

# Adjuvant Stability Tests with Phosphorus Acid Formulations

PPC report for Stefan Gous-Scion



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**Report for Stefan Gous, Scion**

**26 June 2015**

**Adjuvant Stability Tests with Phosphorus Acid Formulations**

This study was undertaken to test the stability of different classes of adjuvants with the phosphorus acid formulations, Agri-fos® 600 and Foschek™ over 24 hours.

**Methods**

Phosphorus acid solutions of both Agri-fos® 600 (600 g/L phosphorus acid, Key Industries) and Foschek™ (400 g/L phosphorous acid, Zelam) were made up at varying use rates (6-24 kg/ha phosphorus acid in 100 L/ha of water) and tested with various concentrations of adjuvants (Tables 1 & 2).

The adjuvants investigated were:

- 1) Actiwett®, a linear alcohol ethoxylate (Etec Crop Solutions)
- 2) LI-700®, a lecithin based, non ionic penetrating surfactant (Etec Crop Solutions)
- 3) LI-1000™, lecithin plus methyl esters of fatty acids & alcohol ethoxylate (Etec Crop Solutions)
- 4) Hasten™ spray oil, a blend of esterified vegetable oil and non-ionic surfactants (Victorian Chemicals)
- 5) Du-Wett®, an organosilicone-blend superspreader containing siloxane polyalkeneoxide copolymers (Etec Crop Solutions).

Solutions were made up in 20 mL glass vials, with a total mix of 14 mL in each vial so as to accurately assess the solutions stability. They were visually monitored from initial mixing (thoroughly for the first 2 hours after mixing) through to 24 hours post-mix.

Droplets of the solutions were also applied onto cabbage (var. Matador) leaves as 5 x 1 µL droplets at: initial mixing, 1 hour and 24 hours after mixing. Photographs of the droplets were taken to visually assess their spreading properties and to indicate if breakdown of the adjuvants was occurring. All tests were carried out at 20°C.

The phosphorus acid formulations were also compared using the physical data from safety data sheet information and with other products found in the marketplace.

**Results and Discussion**

General assessments combining both the visual observations of the solutions and the droplet spreading data from time of initial mixing to 24 hours are collated in Tables 1 and 2. For more detailed information on the results of each assessment see appendices 1 (tabulated stability results) and 2 (photos).

**Stability**

The low rate of Agri-fos 600 (6 kg phosphorus acid) was stable over 24 hours after mixing, with all adjuvants tested (Table 1). Good spreading was observed, especially with the Actiwett adjuvant

(Appendix 2). However, as the rate of phosphorus acid increased the adjuvant solutions became unstable. The Agrifos 600 solutions containing high rates of phosphorus acid (24 kg/ha) broke down all adjuvants tested. At this rate, all treatments formed a viscous clear precipitate near the surface of the solutions within 1 hour of mixing (Appendix 1, Table 5). This result was confirmed by the lack of droplet spreading on the cabbage leaves, confirming that the surfactants were degraded by the Agri- fos 600.

**Table 1: Stability of Agri-fos 600 solutions using both visual monitoring and droplet spreading on cabbage leaves over 24 hours.**

Adjuvant concentration	Concentration of phosphorus acid (kg/ha) in Agri-fos solutions		
	6	12	24
Actiwett 0.1%	stable	some instability	broken down
Actiwett 0.2%	stable	some instability	broken down
LI-700 0.5%	maybe some instability	some instability	broken down
LI-1000 0.125%	stable	some instability	broken down
LI-1000 0.25%	stable	some instability	broken down
Hasten 0.25%	stable	stable	broken down

The Foschek formulation was generally quite stable with all adjuvants tested over 24 hours after mixing (Table 2). Only after 24 hours with the highest rate of phosphorus acid (24 kg/ha) were some clear viscous precipitates observed near the surface of the solutions containing Du-Wett and LI-1000 adjuvants, indicating adjuvant breakdown (Table 2 and Appendix 1-Table 8). However, this did not seem to affect the droplet spreading greatly in either of these treatments at 24 hours (Appendix 2). Foschek already contains surfactants in its formulation (Zelam 2012) and it was observed that as the Foschek rates increased so did the droplet spreading. Generally the addition of adjuvants to Foschek improved the droplet spreading on cabbage; the best of these adjuvants was Du-Wett, and then Actiwett (both at 0.2%).

**Table 2: Stability of Foschek solutions using both visual monitoring and droplet spreading on cabbage leaves over 24 hours.**

Adjuvant concentration	Concentration of phosphorus acid kg/ha in Foschek solutions		
	6	12	24
Foschek alone	stable	stable	stable
Actiwett 0.1%	stable	stable	stable
Actiwett 0.2%	stable	stable	stable
LI-700 0.5%	stable	stable	stable
LI-1000 0.125%	stable	stable	some instability after 24 hours
LI-1000 0.25%	stable	stable	some instability after 24 hours
Hasten 0.25%	stable	stable	stable
Du-Wett 0.2%	stable	stable	some instability after 24 hours

The degradation of adjuvants tested may be due to a chemical reaction with the a.i., particularly when high rates are used. However, the results indicate that a likely cause is due to the (undisclosed) proprietary formulants used in the Agri-fos 600 formulation. These have a greater antagonistic effect on the on adjuvants, degrading them over a shorter duration and at lower phosphorus acid rates than seen with Foschek. Alternatively, the formulants in Foschek protect the tank mix adjuvants more effectively, from chemical interactions with the phosphorus acid.

#### Comparison of technical specifications and physical properties of phosphorus acid products

There are technical and physical differences between the two phosphorus acid formulations Agri-fos 600 and Foschek. The major difference is the amount of a.i. in each formulation, with Agri-fos 600 containing a third more phosphorus acid than Foschek (600 g/L vs 400 g/L phosphorus acid).

Foschek is a green coloured liquid, it has an adjuvant smell upon opening and foams readily. It contains <70% proprietary surfactants (Zelam, 2012) and results in droplets with good spreading ability (at high rates) when applied to cabbage leaves (see Appendix 2). In comparison, Agri-fos 600 is a clear liquid with a neutral odour, undisclosed amounts of surfactant(s) included in the formulation (Key Industries 2012), it does not foam and spreads poorly on plant surfaces (Horgan & Gaskin, 2012).

Overseas, the use of Pentra Bark® adjuvant (a combination of alkylphenol ethoxylate, polysiloxane polyether copolymer, propylene glycol; Quest Products 2007) is recommended for use with the US formulation of Agri-fos® (400 g/L phosphorus acid), in treating sudden oak disease in California. Pentra Bark is an organosilicone class of adjuvant and presumably is stable with this formulation of Agri-fos (even when used at high, >6 kg/ha phosphorus acid, rates). Investigating the safety data sheets of all these products, the US formulation of Agri-fos has similar physical properties to that of Foschek (pH 5.5, density 1.35; Agrichem 2012) while the Agri-fos 600 formulation greatly differs in terms of its pH, density (pH 7.5-8, density 1.55-1.6) and a.i. concentration (Key Industries 2012).

Another phosphorous acid formulation in the New Zealand market, Phosgard™ (400 g/L phosphorus acid, Grochem) also has similar physical properties to Foschek and could be investigated for its compatibility with the adjuvants tested.

## Conclusions

- Adjuvants tested at 6 kg/ha phosphorus acid were stable (or mostly stable) with both formulations of phosphorus acid.
- High rates of Agri-fos 600 (>6 kg/ha phosphorus acid) caused degradation of all adjuvants tested and this occurred very quickly, in less than 15 minutes.
- The Foschek formulation of phosphorus acid was used at higher rates (up to 24 kg/ha) without adjuvant degradation occurring.

## Recommendation

Foschek phosphorus acid formulation should be investigated in uptake studies. Foschek was (mostly) compatible with all adjuvants tested, even when used at high rates, and may thus provide improved uptake of phosphorus acid into *P. radiata* foliage relative to Agri-fos.

## References

Agrichem Manufacturing Industries 2012. Safety Data Sheet Agri-fos® Systemic Fungicide. Issued April 2012. 4pp.

Horgan D. B and R. E. Gaskin 2012. Optimising uptake of phosphorous acid into *Pinus radiata* foliage. Report to Scion. 12 pp.

Key Industries 2012. Safety Data Sheet Agri-fos® 600. Issued 27 July 2012. 4pp.

Quest Products 2007. Safety Data Sheet Pentra-Bark® Surfactant. Issued 2 April 2007. 3pp.

Zelam 2012. Safety Data Sheet Foschek™. Issued 17 April 2012. 2p.

## APPENDIX 1: Stability of adjuvants with phosphorus acid solutions over 24 hours (Tables 3-8)

**Table 3. Visual stability of adjuvants in solution with 6 kg/ha phosphorous acid (Agri-fos 600) at 0-24 h after mixing.**

<b>Treatment</b>	<b>0</b>	<b>15 min</b>	<b>30 min</b>	<b>60 min</b>	<b>2 h</b>	<b>24 h</b>
Agri-fos 600 (6 kg/ha phos. acid) + Actiwett 0.1%	clear	ditto	ditto	ditto	ditto	clear solution, no ppt, <b>Appears Stable</b>
Agri-fos 600 (6 kg/ha phos. acid) + Actiwett 0.2%	clear	ditto	ditto	ditto	ditto	clear, no ppt, <b>Appears Stable</b>
Agri-fos 600 (6 kg/ha phos. acid) + LI-700 0.5%	opaque, tan	ditto	ditto	slight adjuvant separation	ditto	tan solution, adjuvant on top, when shaken, goes mostly into solution
Agri-fos 600 (6 kg/ha phos. acid) + LI-1000 0.125%	opaque	ditto	ditto	clearing slightly, adjuvant separation	ditto	clear solution, adjuvant on top, opaque when shaken <b>Appears Stable</b>
Agri-fos 600 (6 kg/ha phos. acid) + LI-1000 0.25%	opaque	ditto	ditto	clearing slightly, adjuvant separation	ditto	clear solution, adjuvant on top, opaque when shaken <b>Appears Stable</b>
Agri-fos 600 (6 kg/ha phos. acid) + Hasten 0.25%	opaque	ditto	ditto	ditto	clearing, slight adjuvant separation	clear solution, adjuvant on top, opaque when shaken <b>Appears Stable</b>

**Table 4. Visual stability of adjuvants in solution with 12 kg/ha phosphorous acid (Agri-fos 600) at 0-24 h after mixing.**

<b>Treatment</b>	<b>0</b>	<b>15 min</b>	<b>30 min</b>	<b>60 min</b>	<b>2 h</b>	<b>24 h</b>
Agri-fos 600 (12 kg/ha phos. acid) + Actiwett 0.1%	clear	ditto	slight white ppt	ditto	ditto	white ppt, clear solution
Agri-fos 600 (12 kg/ha phos. acid) + Actiwett 0.2%	clear	ditto	slight white ppt	ditto	ditto	white ppt, clear solution
Agri-fos 600 (12 kg/ha phos. acid) + LI-700 0.5%	opaque, tan	ditto	slight adjuvant separation	ditto	ditto	tan solution, adjuvant on top, when shaken, goes mostly into solution
Agri-fos 600 (12 kg/ha phos. acid) + LI-1000 0.125%	opaque	ditto	ditto	clearing slightly, adjuvant separation	ditto	clear solution, adjuvant on top, opaque when shaken but some adjuvant left around meniscus
Agri-fos 600 (12 kg/ha phos. acid) + LI-1000 0.25%	opaque	ditto	ditto	clearing slightly, adjuvant separation	ditto	clear solution, adjuvant on top, opaque when shaken but some adjuvant left around meniscus
Agri-fos 600 (12 kg/ha phos. acid) + Hasten 0.25%	opaque	ditto	ditto	clearing, slight adjuvant separation	ditto	clear solution, adjuvant on top, opaque when shaken <b>Appears Stable</b>

**Table 5. Visual stability of adjuvants in solution with 24 kg/ha phosphorous acid (Agri-fos 600) at 0-24 h after mixing**

<b>Treatment</b>	<b>0</b>	<b>15 min</b>	<b>30 min</b>	<b>60 min</b>	<b>2 h</b>	<b>24 h</b>
Agri-fos 600 (24 kg/ha phos. acid) + Actiwett 0.1%	clear ppt	ditto	ditto	ditto	ditto	clear ppt, clear solution
Agri-fos 600 (24 kg/ha phos. acid) + Actiwett 0.2%	clear ppt	ditto	ditto	ditto	ditto	clear ppt, clear solution
Agri-fos 600 (24 kg/ha phos. acid) + LI-700 0.5%	opaque, tan	slight adjuvant separation	ditto	ditto	ditto	slight clear ppt formed, clear solution, brown surfactant on top, looks to have split
Agri-fos 600 (24 kg/ha phos. acid) + LI-1000 0.125%	opaque	clearing, slight adjuvant separation	ditto	slight clear ppt formed	ditto	clear ppt, clear solution, slightly opaque when shaken
Agri-fos 600 (24 kg/ha phos. acid) + LI-1000 0.25%	opaque	clearing, slight adjuvant separation	ditto	slight clear ppt formed	ditto	clear ppt, clear solution, slightly opaque when shaken
Agri-fos 600 (24 kg/ha phos. acid) + Hasten 0.25%	opaque	clearing, slight adjuvant separation	ditto	slight clear ppt formed	ditto	clear ppt, clear solution, slightly opaque when shaken

**Table 6. Visual stability of adjuvants in solution with 6 kg/ha phosphorous acid (Foschek) at 0-24 h after mixing**

<b>Treatment</b>	<b>0</b>	<b>15 min</b>	<b>30 min</b>	<b>60 min</b>	<b>2 h</b>	<b>24 h</b>
Foschek (6 kg/ha phos. acid)	clear	ditto	ditto	ditto	ditto	clear, light blue/green solution <b>Stable</b>
Foschek (6 kg/ha phos. acid) + Actiwett 0.1%	clear	ditto	ditto	ditto	ditto	clear, light blue/green solution <b>Appears Stable</b>
Foschek (6 kg/ha phos. acid) + Actiwett 0.2%	clear	ditto	ditto	ditto	ditto	clear, light blue/green solution <b>Appears Stable</b>
Foschek (6 kg/ha phos. acid) + LI-700 0.5%	opaque	ditto	ditto	ditto	ditto	opaque light tan/green solution <b>Appears Stable</b>
Foschek (6 kg/ha phos. acid) + LI-1000 0.125%	opaque	ditto	ditto	ditto	ditto	slightly opaque blue solution <b>Appears Stable</b>
Foschek (6 kg/ha phos. acid) + LI-1000 0.25%	opaque	ditto	ditto	ditto	ditto	slightly opaque blue solution <b>Appears Stable</b>
Foschek (6 kg/ha phos. acid) + Hasten 0.25%	opaque	ditto	ditto	ditto	ditto	slightly opaque blue solution <b>Appears Stable</b>
Foschek (6 kg/ha phos. acid) + Du-Wett 0.2%	opaque	ditto	ditto	ditto	ditto	slightly opaque blue/green solution <b>Appears Stable</b>

**Table 7. Visual stability of adjuvants in solution with 12 kg/ha phosphorous acid (Foschek) at 0-24 h after mixing**

<b>Treatment</b>	<b>0</b>	<b>15 min</b>	<b>30 min</b>	<b>60 min</b>	<b>2 h</b>	<b>24 h</b>
Foschek (12 kg/ha phos. acid)	clear	ditto	ditto	ditto	ditto	clear, light blue/green solution <b>Stable</b>
Foschek (12 kg/ha phos. acid) + Actiwett 0.1%	clear	ditto	ditto	ditto	ditto	clear, light blue/green solution <b>Appears Stable</b>
Foschek (12 kg/ha phos. acid) + Actiwett 0.2%	clear	ditto	ditto	ditto	ditto	clear, light blue/green solution <b>Appears Stable</b>
Foschek (12 kg/ha phos. acid) + LI-700 0.5%	opaque	ditto	ditto	ditto	ditto	opaque tan/green solution <b>Appears Stable</b>
Foschek (12 kg/ha phos. acid) + LI-1000 0.125%	opaque	ditto	ditto	ditto	ditto	slightly opaque blue solution <b>Appears Stable</b>
Foschek (12 kg/ha phos. acid) + LI-1000 0.25%	opaque	ditto	ditto	ditto	ditto	slightly opaque blue solution <b>Appears Stable</b>
Foschek (12 kg/ha phos. acid) + Hasten 0.25%	opaque	ditto	ditto	ditto	ditto	slightly opaque blue solution <b>Appears Stable</b>
Foschek (12 kg/ha phos. acid) + Du-Wett 0.2%	opaque	ditto	ditto	ditto	ditto	slightly opaque blue/green solution <b>Appears Stable</b>

**Table 8. Visual stability of adjuvants in solution with 24 kg/ha phosphorous acid (Foschek) at 0-24 hours after mixing**

<b>Treatment</b>	<b>0</b>	<b>15 min</b>	<b>30 min</b>	<b>60 min</b>	<b>2 h</b>	<b>24 h</b>
Foschek (24 kg/ha phos. acid)	clear	ditto	ditto	ditto	ditto	clear, light blue/green solution <b>Stable</b>
Foschek (24 kg/ha phos. acid) + Actiwett 0.1%	clear	ditto	ditto	ditto	ditto	clear, light blue/green solution <b>Appears Stable</b>
Foschek (24 kg/ha phos. acid) + Actiwett 0.2%	clear	ditto	ditto	ditto	ditto	clear, light blue/green solution <b>Appears Stable</b>
Foschek (24 kg/ha phos. acid) + LI-700 0.5%	slightly opaque	ditto	ditto	ditto	ditto	slightly opaque tan/green solution <b>Appears Stable</b>
Foschek (24 kg/ha phos. acid) + LI-1000 0.125%	slightly opaque	ditto	ditto	ditto	ditto	very slight clear ppt, light blue/green solution
Foschek (24 kg/ha phos. acid) + LI-1000 0.25%	slightly opaque	ditto	ditto	ditto	ditto	very slight clear ppt, light blue/green solution
Foschek (24 kg/ha phos. acid) + Hasten 0.25%	opaque	ditto	ditto	ditto	ditto	slightly opaque blue solution <b>Appears Stable</b>
Foschek (24 kg/ha phos. acid) + Du-Wett 0.2%	slightly opaque	ditto	ditto	ditto	ditto	slight clear ppt present around the meniscus, blue/green solution



**APPENDIX 2: Droplet spreading properties of adjuvants in phosphorus acid solutions over time when applied to cabbage leaves**

**6 kg/ha phos. acid, Agri-fos 600**

**0 hrs**



**1 hr**



**24 hrs**



**+ 0.1% Actiwett**



**+ 0.2% Actiwett**



6 kg/ha phos. acid, Agri-fos 600

0 hrs



1 hr



24 hrs



+ 0.5% Li-700



+ 0.25% Hasten



6 kg/ha phos. acid, Agri-fos 600

0 hrs



1 hr



24 hrs



+ 0.125% Li-1000



+ 0.25% Li-1000



12 kg/ha phos. acid, Agri-fos 600

0 hrs



1 hr



24 hrs



+ 0.1% Actiwett



+ 0.2% Actiwett



12 kg/ha phos. acid, Agri-fos 600

0 hrs



1 hr



24 hrs



+ 0.5% Li-700



+ 0.25% Hasten



12 kg/ha phos. acid, Agri-fos 600

0 hrs



+ 0.125% Li-1000

1 hr



24 hrs



+ 0.25% Li-1000





24 kg/ha phos. acid, Agri-fos 600

0 hrs



1 hr



24 hrs



+ 0.1% Actiwett



+ 0.2% Actiwett



24 kg/ha phos. acid, Agri-fos 600

0 hrs



1 hr



24 hrs



+ 0.5% Li-700



+ 0.25% Hasten



24 kg/ha phos. acid, Agri-fos 600

0 hrs



1 hr



24 hrs



+ 0.125% Li-1000



+ 0.25% Li-1000



6 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



Foschek only



+ 0.2% Du-Wett



6 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



+ 0.1% Actiwett



+ 0.2% Actiwett



6 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



+ 0.5% Li-700



+ 0.25% Hasten





6 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



+ 0.125% Li-1000



+ 0.25% Li-1000



12 kg/ha phos. acid, Foschek  
0 hrs



1 hr



24 hrs



Foschek only



+ 0.2% Du-Wett



12 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



+ 0.1% Actiwett



+ 0.2% Actiwett



12 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



+ 0.5% Li-700



+ 0.25% Hasten



12 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



+ 0.125% Li-1000



+ 0.25% Li-1000



24 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



Foschek only



+ 0.2% Du-Wett



24 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



+ 0.1% Actiwett



+ 0.2% Actiwett



24 kg/ha phos. acid, Foschek  
0 hrs



1 hr



24 hrs



+ 0.5% Li-700



+ 0.25% Hasten



24 kg/ha phos. acid, Foschek

0 hrs



1 hr



24 hrs



+ 0.125% Li-1000



+ 0.25% Li-1000