The Extruded Granule Formulation of Selective Rice Herbicide Cyhalofop Butyl

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Abstract: Cyhalofop butyl, [R-(+)-n-butyl - 2 - (4 - (2 - fluoro - 4 - cyanophenoxy) phenoxy) propionate] is a selective rice graminicide which can control up to the 5-6 leaf stage of *Echinochloa crus-galli* by foliar application. The development of granule formulations for rice herbicides is important to strengthen agricultural practices in Japan. One granule system of cyhalofop butyl employs KCl core granules and di-tridecyl phthalate to maximize its bioefficacy. As described in a previous report, this system can enhance plant uptake of the graminicide when a high concentration of cyhalofop butyl plus di-tridecyl phthalate comes into direct contact with a plant. The system does, however, limit the flexibility of one shot granule formulations depending on the KCl core granule compatibility with the partner with which it is combined. Therefore, an extruded granule of cyhalofop butyl is preferable to a KCl granule of cyhalofop butyl to broaden the potential/possible partners for a one shot granule. Several core granule systems and solvent systems were evaluated to develop an efficacious extruded granule of cyhalofop butyl. Among them, the employment of maleic acid polymer type surfactant for the extruded core granule system and di-tridecyl phthalate plus isoparaffin as solvent system showed the best bioefficacy to control the 3

leaf stage of *Echinochloa crus-galli* than did the KCl granule of cyhalofop butyl. Granules extruded by this system also showed a high release rate of the graminicide in the upper layer of the water.

Key words; Cyhalofop butyl, *Echinochloa crus-galli*, granule, maleic acid polymer type surfactant, isoparaffin

Introduction

Cyhalofop butyl, known as XDE-537 or DEH-112, is a new post-emergence aryloxyphenoxy propionate graminicide discovered by Dow AgroSciences which controls a broad spectrum of grass weeds, including genera of *Echinochloa*, *Brachiaria*, *Cynodon*, *Digitaria*, *Eleusine*, *Leptochloa*, *Panicum*, *Setaria* and *Sorghum*. Cyhalofop butyl is highly selective to both Japonica and Indica rice varieties as well as to all broadleaf rotational crop species⁶⁾. It has a broad window of application (1-6 leaf *Echinochloa crus-galli*) and also the ability to mix with a number of other herbicides⁵⁾. Since the 1960s the major formulation type of herbicides used in Japan for paddy fields has been granule formulations⁴⁾. Therefore, a granule formulation of cyhalofop butyl is essential for the Japanese herbicide market⁴⁾. One granule system which employs KCl core granules and di-tridecyl phthalate maximizes the bioefficacy of cyhalofop butyl^{2),3)}. However, this system limits formulation flexibility for one shot

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granule formulations, and depends on KCl core granule compatibility with its combination partners. Therefore, extruded granules of cyhalofop butyl are preferable to the KCl granules⁷⁾, although the conventional type of extruded granules have shown poor bioefficacy. Formulation studies were conducted to find an efficacious extruded granule of cyhalofop butyl which would show equal or at least nearly as good bioefficacy in controlling 3 leaf stage of *E. crus-galli* than the KCl granule system. This report covers evaluations of various extruded granule formulations tested for this purpose.

Materials and Methods

Physical and chemical properties of the active ingredient : Physical and chemical properties of cyhalofop butyl are shown in Fig. 1.

Formulation

Extruded granule formulations for core

Code name : XDE-537, DEH-112

Common name : cyhalofop butyl

Chemical name : [R-(+)-n-butyl-2-(4-(2-fluoro-4-cyanophenoxy)phenoxy)-propionate]

Empirical formula : $C_{20}H_{20}FNO_4$

Molecular weight : 357.39

Structural formula :

Appearance : odorless, white, crystalline solid

Melting point : 50°C

Solubility (at 20°C) : Water: 0.7 ppm (pH 7.0)

Xylene: 47.3 (wt% a.i.)

Acetone: 60.7 (wt% a.i.)

Octanol-water partition coefficient (logP): 3.31

Vapor pressure: 8.8×10^{-9} mmHg at 20°C

Fig. 1. Physical and chemical properties of cyhalofop butyl

granule system optimization : Test formulations containing 0.6% of cyhalofop butyl were prepared to evaluate the core granule system. (Fig. 2)

Extruded granule formulations for solvent system optimization : Test formulations contained 0.6% of cyhalofop butyl. (Fig. 3)

Release rate test for cyhalofop butyl : One-tenth of a gram of each granule was placed into a specially made "funnel flask", to which 20 ml of water was added. After standing for 24 hours, the stopcock was closed and the upper layer of the water was collected by washing with acetone and filled to 50 ml. Cyhalofop butyl was then analyzed by a high performance liquid chromatograph (HPLC). The HPLC used was a HP1090LC (Hewlett Packard) equipped with a UV detector (250 nm, Shimadzu model SPD-6A). The column was an Apex-ODS (250×4.6mm). Mobile phase consisted of 50% acetonitrile and 50%

(1) Extruded Core Granule

(2) Test Formulations

*Selected surfactant : Meleic acid polymer type, Acetylene glycol type, Naphthalene sulphonic acid sodium salt

Fig. 2. Formulation process on test formulations for core granule system optimization

Fig. 3. Formulation process on test formulations for solvent system optimization

water containing 0.1% of acetic acid, and the flow rate was 1 ml/min. The procedure of the release rate test is shown in Fig. 4.

Herbicidal efficacy trials

1) Greenhouse trial 1 : For core granule system optimization

The bioefficacy of extruded granule formulations of 0.6% cyhalofop butyl was evaluated in comparison with that of KCl granules of 0.6% cyhalofop butyl under a greenhouse condition at the Gotemba laboratory of Dow AgroSciences. A Wagner's pot 1/5000 in size was used for the trial and the water level was maintained at 3 cm. *E. crus-galli* at the 2.0–2.5 leaf stage was treated with cyhalofop butyl granule formulations at 180 g ai/ha. Visual assessment of herbicide activity was made 28 days after the application with 3 replications (0% : no effect–100% : complete kill).

2) Greenhouse trial 2 : For solvent system optimization

The bioefficacy of 0.6% extruded granule formulations of cyhalofop butyl was evaluated to select the best solvent system under a greenhouse condition at the Fukuoka field station of Dow AgroSciences. A 1/5000 Wagner's pot was used and the water level was maintained at 3 cm. *E. crus-galli* at the

Fig. 4. Method for release rate test

3 leaf stage was treated with the formulations, and visual assessment of herbicide activity was made 27 days after the application with 3 replications (0% : no effect–100% complete kill)

Results and Discussion

Herbicidal efficacy trials

1) Greenhouse trial 1 : Cyhalofop butyl granules containing 3% maleic acid polymer type surfactant in the core granule system showed the highest efficacy in controlling the 2.0–2.5 leaf stage of *E. crus-galli* and was superior to the reference formulation, KCl granules of cyhalofop butyl under a greenhouse condition (Table 1).

Based on these results, the core granule system containing 3% maleic acid polymer type surfactant was determined to be the best system for cyhalofop butyl extruded granules.

2) Greenhouse trial 2 : Cyhalofop butyl granules containing 3% isoparaffin, solvesso 200 and cycloparaffin as solvent system

Table 1. Core granule system optimization on cyhalofop-butyl granule formulations-efficacy against *E. crus-galli*

Formulation*	Surfactant for core granule	Rate g a.i./ha	% Control of <i>E. crus-galli</i> at 28DAA**
Cyhalofop butyl 0.6% Gr	Maleic acid polymer type	180	90
Cyhalofop butyl 0.6% Gr	Acetylene glycol type	180	47
Cyhalofop butyl 0.6% Gr	Naphthalene sulphonic acid sodium salt	180	73
Cyhalofop butyl 0.6% KCl Gr (reference)	—	180	73
Leaf stage at application		2.0-2.5 leaf	

Formulation* : 6% Di-tridecyl phthalate as oil system

DAA** : Days After Application

Table 2. Solvent system optimization on cyhalofop butyl granule formulations-efficacy against *E. crus-galli*

Formulation	Solvent system	Rate g a.i./ha	% control of <i>E. crus-galli</i> at 27DAA*
Cyhalofop butyl 0.6% Gr	9% Di-tridecyl phthalate	180	95
	+	120	86
	3% Isoparaffin	60	72
Cyhalofop butyl 0.6% Gr	9% Di-tridecyl phthalate	180	85
	+	120	75
	3% Ditolyl methyl methane	60	65
Cyhalofop butyl 0.6% Gr	9% Di-tridecyl phthalate	180	85
	+	120	67
	3% Solvesso 150	60	60
Cyhalofop butyl 0.6% Gr	9% Di-tridecyl phthalate	180	96
	+	120	87
	3% Solvesso 200	60	68
Cyhalofop butyl 0.6% Gr	9% Di-tridecyl phthalate	180	97
	+	120	77
	3% Cycloparaffin	60	63
Cyhalofop butyl 0.6% Gr	9% Di-tridecyl phthalate	180	88
	+	120	78
	3% Paraffinic petroleum hydrocarbons	60	57
Cyhalofop butyl 0.6% Gr	9% Di-tridecyl phthalate	180	99
	(KCl core Gr.)	120	99
		60	93
Leaf stage at application		3.0 leaf	

DAA* : Days After Application

showed stable efficacy in controlling the 3.0 leaf stage of *E. crus-galli* from 180 g ai/ha to 60 g ai/ha application among the formulations evaluated under a greenhouse condition in comparison with 0.6% KCl granules of cyhalofop butyl (Table 2).

This suggested there would be a clear enhancement of plant uptake of the graminicide by employing the appropriate surfactant and solvent in the granule composition. More finely tuned studies should permit reduction in the amount of cyhalofop butyl used in the extruded granule, and the solvent system containing 3% isoparaffin was selected for further studies.

3) Release rate of 0.6% cyhalofop butyl extruded granule formulations for solvent system optimization

The release rate of each selected formulation before and after storage at 50°C×2 weeks was analyzed to identify the one with the most stable release rate performance even after storage at 50°C.

The results showed there was no close correlation between bioefficacy and release rate performance. Three formulations containing 3% each of isoparaffin, or ditolyl methyl methane or cycloparaffin showed a

relatively high and stable release rate before and after the storage test at 50°C×2 weeks from a stability point of view (Table 3).

4) Release rate pattern of 0.6% cyhalofop butyl extruded granule formulations for 3, 6 and 24 hours

The release rate of the 3 formulations containing 3% each of isoparaffin, ditolyl methyl methane, or cycloparaffin was analyzed after standing for 3, 6 and 24 hours to show the release rate pattern of each extruded granule. The granules containing 3% isoparaffin showed a higher release rate than those containing 3% cycloparaffin or 3% ditolyl methane for the 3-24 hour period and a rate almost equal to KCl Gr. at 24 hours (Fig. 5.)

In conclusion, by employing maleic acid polymer type surfactant for the extruded core granule system and isoparaffin as solvent system in tested granule formulations better bioefficacy was shown in controlling the 3 leaf stage of *E. crusgalli*. This granule system also showed relatively quick and stable release rate performance before and after 50°C×2 weeks storage.

The composition of the best extruded granule would be applicable to a one shot granule

Table 3. Optimization of solvent system*

Formulation	Solvent	Release rate (%) at 24 hrs after application	
		Initial	50°C×2-week
Cyhalofop butyl 0.6% Gr	Isoparaffin	96	92
Cyhalofop butyl 0.6% Gr	Ditolyl methyl methane	90	89
Cyhalofop butyl 0.6% Gr	Solvesso 150	95	88
Cyhalofop butyl 0.6% Gr	Solvesso 200	62	63
Cyhalofop butyl 0.6% Gr	Cycloparaffin	92	90
Cyhalofop butyl 0.6% Gr	Paraffinic petroleum hydrocarbons	100	87

*Solvent system : 9% Di-tridecyl phthalate +3% solvent

Fig. 5. Difference in release rate pattern among 3 solvent systems versus KCl granule

formulation of cyhalofop butyl due to there being better compatibility and more flexibility than with the KCl granule, although the latter is appropriate for a single granule of this graminicide because of its stable bioefficacy.

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水稻用選択性除草剤シハロホップブチルの押し出し粒剤化

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摘 要

シハロホップブチル, [R-(+)-n-butyl-2-(4-(2-

fluoro-4-cyanophenoxy)phenoxy) propionate] はダウ・アグロサイエンスにより開発中の水稻用選択性除草剤である (Fig. 1)。本剤は、茎葉処理において5-6葉期までのイヌビエ等に卓効を示すものの、現在の日本の稲作の現状を考えると、シハロホップブチルの粒剤の製剤開発が必須である。しかしながら、これまでシハロホップブチルの一般的な押し出し粒剤では、期待された十分な効果を発揮させることは困難であった。そこで、押し出し粒剤の粒基剤の界面活性剤及びその粒基剤にシハロホップブチルを含浸させる際に使用する溶剤の組み合わせを変えることにより、生物効果の向上が図れることが判明

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した。これらの組み合わせからなる各種シハロホップブチル0.6%押し出し粒剤の生物効果を温室内にて評価した。押し出し粒剤の粒基剤中に3%のマレイン酸ポリマー系界面活性剤を添加することにより、シハロホップブチルのイヌビエに対する効果が増強されることがわかった (Table 2)。また、溶剤の組み合わせの中では、9% di-tridecyl phthalate に3%のイソパラフィンを添加したものが最も安定したシハロホップブチルの生物効果を示し (Fig. 3, Table 2, 3), また、シハロホップブチルの水面浮上率の改

善に貢献した。

これらの結果より、シハロホップブチル押し出し粒剤の粒基剤及びシハロホップブチルの含浸用の溶剤を工夫することにより、期待されるシハロホップブチルの生物効果を引き出すのが可能であることが判明した。

キーワード：シハロホップブチル, イヌビエ, 粒剤, マレイン酸ポリマー系界面活性剤, イソパラフィン