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Phytotoxicity and adjuvancy of lactate esters in 2,4-D based agrochemical formulations

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ABSTRACT

Application of n-propyl lactate, n-butyl lactate and 2-ethylhexyl lactate on tomato seedlings did not result in phytotoxic effects when applied at 0.05 and 0.5% (*wt/wt*). The results of this study show that lactate esters can strongly enhance the performance of the herbicides 2,4-D-dimethylamine (salt) and 2,4-D-2-ethylhexyl (ester) on *Chenopodium album* (fat-hen).

INTRODUCTION

Lactate esters are used as 'green' solvents in many industries. In the agrochemical industry there is also a tendency towards the use of 'green' solvents due to environmental and safety issues. Lactates are known to show good compatibility with 'natural' substrates such as wood, leather or fibres. Lactate esters may enhance the foliar penetration of agrochemicals by serving as a solvent in the drop deposit. A second option is that the solvents themselves penetrate into the waxy leaf cuticle and enhance the mobility of the chemicals in the cuticle. The solvents also reduce surface tension so that an influence of both wetting and spreading will be possible. The solvents used in this study are n-propyl lactate (NPL), butyl lactate (BL) and 2-ethylhexyl lactate (EHL). Table 1 provides an overview on some relevant physical properties of these esters.

Table 1. Physical properties of some lactate esters

Lactate ester	Solubility in water (% (*wt/wt*) at 20 °C)	Viscosity (cP at 20 °C)	Vapour pressure (mbar at 20 °C)	Surface tension (mN/m at 25 °C)	Flash point ISO 2719 (°C)
NPL	100	3.3	1	30.4	69
BL	4.5	3.9	0.4	29.5	79
EHL	0.03	7.7	0.02	29.8	113

The aim of this study is to compare different lactate esters on their bio-enhancement potential in 2,4-D dimethylamine salt (DMA) and 2-ethylhexyl ester (2-EH) formulations. Such adjuvancy can be beneficial in the development of more cost-effective and environmentally friendly formulations. To complete the set of data, the phytotoxicity of these solvents was measured.

MATERIALS AND METHODS

Plant material

Adjuvant studies were performed on fat-hen (*Chenopodium album* L.), while phytotoxicity studies were performed on tomato.

Tomato seeds (cv. Astona F1) were germinated under the same conditions as used for fat-hen (see below). At 12-14 days after germination the tomato seedlings were transferred (one plant per pot) to 11-cm-diameter plastic pots filled with a mixture of sand and humic potting soil (Soil no. 12, Colent, Lent, The Netherlands) (1:2 by volume). The pots were placed on sub-irrigation matting that was wetted daily with a nutrient solution. The tomato plants were brought to the greenhouse with the same conditions regarding temperature and relative humidity regime. Additional artificial light was provided when necessary. The tomato seedlings were treated 26-28 days after the seeds were sown. Then, the tomato plants had 4 unfolded leaves and were 16 cm tall.

Fat-hen was grown in a growth chamber under 14 h of light, at 18/12 (±0.5)°C (day/night) temperature, and in 70/80 (±5)% (day/night) relative humidity. Light was provided by high-pressure mercury lamps and fluorescent tubes to give 70 W/m2 (PAR) at leaf level. After emergence, the fat-hen plants were thinned to two plants per pot. Fat-hen was treated at the four-leaf stage. The fresh weight of fat-hen was measured 21 days after treatment (21 DAT).

Application of treatment solutions

The solutions are applied with an air-pressured laboratory track sprayer having 1.2-mm nozzles fitted with a perforated (0.6 mm) whirling pin and delivering 200 litre/ha at 303 kPa.

Phytotoxicity

The reference product used for phytotoxicity studies was 'Arkopal N 080' (nonylphenol polyoxyethylene (8) from Clariant). The solvents and reference product were included at 0.05 (*v/v*) and 0.5% (*wt/v*) respectively. The treatment solutions were shaken just before application to ensure a homogeneous distribution of the products. It was checked before, that a homogeneous distribution was obtained also with the more lipophilic solvents like 2-ethylhexyl lactate ester. Leaves were inspected visually at 3-4 days after treatment (DAT) and a phytotoxicity rating (1 to 5) was recorded. The scale used for the phytotoxicity rating was: 1 = no discoloration or necrosis to 5 = complete necrosis of the wetted plant surface plus loss of leaf turgor. A score of 4 was given when there was complete necrosis without loss of leaf turgor. The fresh weight of the aerial plant parts was measured 7 DAT.

Adjuvancy

The solvents n-propyl lactate, n-butyl lactate and 2-ethylhexyl lactate ('PURASOLV' NPL, -BL and –EHL, respectively) all supplied by PURAC Biochem, The Netherlands, were added to the herbicides or applied alone (NPL) at a concentration of 0.5% (*v/v*). The carrier was demineralized water.

A sub-optimal rate of the herbicides, giving a 0-20% growth reduction without solvents, was used to demonstrate the adjuvant effects. We applied 2,4-D 2-EH (solvent-free EW formulation; 'Lentemul D' 450 g a.e. /litre) and 2,4-D DMA (SL formulation; 'Spritz Hormin 500' g a.e. /litre) both supplied by Nufarm, Austria.

Experimental design and data analysis

The phytotoxicity experiments were conducted as a randomized complete block with four replicates on two separate occasions. The variance between treatments was very low over the experiment as there was little phytotoxicity. The adjuvancy experiments were also conducted with four replicates in a completely randomized design on two separate occasions. The data were subjected to analysis of variance using the statistical package 'Genstat' Release 6.1; Rothamsted Experimental Station. The means of treatment were compared according to Fisher's LSD (0.05). LSD (0.05) is the Least Significant Difference between mean values at the 5% level.

RESULTS AND DISCUSSION

Phytotoxicity

The visual assessment and the fresh weight measurement (Table 2) demonstrated that most treatments were not phytotoxic and looked the same as the untreated plants. Alone, the reference product at 0.5% (*wt/v*) demonstrated a low but clearly visible level of phytotoxicity. This was not reflected in a reduction of fresh weight. Fresh weight levels in the second experiment were higher than in the first experiment because the second experiment was conducted in April and the first experiment in March when less light is available for growth.

EHL is the most lipophilic solvent and, as a consequence, may penetrate into both the lipophilic leaf cuticle and the lipophilic cell membrane. The observation that phytotoxic effects are not observed at the 0.5% (*v/v*) level indicates that either the penetration of EHL into the plant or its interaction with the cell membrane is rather limited at this concentration. Application of the solvents and the reference product at the somewhat unrealistic concentration of 5%, demonstrated severe phytotoxic symptoms from the reference product but EHL. NPL and BL were not phytotoxic at 5% (*v/v*).

This study provides indirect evidence that lactate esters exert their activity on the leaf surface. This can be beneficial in situations where any risk on plant phytotoxicity has to be excluded (ornamentals, fruit, vegetables etc.). Application of EHL may result in phytotoxic effects in situations where accumulation of solvents may occur.

Table 2. Phytotoxicity (means of four replicates) of solvents and reference product

No.	Product	Conc. (%) a	Phytotoxicity visual assessment b Experiment 1	Phytotoxicity visual assessment b Experiment 2	Phytotoxicity fresh weight (g) Experiment 1	Phytotoxicity fresh weight (g) Experiment 2
1	Untreated	-	1.0	1.0	8.6	10.5
2	Demin water	-	1.0	1.0	8.1	9.6
3	NPL	0.05	1.0	1.0	9.1	8.2
4	NPL	0.5	1.0	1.0	7.9	10.0
5	BL	0.05	1.0	1.0	9.0	10.0
6	BL	0.5	1.0	1.0	8.5	10.2
7	EHL	0.05	1.0	1.0	7.6	9.9
8	EHL	0.5	1.0	1.0	8.1	10.3
9	Arkopal N-080	0.05	1.0	1.0	8.3	10.7
10	Arkopal N-080	0.5	2.3	2.5	8.1	9.6

a *v/v* for PL, BL and EHL solvents and *wt/v* for Arkopal N-080
b 1-5 rating; 1 = no phytotoxic effects, 5 = necrosis and loss of leaf turgor;

Adjuvancy

NPL enhanced the performance of 2,4-D DMA salt (Figure 1; Table 3).

Table 3. Influence of PL, BL, EHL solvents on 2,4-D efficacy when tested on fat-hen as fresh foliar weight (g), (mean of 4 replicates)

No.	Herbicide	Adjuvant 0.5% *v/v*	Fat-hen Means (g)
1	Untreated	-	13.53
2	-	NPL	15.23
3	2,4-D DMA[1]	-	9.70
4	2,4-D DMA	NPL	5.53
5	2,4-D 2-EH [2]	-	11.16
6	2,4-D 2-EH	NPL	9.01
7	2,4-D 2-EH	BL	8.11
8	2,4-D 2-EH	EHL	6.53
	LSD (0.05)		1.3

[1] dimethylamine salt of 2,4-D (500 g a.e. /litre); dose 0.3 mM (equiv. to 13.3 g a.e. /ha at 200 litres/ha).
[2] 2-ethylhexyl ester of 2,4-D (450 g a.e. /litre); dose 0.1 mM (equiv. to 4.4 g a.e. /ha at 200 litres/ha).

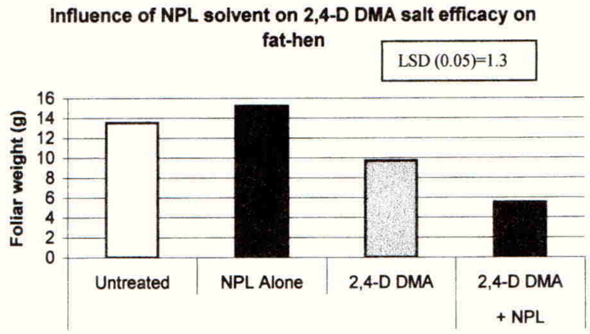

Figure 1. Influence of NPL on 2,4-D DMA salt efficacy

NPL, BL and EHL also enhanced the performance of 2,4-D 2-EH (Figure 2; Table 3). EHL was significantly better than NPL and tends to be better than BL in enhancing efficacy of 2,4-D 2-EH. We did not observe phytotoxic symptoms caused by the solvents applied.

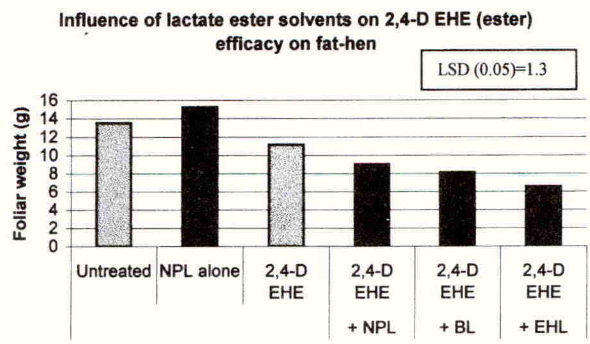

Figure 2. Influence of lactate ester solvents on 2,4-D 2-EH efficacy

These efficacy data do not reveal the exact mechanism(s) involved in the activity of the PURAC solvents. Below, a discussion is started based on the data so far. Fat-hen is somewhat wettable. The similarity in surface tension of the various solvents (Table 1) and the differences in performance between NPL with the DMA salt and the 2-EH ester (Figure 2; Table 3) indicate that it is not just a matter of improved retention of spray solution on the foliage of fat-hen. An adjuvant that increases foliar uptake may serve as a solvent for the active ingredient in the visually dry drop deposit or may enhance the permeability of the leaf cuticle or provide both functions. Penetration of the adjuvant into the leaf cuticle is required to fulfil the latter function.

Based on studies with other carbohydrate-based adjuvants and the structure of the lactate esters, it seems likely that the lactate esters will not or hardly move into the waxy leaf cuticle. This means that the action of the lactate ester solvents is most likely located on the leaf surface. We suggest that they improve the availability of the active ingredient for uptake. This is reasonable for the solid DMA salt of 2,4-D. The 2,4-D 2-EH (ester) is a liquid and very lipophilic.

The concentration of the 2,4-D ester in the treatment solution is 0.15 g a.e. /litre - much lower than the 5 g/litre (approximately) of the solvent. It is suggested that the greater amount of solvent provides a more intimate contact between ester and the leaf surface. That the EHL solvent (as the most lipophilic solvent) is the most effective one with 2,4-D 2-EH agrees with this view. More sophisticated experiments with isolated leaf cuticles and spray retention measurements are required to explain in detail the mechanism(s) involved with the lactate ester solvents.

NPL applied at 0.5% (*v/v*) did not reduce growth of fat-hen (Table 3; Figures 1, 2). In the other experiments with herbicides we also did not observe local leaf necrosis caused by BL or EHL. This preliminary observation agrees with the suggestion above that the lactate esters will not or hardly move into the leaf cuticle and subsequently to the plant tissue.

CONCLUSIONS

Application of the solvents NPL, BL and EHL on tomato seedlings did not result in phytotoxic effects up to 0.5% (*wt/wt*).

This study has shown that lactate esters can strongly enhance the performance of 2,4-D DMA salt and 2,4-D 2-EH (ester) on fat-hen.

REFERENCES

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Adjuvant improves performance of pre-emergence residual herbicides in cereals

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ABSTRACT

Previous studies have reported that adjuvants can enhance the performance of pre-emergence residual herbicides in a range of broadleaved crops by reducing spray drift, improving spray deposition and reducing leaching. This paper reports a trial investigating the effect of the adjuvant HM 9679-A on the efficacy of five pre-emergence herbicide treatments applied via four nozzle types on the control of blackgrass (*Alopecurus myosuroides*). The addition of HM 9679-A to each of the five herbicide treatments significantly reduced the number of blackgrass plants assessed 43 days after application. This effect was maintained after the application of a standard post emergence herbicide. The number of blackgrass heads/m^2 recorded in the following spring, 273 days after the pre emergence treatment, was reduced in comparison to the herbicide alone.

INTRODUCTION

Blackgrass (*Alopecurus myosuroides*) is a widespread weed in England and in 2002 it was estimated that there were over 1000 confirmed cases of herbicide resistance spread across 30 counties in England (WRAG, 2003). Enhanced metabolism resistance is widespread affecting many cereal herbicides (e.g. isoproturon, pendimethalin and flupyrsulfuron-methyl), and target site resistance to “fops” and “dims” is increasing and remains a potential threat to ALS inhibitors (e.g. mesosulfuron). High levels of control can be achieved only by a combination of cultural practices and the use of an integrated herbicide programme. A key principle is to treat blackgrass at an early growth stage to reduce the effects of enhanced metabolism resistance, and one important component is the use of a pre-emergence herbicide. The combination of increased blackgrass resistance, the trend towards earlier establishment using reduced tillage and the introduction of flufenacet based herbicides has resulted in increased use and it is currently estimated that 0.5 million hectares of winter wheat are treated with pre-emergence herbicides annually (Market research data from 2005, BASF, *pers. comm.*). The efficacy of pre-emergence herbicides can be affected by a number of environmental factors, for example, spray drift, poor deposition over the soil surface, volatilisation from the soil surface and leaching of the active ingredient below the active zone. The addition of an adjuvant can improve their performance by reducing spray drift, improving spray deposition and reducing leaching (McMullan *et al.*, 1998). Previous studies have demonstrated that the addition of the adjuvant ‘Grounded’ can enhance the performance of pre-emergence herbicides when applied in maize and a range of broad-leaved crops (McMullan *et al.*, 1998; Thomas & Morgan, 2001). In this study the effect of this adjuvant when applied in mixture with a range of pre-emergence herbicides via four different nozzle types in cereals was investigated.

MATERIALS AND METHODS

Winter wheat (cv. Robigus), was drilled to a depth of 25-30mm on 16 September 2004 at 250 seeds/m^2, and subsequently rolled to create a fine firm seedbed. The following herbicide treatments were applied:

1) Untreated
2) 'Alpha Trifluralin 48EC' (480 g/litre trifluralin) at 2 litres/ha
3) 'Crystal' (flufenacet/pendimethalin 60/300 g/litre) at 4 litres/ha + trifluralin at 2 litres/ha
4) 'Stomp 400' (pendimethalin 400 g/litre) at 5 litres/ha
5) 'Liberator' (flufenacet/diflufenican 240/100 g/litre) at 0.6 litres/ha
6) 'AUK 10560' (experimental product) + trifluralin at 2 litres/ha

Each treatment was applied either alone or in conjunction with 0.2 litres/ha 'Grounded' (a proprietary blend of $C_8 - C_{12}$ aliphatic hydrocarbons, hexahydric alcohol ethoxylates, and $C_{18} - C_{20}$ alkanoic acids, hereafter coded HM 9679-A) using a Martin Lishman sprayer mounted on an ATV via a range of nozzles detailed in Table 1. Application date was on 22 September 2004, 6 days after drilling.

Table 1. Application details of nozzles used to apply pre-emergence herbicides

Nozzle	Specification	Application volume (litres/ha)	Spray quality	Pressure (kPa)
Flat fan	04 F110	200	Medium	200
Lo-Drift	02 F110	100	Medium	200
Air inclusion	02 F110	100	Medium	200
Variable pressure	02 F110	100	Medium	200

Each plot measured 3m x 3m and was replicated five times. The trial was located near Maidwell, Northampton on a clay soil. Resistance testing in 2004 established that the field blackgrass population had enhanced metabolism resistance, R? to "fop" herbicides and RR to pendimethalin as defined by the Weed Resistance Action Group classification. The efficacy of the pre-emergence treatments on the control of blackgrass was assessed on 4 November 2004 (43 DAT), by counting the number of blackgrass plants in five 0.1m^2 quadrats per plot, and then calculating the mean plants/m^2.

All plots were then oversprayed with a post emergence application of 0.4 kg/ha 'Atlantis WG' (mesosulfuron-methyl/iodosulfuron-methyl-sodium 30/6 g/kg) + 2 litres/ha trifluralin + 1.0 litres/ha 'BioPower' (an adjuvant containing 6.7% *wt/wt* 3,6-dioxaeicosylsulphate sodium salt and 20.2% *wt/wt* 3,6-dioxaoctadecylsulphate sodium salt), applied on 23 March 2005 via a flat fan nozzle in 200 litres/ha spray volume. Subsequently, the number of blackgrass heads in five 0.1m^2 quadrats per plot was recorded on 22 June 2005 (273 days after the pre-emergence treatments, 91 days after the post emergence application) and the number of heads/m^2 calculated.

RESULTS

Germination of blackgrass was rapid in the mild wet autumn, and in the untreated plots a mean of 1780 plants/m^2 was recorded in the November assessment (Table 2). With the exception of trifluralin 2.0 litres/ha applied via a variable pressure nozzle, all pre-emergence herbicides significantly reduced the number of blackgrass plants/m^2 assessed 43 days after application. Factorial analysis was used to compare pre-emergence herbicide performance (Table 3). There was a clear hierarchy in the performance, with pendimethalin-based treatments (either alone or in combination with flufenacet + trifluralin) giving significantly the greatest reduction in blackgrass numbers The next most effective treatment was flufenacet/diflufenican, which in turn gave a significantly lower number of blackgrass plants/m^2 in comparison with either the experimental tank mixture (AUK 10560 + trifluralin) or trifluralin (Table 3). The addition of the adjuvant HM 9679-A tended to enhance the performance of the pre-emergence herbicides. The adjuvant effect was statistically significant in specific herbicide-nozzle combinations (Table 2). For example when applied via a flat fan nozzle, use of the adjuvant reduced the blackgrass population from 600 to 375 plants/m^2 with trifluralin and from 145 to 70 plants/m^2 with the mixture of flufenacet/pendimethalin + trifluralin (Table 2). In contrast, there was no clear effect when applied with pendimethalin alone. The effect of the adjuvant on overall herbicide performance was significant (Table 3).

Table 2. The effect of pre-emergence herbicide, adjuvant and nozzle type on the number of blackgrass plants/m^2. Assessed 43 DAT. LSD (p =0.05) = 354.9. Statistical analysis was carried out on the log-transformed data

Treatment (dose rate product litres/ha)	Flat Fan (04F110) 200litres/ha	Lo-Drift (LD02F110) 100litres/ha	Air inclusion (BBJ02F110) 100litres/ha	Variable Pressure (VP02F110) 100litres/ha
Untreated	1780.0 a			
Trifluralin (2.0)	600 bc	702.5 bc	750.0 bc	775.0 ab
Trifluralin + HM 9679-A (2.0 + 0.2)	375.0 b-h	532.5 bc	505.0 bcd	305.0 c-j
Flufenacet/pendimethalin + trifluralin (4.0 + 2.0)	145.0 g-m	182.5 e-i	145.0 h-m	60.0 mn
Flufenacet/pendimethalin + trifluralin + HM 9679-A (4.0 + 2.0 + 0.2)	70.0 k-n	85.0 k-n	65.0 lmn	75.0 lmn
Pendimethalin (5.0)	100.0 i-n	77.5 k-n	80.0 k-n	60.0 n
Pendimethalin + HM 9679-A (5.0 + 0.2)	50.0 n	92.5 j-n	90.0 k-n	217.5 e-l
Flufenacet/diflufenican (0.6)	315.0 c-j	237.5 c-j	450.0 b-e	275.0 b-i
Flufenacet/diflufenican + HM 9679-A (0.6 + 0.2)	215.0 d-k	77.5 k-n	140.0 h-m	155.0 f-m
AUK10560 + trifluralin (2.0)	355.0 b-h	412.5 b-f	440.0 b-e	440.0 b-e
AUK10560 + trifluralin (2.0) + HM 9679-A (0.2)	270.0 b-i	387.5 b-g	255.0 c-l	300.0 b-h

In this trial the effect of nozzle type on the performance of the pre-emergence herbicide was not significant in relation to the number of blackgrass plants/m^2 recorded in November.

Table 3. Factorial analysis on blackgrass plants/m^2 assessed on 43 DAT. Means followed by the same letter do not significantly differ, ns = not significant

Factor	Blackgrass plants/m^2	Log LSD (p=0.05)	
Pre-emergence herbicide (product litres/ha)		LSD = 0.16	
Trifluralin (2.0)	568.1	2.70	a
Flufenacet/pendimethalin + trifluralin (4.0 + 2.0)	103.4	1.96	d
Pendimethalin (5.0)	95.9	1.91	d
Flufenacet/diflufenican (0.6)	233.1	2.28	c
AUK 10560 + trifluralin (2.0)	357.5	2.54	b
Pre-emergence adjuvant		LSD = 0.10	
No adjuvant	330.1	2.36	a
+ adjuvant	213.1	2.20	b
Nozzle / water volume (litres/ha)		LSD = 0.14	
Flat fan (200)	249.5	2.26	ns
Lo-Drift (100)	278.8	2.30	ns
Air inclusion (100)	292.0	2.31	ns
Variable pressure (100)	266.2	2.25	ns

The effect of the performance of the pre-emergence herbicide as a component of an integrated blackgrass control programme, was assessed by overspraying the trial with a standard post emergence herbicide mixture, and then assessing the heads/m^2 recorded in June (Table 4). The blackgrass population in the untreated was high at 2400 heads/m^2 and applying only a post emergence application of mesosulfuron-methyl/iodosulfuron-methyl-sodium + trifluralin + 'Biopower' reduced this to 411 heads/m^2 equivalent to 83% control. All the pre-emergence treatments applied in sequence with a post-emergence spray application, significantly reduced the number of heads/m^2 in comparison to the post-emergence only treatment, and control ranged from 88 – 98%.

Factorial analysis was used to compare performance of the herbicides, adjuvant and nozzle type (Table 5). A pre-emergence application of flufenacet/pendimethalin gave significantly the greatest reduction in blackgrass heads/m^2 and this equated to 97% control. The development combination (AUK 10560 + trifluralin), trifluralin or pendimethalin alone all gave similar levels of control and were significantly better than the flufenacet/diflufenican (Table 5). The addition of HM 9679-A improved the levels of control of blackgrass achieved, reducing the number of heads/m^2 recorded from 236.0 to 130.6 when applied in combination with trifluralin via a flat fan nozzle (Table 4), and from 262.8 to 114.2 with flufenacet/diflufenican via an air inclusion nozzle.

Overall the addition of the adjuvant HM 9679-A to pre-emergence herbicides significantly reduced the number of blackgrass heads recorded (Table 5). In this trial the performance of the flat fan, Lo-Drift and air inclusion nozzles overall was similar, and significantly better than the variable pressure nozzles in terms of the number of blackgrass heads/m^2 assessed in June (Table 5).

Table 4. The effect of pre-emergence herbicide, adjuvant and nozzle type on the number of blackgrass heads/m^2. The percentage control is given in parenthesis. All treatments (including the untreated) received a post emergence herbicide treatment. Assessment on 22 June 2005 (91 DAT with the post-emergence herbicide). LSD (p=0.05) = 83.8

Treatment (litres/ha)	Flat Fan (04F110) 200litres/ha	Lo-Drift (LD02F110) 100litres/ha	Air inclusion (BBJ02F110) 100litres/ha	Variable Pressure (VP02F110) 100litres/ha
Untreated (no post emergence)	2400			
Untreated	411.4 a (83)			
Trifluralin (2.0)	236.0 bcd (90)	90.6 l-p (96)	156.8 d-m (93)	226.2 b-f (91)
Trifluralin + HM 9679-A (2.0 + 0.2)	130.6 h-p (95)	119.8 i-p (95)	130.8 h-p (95)	182.8 c-j (92)
Flufenacet/pendimethalin + trifluralin (4.0 + 2.0)	63.8 op (97)	99.8 j-p (96)	73.4 m-p (97)	65.6 nop (97)
Flufenacet/pendimethalin + trifluralin + HM 9679-A (4.0 + 2.0 + 0.2)	59.4 p (98)	97.6 k-p (96)	67.0 nop (97)	86.0 l-p (96)
Pendimethalin (5.0)	128.8 l-p (95)	105.8 i-p (96)	137.0 g-p (94)	184.8 c-i (92)
Pendimethalin + HM 9679-A (5.0+0.2)	99.6 j-p (96)	112.8 i-p (95)	178.2 d-k (93)	180.0 c-k (93)
Flufenacet/diflufenican (0.6)	218.8 b-g (91)	281.0 b (88)	262.8 bc (89)	236.6 bcd (90)
Flufenacet/diflufenican + HM 9679-A (0.6 + 0.2)	213.0 b-h (91)	162.8 d-l (93)	114.2 i-p (95)	229.4 b-e (90)
AUK10560 + trifluralin (2.0)	145.6 f-o (94)	130.4 h-p (95)	121.4 i-p (95)	151.4 e-m (94)
AUK10560 + trifluralin (2.0) + HM 9679-A (0.2)	129.6 h-p (95)	121.8 i-p (95)	141.0 g-p (94)	147.6 e-n (94)

Table 5. Factorial analysis on blackgrass heads/m^2 assessed on 22 June 2005 (273 DAT with the pre-emergence herbicides). Means followed by the same letter do not differ significantly

Factor	Blackgrass heads/m^2 LSD (P=0.05)
Pre emergence herbicide (product litres/ha)	LSD = 29.7
Trifluralin (2.0)	159.2 b
Flufenacet/pendimethalin + trifluralin (4.0 + 2.0)	76.6 a
Pendimethalin (5.0)	140.9 b
Flufenacet/diflufenican (0.6)	214.8 d
AUK 10560 + trifluralin (2.0)	136.1 b
Pre emergence adjuvant	LSD = 18.8
No adjuvant	155.8 a
+ adjuvant	135.2 b
Nozzle / water volume (litres/ha)	LSD = 26.5
Flat fan (200)	142.5 a
Lo-Drift (100)	132.2 a
Air inclusion (100)	138.3 a
Variable pressure (100)	169.0 b

DISCUSSION

The addition of the adjuvant HM 9679-A to a range of pre-emergence herbicides significantly improved the control of blackgrass. The number of blackgrass plants recorded in the autumn was reduced in comparison to the herbicide alone, and this effect was still apparent when the number of heads/m^2 was assessed in the following June, 273 days after application. Previous studies in a range of broad-leaved crops have also reported improvements in the performance of trifluralin, pendimethalin and other herbicides when applied with HM 9679-A (McMullan *et al.*, 1998; Thomas & Morgan, 2001). Improving the performance of the pre-emergence component of the herbicide programme, has some important implications. Firstly, the selection pressure exerted on the subsequent post-emergence herbicide is reduced as the number of weed plants per unit area is reduced. Secondly, a reduction in the number of post-emergence herbicides or the selection of lower cost option may be possible. Finally, this has ramifications on the population dynamics of blackgrass. Typically 98% control is required to maintain or start to reduce the blackgrass population, and as this trial demonstrates in high-pressure sites this level of control is difficult to achieve. The addition of HM 9679- A to the pre-emergence herbicide to enhance activity can, in conjunction with an integrated control strategy, enable this level of control to be achieved, reducing the blackgrass population in future years.

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Amido propyl amines – new adjuvant class for agrochemicals

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ABSTRACT

Amido propyl amines (APAs) are a new chemistry class explored to meet the demand of increased efficacy and improved environmental properties of agrochemical formulations. For a series of various amido propyl amines based surfactants, physical and chemical properties have been determined and are shown to be dependant on the pH environment. The adjuvancy has been investigated using glyphosate and strobilurin as active ingredients. The efficacy of APA derivatives was determined in glass house trials. The studies showed excellent adjuvant properties for both glyphosate and azoxystrobin, compared to standard products on the market. Furthermore, it is shown that APAs have excellent compatibility with high loading glyphosate formulations.

INTRODUCTION

Due to consumer's interest and agricultural policies, there is a huge incentive for the agrochemical industry to develop formulations with increased efficacy and improved environmental profiles. One way of meeting these demands is to further explore the use of adjuvants in pesticide formulations. The use of fatty amine based surfactants as adjuvants for foliar pesticides, particularly hydrophilic herbicides like glyphosate and paraquat, is well known. However, the use of adjuvants to enhance the performance of fungicides and insecticides is less explored.

This paper will describe a new type of adjuvant explored to meet the demand of increased efficacy and improved environmental profile. It has been shown by other authors that the amine functionality in an adjuvant is important for adsorption to the foliar, the interaction with the plant cuticle and the penetration of the active ingredient (Coret & Chamel, 1993). The amido propyl amines are believed to possess these properties and, at the same time, offer environmental and compatibility benefits.

MATERIALS AND METHODS

Three different amido propyl amines (APA) based on C8/C10 fatty acid (APA C8/10), coco fatty acid (APA C), commercial available as 'Adsee C-80/W', and soy fatty acid (APA S) have been synthesised by Akzo Nobel Surfactants AB, Stenungsund, Sweden. Dimethyl amino propylamine was converted into the alkyl amide by condensation with the different fatty acids. Polyethoxy (15) tallow amine (TA 15) and a commercial available phosphate ester (PhE) were used as model adjuvant for comparative purposes in the glyphosate tests.

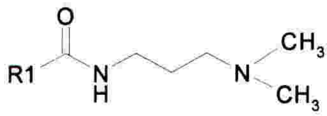

Figure 1. Amido propyl amines (APA) are fatty acid compounds with N,N-dimethyl-1,3 propanediamine. R1 can be C8/C10, coco or soy fatty acids

Equilibrium surface tension was measured by the Du Noüy ring method, with a Sigma 70KSV instrument. Contact angle measurement was made using a FTÅ 200 instrument, equipped with a video camera and an image analysis software, on a hydrophobic surface consisting of 'Parafilm PM-992' (American Can Company). As a reference, equilibrium surface tension of distilled and deionized water is 72 mN/m and contact angle on Para film after 60 s equals 102°. The concentration of surfactant used for contact angle and surface tension measurements, has been 0.1% and the contact angle after 60 s is given. All measurements were done at a temperature of 20°C and a humidity of 53%. The water used was distilled and deionized. Glacial acetic acid or phosphoric acid (Merck) was used to adjust the pH.

All surfactants were blended with glyphosate [N-(phosphonomethyl)glycine] as the isopropylamine salt, (62% *wt/wt*, Monsanto) for compatibility tests and greenhouse trials. Three different concentrations of the surfactant were used, 6, 10 and 15% of active content respectively, while the glyphosate was kept at a concentration of 30% a.e.. The formulations had a pH between 5 and 6. The biological efficacy was tested on pot-grown couch grass (*Elymus repens)*, winter oilseed rape (*Brassica napus*) cv. Apex and Mediterranean ryegrass (*Lolium rigidum*). The formulations were sprayed at 0.20, 0.40 and 0.75 kg a.e./ha on *B. napus* and *E. repens*. A lower dose range was used on the L. rigidum, 0.08, 0.15 and 0.25 kg a.e./ha. The treatments were applied at a spray pressure of 210 kPa delivering 200 liters/ha. There were three replicates of each treatment. Damage as a % compared with the best untreated was assessed on the three species at 11, 19 and 30 days after spraying. The test was performed by Castan Consultants, Bristol, UK.

The fungicide trial was performed as curative treatment of wheat infected with *Mycosphaerella graminicola (Septoria tritici)*. Surfactant (0.25%) was added to the commercially available 'Ortiva' (azoxystrobin 250 g/litre SC) from Syngenta which was sprayed at 62.5 g a.i./ha with a water volume of 200 litres/ha. The pH of the spray liquid was between 8 and 10. The biological efficacy was expressed as the degree of plant infections, i.e. leaf necrosis, in %. The test was performed by Surfaplus and Plant Research International, Wageningen, Netherlands.

RESULTS

Surface chemistry properties and different pH

As can be seen from Figure 1, the chemistry of amido amines will be sensitive to pH and protonation. At high pH, the molecule will be nonionic, but at lower pH the amine will protonate and be more cationic. This process could be followed by monitoring the viscosity versus pH (Figure 2). Protonation starts close to pH 8 and below pH 6, the molecules are predominately protonated. The protonation degree of the molecule will have a huge impact on the physical properties such as adsorption properties and solubility properties. Most natural surfaces (such as a leaf surface) are negatively charged and a cationic adjuvant will adsorb more readily to such a surface.

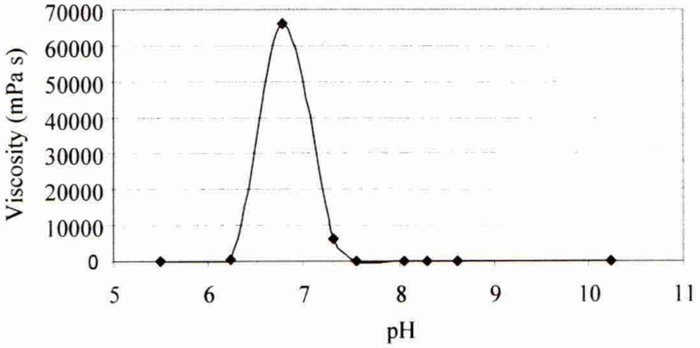

Figure 2. The pH versus viscosity for APA C. Phosphoric acid is used to lower the pH

The influence of pH is clearly seen in the surface chemistry properties (Table 1) and the data confirms that protonation takes place. Solubility will increase upon protonation, as seen for APA C and APA S. CMC (critical micelle concentration) is higher for cationic surfactants (at pH=5) compared to nonionic (at pH = 10). As can be seen, surface tension and wetting properties will also be influenced by pH. The data suggests that specific interactions are taking place between the surface and the surfactants, most likely due to different types of aggregates formed at different pH.

Table 1. Surface Chemistry properties for APAs at different pH

Alkyl chain	Surface tension (mN/m)		CMC (g/litre)		Contact Angle (°, 60 sec)		Water Solubility	
	pH =5	pH=10	pH =5	pH=10	pH =5	pH=10	pH =5	pH=10
C 8/10	28	27	1.0	0.4	86	49	Yes	Yes
Coco	32	27	0.05	0.05	65	41	Yes	Disp
Soya	39	29	0.03	0.03	73	43	Yes	No

Glyphosate compatibility

All three APAs tested in this study have an extremely good compatibility with isopropylamine (IPA) - glyphosate salt. A standard glyphosate adjuvant, such as the tallow amine 15 EO, suffers from a salting out effect in most electrolyte solutions that is related to the cloud point phenomena of ethylene oxide containing surfactants (Holmberg *et al.*, 2003). Thus, increasing the glyphosate concentration in a formulation containing an ethoxylated surfactant, will lead to incompatibility between the adjuvant and the glyphosate – the formulation will phase separate. The sensitivity towards electrolyte salts can be monitored by measuring the temperature at which the formulation becomes cloudy upon heating (cloud point). The APA surfactants on the contrary, contain no ethylene oxide and have no cloud point. They have been shown to be very insensitive to high salt concentrations and could thus be used in highly concentrated glyphosate formulations. Figure 3 shows the effect on cloud point between different IPA-glyphosate formulations containing two different adjuvants, APA C or TA 15. APA C gives a stable and clear formulation at all concentrations up to 470 g/litre a.e. while a formulation containing TA 15 will be separated at 40°C in 470 g/litre formulation.

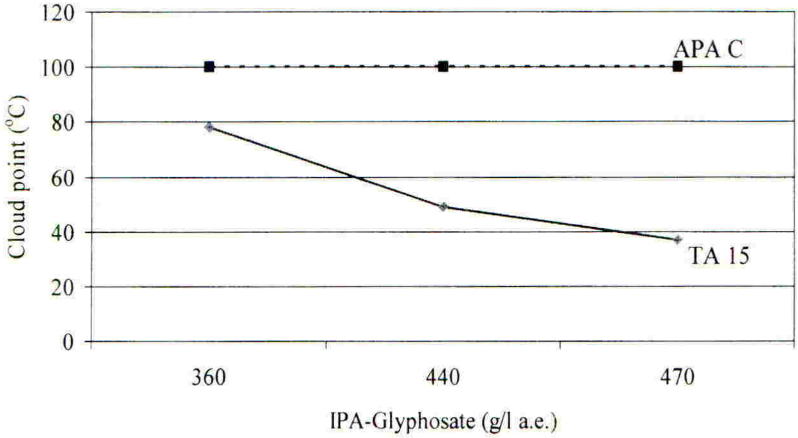

Figure 3. Compatibility between IPA-glyphosate and two different surfactants; TA 15 and APA C. Surfactant concentration is 10% in all formulations

Green house trials - Glyphosate

Several formulations have been tested at different concentrations in green house trials. Figure 4 shows the comparison between the three APAs at low surfactant concentration (6%) and low glyphosate rate concentration (0.20 kg a.e./h for *B. napus* and *E. repens*, 0.08 kg a.e./h for *L. rigidum*) . As can be seen, the coco based APAs are outperforming both the soy and C8/10 derivatives. It is also ranked over the reference TA 15 for *B. napus* and *E. repens*, but this was not statistically significant. All APA derivatives are superior over the commonly used phosphate ester (PhE).

Furthermore, the study showed that the APA C can be diluted to low concentrations, while maintaining the bioefficacy (Figure 5). This opens possibilities for efficient high loading formulations. An additional advantage is the shortened burn down time seen in Figure 5. The plant damage at 11 DAT seen in the formulations based on APA C compared to TA 15 is significantly higher. However, at high spray concentrations and at high surfactant loadings, no differences are seen between the APA C and TA 15 after 30 DAT. The advantage is at low surfactant concentrations and at low spray concentrations.

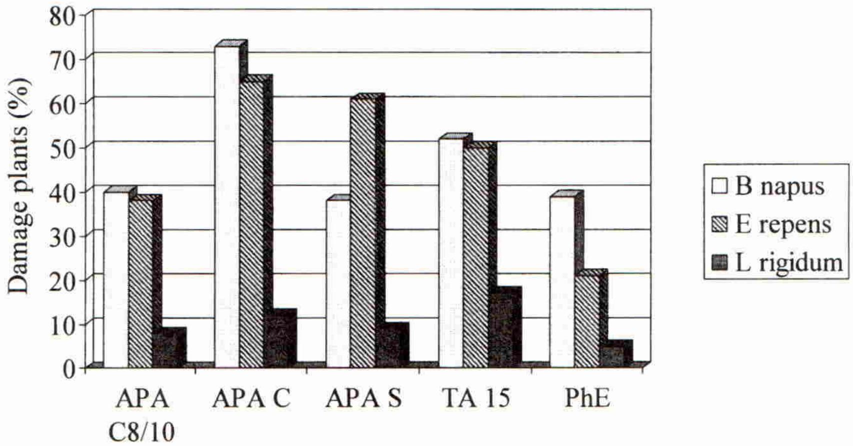

Figure 4. Green house trials with IPA-Glyphosate and three different APA derivatives. TA 15 and PhE are used as references

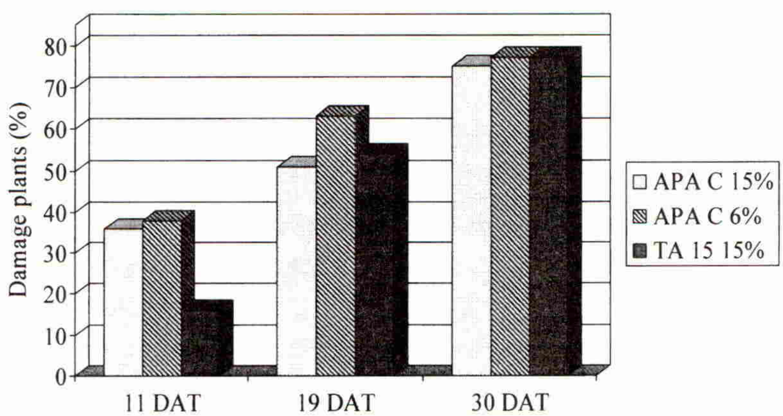

Figure 5. Green house tests with IPA-Glyphosate on *B. napus* with two different surfactants. Glyphosate application rate 0.40 kg a.e./ha.

When surfactants are used as adjuvants in agrochemical formulations, a number of different surfactant properties contribute to the final result and act together both in a positive and negative manner. Multivariate data analysis has been used in earlier studies and has showed that high surface tension and low CMC are some of the most important parameters for a good glyphosate adjuvant (Strandberg *et al.*, 2004). Thus, the data in Table 1 suggest that both the soy and coco based derivatives should be good adjuvants for glyphosate, at pH close to 5. This was confirmed in the green house trials. It seems that the APA C delivers the right balance between wetting, adsorptivity and penetration enhancement at low concentrations to become a next generation adjuvant for glyphosate.

Green house trials – Strobilurin

Short-chained APA showed an extremely good adjuvancy on the performance of azoxystrobin, increasing the fungicidal efficacy by over 50% (Figure 6). The most hydrophilic APA derivative, giving the lowest surface tension, showed to be the best adjuvant for the water insoluble fungicide. The efficacy seems to be directly related to the length of the surfactant alkyl chain. The efficacy of 'Ortiva' was increased by the addition of all APAs.

The azoxystrobin 'Ortiva' formulations have a pH above 8. This means that the character of the surfactant will be more nonionic in the fungicide formulation compared to cationic in the case of glyphosate. The data suggest that a water insoluble systemic fungicide needs a small, water soluble adjuvant that reduces the surface tension and enables good contact between the strobilurin particles and the plant, such as the C8/10 APA.

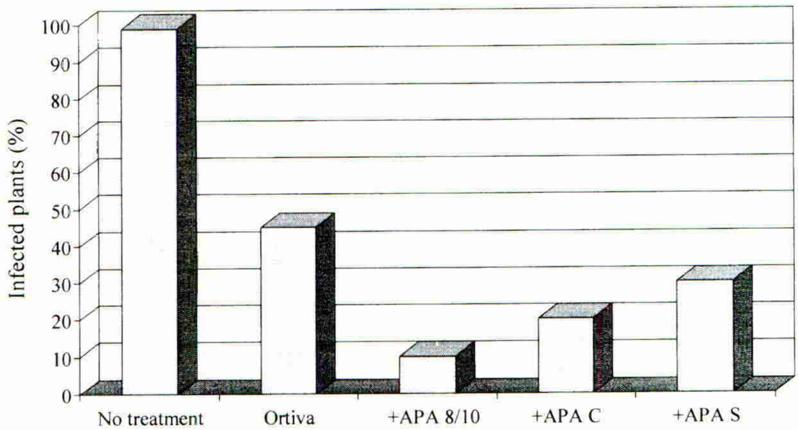

Figure 6. Efficacy of the strobilurin based formulation 'Ortiva' on *Mycosphaerella graminicola* infected wheat. The different APA derivatives were added to the Ortiva treatment solution.

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