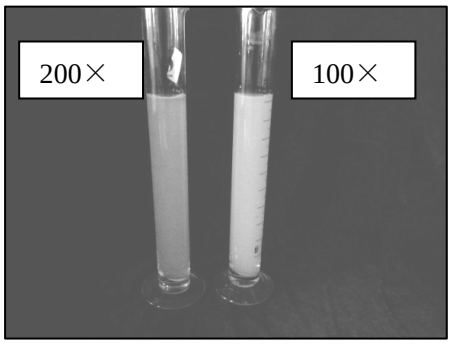

Fig1 the dilution stability of the 5% abamectin EW

Determination of heat storage stability

The stability of heat storage of 5% abamectin EW were characterized with decomposition rate of abamectin and emulsifying properties. The decomposition rate of abamectin was determined by high performance liquid chromatography. Table 8 showed that the decomposition of three parallel tests of EW samples were less than 5% and the thermal stability of sample meet the requirements.

Table 8 Heat storage stability of 5% abamectin EW

sample	Before heat storage		heat storage for 14d		Decomposition %
	The content of abamectin %	Emulsion stability	The content of abamectin %	Emulsion stability	
1	5.05	up to standard	4.90	up to standard	2.97%
2	5.04	up to standard	4.87	up to standard	3.37%
3	5.01	up to standard	4.83	up to standard	3.36%

CONCIUSION

EW is a kind of water-based formulation of environmental and security because it uses water to replace all or most organic solvents, improves the safety of preparation, and greatly reduces the cost of production. However, because EW is unstable system of thermodynamic, so stability control of EW is the key to the development and production of EW formulation. Screening and optimization of preparation is the foundation to guarantee the stability of EW system. In this study, stable formulation of 5% abamectin EW was obtained through the orthogonal optimization method. The obtained product has good cold storage, heat storage and stability with time, is in conformity with the EW quality standard.

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