MULTIPURPOSE AGRIMAX ADJUVANT SYSTEM

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Summary. Agrimax™ 3, 4, and 5 are proprietary multipurpose adjuvant compositions for pesticide formulations microemulsified as homogeneous, thermodynamically stable systems dilutable at all concentrations without separation. These formulations have imparted rainfastness and enhanced biological activity with several herbicides on many broad leaf and grass weed species when used as tank mix additives at 0.1-0.25% v/v.

INTRODUCTION

Some of the benefits derived from the proper use of adjuvants are enhanced biological activities resulting in a reduction in total use while maintaining efficacy, increased rainfastness, improved penetration, better wetting and spreading, and protection against UV radiation for the active ingredients. Agrimax™ adjuvant systems show many of these benefits. These adjuvants are based on N-alkylpyrrolidones and possess excellent physical profiles such as low surface tension, low contact angle, and low wetting time. Recent studies also showed that some pyrrolidones increase cuticular penetration and enhance translocation (1).

Stability. Agrimax™ 3 and 5 are water based optimized proprietary compositions. At appropriate dilutions, the particle size distribution was centered around 200-300 A°, well within the microdispersion range. Agrimax™ 4 is formulated in hydrocarbon and also contains water insoluble polymers. Dilution with water to 10%, 2%, 1% and 0.1% produced stable emulsions without separation even for weeks. The droplet size of the emulsion was <2 μm.

Surface properties. Table 1 summarizes the surface properties of Agrimax™ 3 and 5 in aqueous solutions as a function of dilution. Agrimax™ 5 has similar properties. If droplet dry-down is considered, assuming a reasonable estimate of 50% evaporation during flight, the effective values for the surface properties for Agrimax™ 3 are: instantaneous wetting time, surface tension of <28 dynes/cm, and contact angle of approximately 46 degrees. The effective values at 0.5% dilution for Agrimax™ 5 are 8 s wetting time, surface tension of <29 dynes/cm, and contact angle of approximately 46 degrees.

Ease of emulsification of actives. In the concentrated form Agrimax™ systems can solubilize a variety of active ingredients, especially those containing aromatic (benzenoid) compounds, carbamates, and hydrophobic esters at concentrations as high as 30%. Such systems are believed to be microemulsion/emulsion concentrates. On dilution in water these concentrates produced very stable emulsions with submicron droplet size, with unchanged particle size distribution even after standing for 2 weeks.

METHODS

Rainfastness evaluations. Commercial formulations of pendimethalin (as Prowl®) phosphonomethylglycine isopropylamine salt (as (Rodeo®), and carbaryl (as Sevin®) were diluted to end use concentrations and the appropriate Agrimax™ system added at 0.125-0.05% of final dilution. An aliquot (0.1-0.5 g) was applied to a glass/parafilm plate uniformly as a

2.5-7.5 cm square patch. After a dry film was obtained, a fine spray of water was applied to simulate 0.5-2.0 cm of rain wash-off. The washings were collected in a waste jar. The remaining washed patch was quantitatively extracted. The ethanol was analyzed by UV spectral analysis in the case of Prowl® and Sevin® and by potentiometric titration for Rodeo®.

Biological evaluations. The same rates of Agrimax® system adjuvants were added to commercial samples of paraquat (Gramoxone®) and glyphosate (Roundup®) and sprayed onto weeds under two year old citrus trees at Lake Alfred, Florida. The major grass weed was Bahia grass (*Paspalum notatum*) and the major broad-leaf weed species included *Heterotheca subaxillaris*, white eye *(Richardia brasiliensis)*, Mexican tea *(Chenopodium ambrosiodes)*, fat hen *(Chenopodium album)*, green amaranth *(Amaranthus viridis)*, cobbler's pegs *(Bidens pilosa)* and spiny head sida *(Sida acuta)*.

The plots were visually rated 3, 7, 21, 42 and 63 days after spraying.

RESULTS

Table 1. Surface properties of aqueous Agrimax™ 3 and 5

% Dilution	Concentration ratio	Surface tension (dynes/cm)	Contact angle[a] (degree)	Wetting time (S)
	Agrimax™ 3			
1/100	1.0	26.5 ± 0.1	41.6 ± 5	0
1/133	0.75	26.1 ± 0.1	42.6 ± 4	0
1/200	0.50	27.9 ± 0.1	46.2 ± 7	0
1/400	0.25	29.7 ± 0.08	55.6 ± 7	8.0 ± 1
1/666	0.15	30.6 ± 0.08	65.1 ± 7	45.6 ± 11.5
1/1000	0.10	32.5 ± 0.09	79.3 ± 5	573 ± 185
1/1330	0.075	33.1 ± 0.09	79.6 ± 5	1600 ± 707
1/2000	0.050	35.0 ± 0.05	83.0 ± 4	> 3600
	Agrimax™ 5			
1/100	1.0	28.3 ± 0.4	47.4 ± 3	3.5 ± 0.4
1/133	0.75	28.3 ± 0.4	48.2 ± 6	4.5 ± 0.3
1/200	0.50	28.3 ± 0.6	57.0 ± 5	8.3 ± 0.6
1/400	0.25	29.7 ± 0.09	55.3 ± 6	18.6 ± 1.2
1/666	0.15	30.9 ± 0.08	60.2 ± 3	50.1 ± 6.8
1/1000	0.10	31.6 ± 0.04	70.0 ± 5	184 ± 42
1/1330	0.075	33.2 ± 0.12	74.9 ± 7	677 ± 226
1/2000	0.050	33.60 ± 0.04	82.0 ± 6	> 3600

[a] contact angles are on a parafilm surface

Rainfastness. When commercial Prowl® was diluted to 1% with water with the addition of either Agrimax™ 3 added at 0.125% and 0.25% or a commercial sticker based on alkyd resin at 0.25%, all Agrimax™ treatments produced significantly higher recoveries than the commercial sticker formulation. Agrimax™ 5 and 4 also produced similar results. The addition of Agrimax™

3 increased retention by three times (78.8 ± 7.4%) more than the commercial formulation alone (21.3 ± 3.3%). It is interesting to note that lower recoveries were obtained at higher doses of Agrimax™ 3. This trend was confirmed by using 0.5% Agrimax™ 3, when the recovery was (38.3 ± 3.2%). Increased rainfastness at lower adjuvant concentrations suggests that the formulation contains an optimized surfactant system and film forming polymer which will act in opposite directions. The surfactant system will have a washing tendency whereas the polymer will retain the active ingredient. Proper adjustment of the dosage balances these opposing forces.

When adjuvants were added to the concentrate, the retention of Rodeo® was influenced by Agrimax™ 3 and was compared with a commercial sticker. The adjuvants were added to the concentrate followed by dilution to 2.1% a.i. Agrimax™ 3 doubled active ingredients retention (49.4 ± 2.6%) relative to the standard commercial formulation (27.1 ± 1.5). The commercial sticker produced much lower recovery at both 0.125 and 0.5%. Once again, Agrimax™ 3 gave higher (41 ± 4%) retention at 0.25% as compared to the commercial formulation (26.4 ± 5%). The commercial sticker produced only 9.1 ± 2.7% recovery. The wash off effect from the high surfactant levels in the commercial sticker was evident in this study. Rainfastness data for Rodeo® applied on a parafilm surface shows surface properties similar to plant leaf surfaces (2). The results were similar to those obtained for glass surfaces.

An increase in the retention of carbaryl was shown when Agrimax™ 4 was added at the rate of 0.13%, and 0.32% v/v to the end-use dilution (1/200) commercial Sevin®. The retention was increased from 39.2 ± 4% for the commercial formulation to 55.4 ± 7% and 59 ± 8% when Agrimax™ 4 was added at the rate of 0.13%, and 0.32% v/v, respectively.

Greenhouse evaluations. Agrimax™ 3 was evaluated with Bravo™ 500. Aqueous suspensions of Bravo® 500 were prepared at 50 ppm and 10 ppm a.i. Agrimax™ 3 was added to each fungicide at 0.25% v/v. The treatments were sprayed to run off on four week old tomato plants. Check plants were sprayed with water only. After drying, separate samples of 4 replicate plants were exposed to 0, 1, 5 and 10 cm of simulated rainfall. The plants were then inoculated with propagules of *Phytophthora infestants* and incubated. Each plant was evaluated by estimating disease control based on a scale where plants not exhibiting lesions were given a rating of 100% control and the check plants were rated as 0% control. The Agrimax™ 3 showed increased control of late blight on tomatoes from 30% to 60%. Comparative enhancement was more pronounced when the dose of Bravo® 500 active was reduced to 10 ppm.

Field tests. These showed efficacy enhancement by Agrimax™ 3 at 0.25% by volume in a tank mix with commercial Paraquat® and Roundup®, with a doubling of efficacy against Bahia grass and broad leaf weeds, with an extended period of control to 21 days, by the addition of Agrimax™ 3 at 0.25%.

Agrimax™ 3 shows biological enhancement of Roundup®. It is clear that both the rate and ultimate % control were enhanced considerably by the addition of Agrimax™ 3 (0.25% with Roundup® at 1200 g a.i./hectare). When Roundup® was used alone, the maximum effect at 21 days after application were 50% control of Bahia grass and broad leaf weeds. Addition of Agrimax™ 3 enhanced the control as early as 7 days after application (50% control versus 10-25% by commercial Roundup®). Further, at the peak effect, 21 days after application, 100% control was obtained when Agrimax™ 3 was added versus 50% control with commercial Roundup alone.

Interpretations. Agrimax™ 3 and 5, in their concentrated form, are believed to be in a state wherein the system consists of reverse micelles with hydrophobic components as the continuous phase, with the polymer oriented in the core in their coiled state with hydrophobic groups outside. During dilution with water, this first state would go through to a second state in which the reverse micelles would open up, going through a lamellar phase in which the surfactants would orient in a head-to-head and tail-to-tail configuration. The polymer molecules open up to an uncoiled state with its minimum energy conformation. On high dilution, state 2 would further transform to a third state in which the lamellar structure would reorient to form micelles with water as the continuous phase. The polymer would assume a coiled conformation with hydrophilic groups preferably pointing outside.

The above changes can be monitored via viscosity and conductance as a function of dilution. One should see the system going through a maximum region of viscosity corresponding to the lamellar phase. The lamellar region should also show increased conductance in spite of the viscosity being high. Conversely, in a true solution viscosity is inversely proportional to conductance. Thus, a corresponding maximum in conductance and viscosity are consistent with a lamellar structure. The maxima are pronounced for Agrimax™ 3 at about 40% added water.

The hypothesized oil-out micelle initial state for Agrimax™ 3 and 5 would explain their capacity to solubilize high concentrations of certain hydrophobic actives. The film forming capacity of the polymers, with the active contained under the film, is a possible mechanism for enhanced biological activity and rainfastness. Work continues to understand mode of action via cuticular penetration, diffusion and plant translocation.

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