## ADJUVANTS OILS, SURFACTANTS AND OTHER ADDITIVES FOR FARM CHEMICALS USED IN GRAIN PRODUCTION



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This report can be downloaded from the GRDC's website. Go to: https://grdc.com.au/AdjuvantsBooklet and copies are also available from GroundCover Direct on Freephone 1800 11 0044 (Quote Order Code GRDC210).





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## FOREWORD

Spray adjuvants are used within formulations and in tank mixes to improve the efficiency and effectiveness of agricultural chemical application. The Grains Research and Development Corporation (GRDC) has developed this publication to equip consultants, agronomists and growers with a greater understanding of adjuvant attributes and their properties.

Annual worldwide spray adjuvant sales are currently estimated to be worth more than \$1.5 billion. In Australia alone, more than 400 branded products are currently registered for use as spray adjuvants, surfactants or wetting agents and these products have more than 30 different "active ingredients" providing different functions for enhanced agricultural chemical or nutrient efficacy.

The publication is divided into three main sections a) the major adjuvant groups b) adjuvants for the main groups and sub groups of agricultural chemicals and c) question and answers. In addition to these, the booklet provides tips and tactics on spraying, the effect of adjuvants on spray droplet quality, how to manage water quality and a quick guide to which agricultural chemicals need adjuvants and which do not.

By providing more information on adjuvants, and under what circumstances they are best used, will improve agricultural chemical application and efficacy leading to enduring profitability for the Australian grain grower

The GRDC would like to acknowledge the expert assistance of agricultural consultants and industry experts Mark Congreve Independent Consultants Australia Network, Andrew Somerville, Graham Betts, Bill Gordon, Vicki Green and Protech Consulting in compiling this publication or previous editions.



Steve Jefferies Managing Director Grains Research and Development Corporation www.grdc.com.au

## **1. BACKGROUND**

Annual worldwide spray adjuvant sales are currently estimated to be worth more than \$1.5 billion. A significant part of this estimate represents the value of adjuvants built into pesticide formulations. But many millions of dollars are also spent on stand-alone products retailed as adjuvants, surfactants and wetting agents.

In Australia, more than 400 branded products are registered for use as spray adjuvants (208), surfactants (72) or wetting agents (165) (APVMA Pubcris). These include about 30 different 'active ingredients', some of which are combined in individual products to provide different functions.

While there are many adjuvants available for use with farm chemicals, a much smaller number of products are recommended by the manufacturers or distributors of farm chemicals.

This can cause some confusion particularly where there are a large number of branded products providing identical – or near to identical – active constituents.

Adjuvants are used in a variety of farm chemicals, including herbicides, fungicides, insecticides and growth regulator products.

In recent years, the major growth area in the use of adjuvants has been with herbicides. There has been an economic incentive to optimise effectiveness of the more expensive herbicides, under a wide range of conditions.

#### What are adjuvants?

An adjuvant is any material that, when added to a spray solution, enhances or modifies the action of a pesticide. Many adjuvants are included (or 'factory-fitted') in the formulations of various products to facilitate the stability and functionality of the active ingredient(s) in a spray solution.

In addition to adjuvants in-built into formulations, users are keenly interested in those adjuvants that can be added to the spray solution on-farm to help get the most out of their dollars spent on spraying programs.

#### **Classification of adjuvants**

The most useful classification of adjuvants is by chemical group with the adjuvants divided into the broad categories of surfactants, oils, acidifiers and buffers, fertiliser adjuvants and 'others'.

An alternative classification can be made on the basis of spray adjuvant function. This can be confusing since some adjuvants may have more than one function (for example, spreader and buffer).

#### **GLOSSARY OF TERMS**

To help understand the terms used in describing the types and functions of spray adjuvants, a glossary of terms and definitions, based on standard terminology relating to agricultural tank mix adjuvants developed by the American Society for Testing of Materials, is provided on page 42.

#### How do adjuvants work?

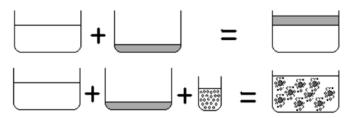
Adjuvants work at three levels in the application of farm chemicals.

- 1. Modifying how chemical components or products interact in the spray tank
- 2. Modifying how a product interacts with the target surface
- 3. Modifying how a product moves into the target

## 1. Modifying how chemical components or products interact in the spray tank

The two most common properties influenced by adjuvant products when included in the spray mix are emulsification/ compatibility and the subsequent effect on droplet size.

Emulsifiers/compatibility agents are usually surfactants that enable active and inert materials to co-exist in a stable solution. These products are normally factory fitted into the formulation and are particularly important in formulations where the active ingredient is insoluble in water.



#### **Figure 1a:** How oil and water solutions can be made to mix using emulsifying adjuvants

Without an emulsifier, the addition of an oil-based formulation to water in the spray tank will see the formulation settle to the top of the spray tank (top image). When an emulsifier is included (bottom image) the pesticide formulation can remain suspended in the water.

Matching the correct choice of adjuvant to the pesticide can be challenging as it can be influenced by many factors, i.e. the chemical properties of both the pesticide and the target



Best suited to		esters, Group A, C & G herbicide, many fungicides and contact insecticides				glyphosate, paraquat, glufosinate, salt/amine & soluble liquid formulations												
Adjuvant type		Spra (2-5% si	y oils Irfactan	t)				op oil co 5-20% s					_I-700® rfactants	5				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
HLB value	Lipophilic (oil soluble)				Water dispersible Hy			Hydro	Hydrophilic (water soluble)									
		anti-	foam				wet	ter/spre	ader				d	etergen	ts			
	water in oil emulsifier					oil in water emulsifier												
Appearance in water	no			stable m ispersio		translucent to clear dis		persion										
				poor dis	persion			stable r	nilky dis	persion					clear s	olution		

Figure 1b: Hydrophilic-lipophilic balance and adjuvant type (Adapted from: Wikipedia, 2019; Hess, 1999).

surface and the role that the adjuvant is required to undertake (e.g. mixing in water, spreading on the leaf, penetrating the cuticle). For these reasons, it is common to find that a blend of adjuvants is often built into pesticide formulations.

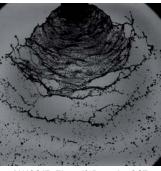
Hydrophilic-lipophilic balance (HLB) is a measure of the relative contribution of the hydrophilic and lipophilic component of the adjuvant.. It can have a distinct influence on the performance of adjuvants with different pesticides. Both the type and size of the hydrophilic (water soluble) and lipophilic (oil soluble) components of a surfactant may influence droplet spread, droplet bounce, evaporation and pesticide absorption. The pesticide needs to be able to be solubilised in the adjuvant so generally it is more effective to match a lipophilic adjuvant with a lipophilic pesticide and vice versa (Figure 1b).

It is common for more than one pesticide to be tank mixed at application. Different pesticides may have different adjuvant requirements, meaning a compromise is often required. For this reason, adjuvants such as crop oil concentrates (COCs), (particularly those with a high surfactant load) are often popular for many herbicides that are likely to be tank mixed.

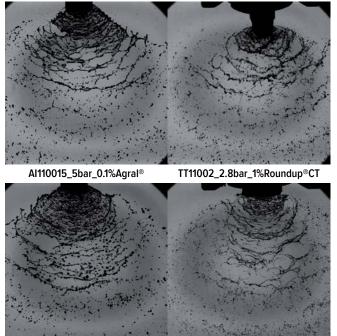
There are a number of adjuvants which, when combined with pesticides, alter the surface tension properties of the solution. For example, adjuvants which increase the surface tension of solutions will tend to reduce the atomisation of sprays which alters the spectrum of spray droplets formed.

A coarser spray can be achieved by increasing the viscosity of the spray mix. This results in an upward shift of the droplet spectrum to reduce driftable 'fines'. Commercially available drift retardant products often include long chain polymers or gums that increase the viscosity of the spray mix. Some studies have found that some of these polymers may be subjected to shearing (breaking droplets into smaller droplets) following multiple passes through a sprayer pump, as would occur in a normal bypass, or the hydraulic mixing in common agricultural sprayers (Zhu et al., 1997). Gums are not sheared as easily as the long chain polymers. Some types of polymers (e.g. polyethylene oxide) are sheared in fewer passes through a pump than other types of polymers (e.g. polyacrylamides).

Although drift retardants are generally effective in reducing the number of driftable fines, in most cases users are better off using the appropriate nozzle, operating the sprayer at low pressure to obtain the desired droplet size and spraying when the environmental conditions are right. Figure 1c: Using high speed photography, various droplet formation patterns depending on nozzle type, spray pressure and spray mixture are illustrated.



AI110015\_5bar\_1%Roundup®CT



Al110015\_5bar\_Water

XR11002\_2.8bar\_1%Roundup®CT

Some adjuvants by their nature increase atomisation, e.g. surfactants, which reduce surface tension, increase the tendency of droplets to break up in the process of atomisation.

This property varies with different surfactants and concentrations so that there may be an apparent variation in the tendency of a spray solution to 'driff' under a given set of conditions, depending on the surfactant type and the concentration present in the spray solution.



**Figure 1d:** The images above show how two adjuvants with the same nozzle set-up and environmental conditions can result in completely different characteristics of the spray solution. Droplet size is changed causing drift and less product reaching its target. The top image is a spray solution with the surfactant LI-700<sup>®</sup> at 250 ml/100L while the bottom image is Chem-wett 1000 at 200 ml/100L.

A GRDC study (Figure 1e) conducted by the Centre for Pesticide Application and Safety (CPAS) at its wind tunnel facility at University of Queensland, Gatton, evaluated the droplet spectrum produced by a range of adjuvant and fallow herbicide combinations across three different nozzle types (all 110-02 (yellow) nozzle size, operating at 4 bar pressure):

- Turbo TeeJet<sup>®</sup> (TT) fine end of medium
- Air Induction Extended Range TeeJet<sup>®</sup> (AIXR) coarse end of medium
- Turbo TeeJet<sup>®</sup> Induction (TTI) ultra coarse.

As can be seen from the graph below, the selection of nozzle type has the greatest impact on the percentage of driftable fine droplets produced.

The addition of ammonium sulphate (AMS and Kombo® type products) typically had minimal effect on droplet size, where it was not mixed with an additional surfactant.

Adjuvants that contain significant levels of surfactant (BS1000®, LI-700®, Liberate®, Hasten®) all increased the volume of spray present as droplets <150 micron with the finest of the nozzles tested (Turbo Teejet). As the nozzles became coarser, this effect diminished.

The guar gum-based adjuvant Dead Sure® consistently provided a reduction in volume of droplets <150 micron across all the various nozzles and herbicides tested.

A wide range of herbicide combinations were also tested in this study (data for all herbicides and combinations grouped in the graph below). Generally, solvent-based herbicides (such as emulsifiable concentrates) or herbicides with in-built surfactant tended to slightly increase the volume of droplets <150 micron, however, the effect of herbicides was typically third in order of importance behind selection of nozzle type and adjuvant, respectively.



**Figure 1e:** Effect of adjuvant type on the volume of 'driftable fine' droplets (volume mean diameter (VMD) less than 150 micron) produced by three different nozzles.



Adjuvants may also modify the evaporation of spray droplets as they are released. As droplets containing surfactants or oils are released into the atmosphere, evaporation of the spray droplet continues until the surface tension of the droplet 'skin' prevents further evaporation.

Medium and large size droplets are more likely to reach the target under the influence of gravity, compared to droplets that are initially very small (or evaporate to a small size), which makes them more vulnerable to the influence of air movement.

## 2. Modifying how a product interacts with the target surface

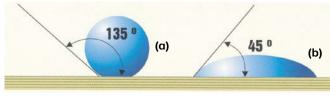
The most common way of modifying the interaction of spray droplets and the target surface is by altering the surface tension of the droplet.

Droplets with a high surface tension will be more likely to bounce off target surfaces while those with a lower surface tension will tend to collapse and spread on contact and be retained on the leaf surface (Figure 1c).

Surfactants lower the surface tension of the spray droplet by moving to the surface where they form a 'micelle' layer.

Surface tension decreases until the surfactant concentration reaches a point known as the Critical Micelle Concentration (CMC). At this point, addition of more surfactant does not decrease surface tension further, though enhancement of pesticides (particularly herbicides) may continue with additional surfactant (Hess, 1999).

Reducing surface tension to as low a level as possible may not always be beneficial. Droplets may run off the target surface as droplets coalesce (due to very low surface tension or where a high volume application causes droplets to run together).



**Figure 1f:** Contact angle of droplet on a difficult-to-wet leaf surface without (a) and with (b) surfactants (Source: Devine et al., 1993 adapted by Hall, 1999).

As well as affecting droplet spread, surface tension can influence the formation of spray droplets, rate of evaporation and retention on sprayed surfaces.

Dynamic surface tension is the measure of how quickly surfactants migrate to the surface of the droplet at the point of impact. Unlike static surface tension (measured after a spray droplet has been deposited on a surface for a period of time), dynamic surface tension can decrease at concentrations greater than the CMC.

Recent evidence has shown that the effects of adjuvants on post-emergent herbicide performance are due more to dynamic surface tension than static surface tension. Retention of sprayed solutions on a target is usually at an optimum when surfactant levels are well above the CMC, particularly if the surface is hairy.

Decreasing the surface tension of a solution will result in a decrease in the size of spray droplets produced by a nozzle. Many non-ionic surfactants may do this. While this may

increase potential for spray drift, retention on leaf surfaces (particularly on 'difficult to hit' targets such as narrow, upright leaves of small grasses) is improved. These smaller droplets have less velocity, there is increased movement through the canopy and lower impact energy when contacting the leaf surface.

Decreased surface tension and increased spreading does not always equate to improved herbicide performance. The opposite trend (improved weed control with reduced droplet spreading) may occur in some situations. For example, hydrophilic herbicides (e.g. glyphosate) that are slow to penetrate the leaf can benefit from a larger droplet that doesn't spread and is slower to evaporate, by allowing increased time in a semi-liquid state on the leaf surface.

## 3. Modifying how a product moves into the target

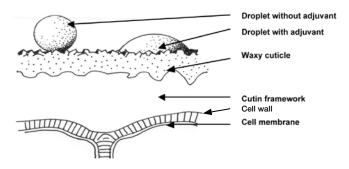
Uptake of pesticides across a target surface is complex, and often involves more than one pathway.

For example, with a hydrophilic herbicide such as glyphosate, some movement of the active ingredient is due to a simple process of diffusion across the leaf cuticle (Figure 1g). Diffusion appears to be improved when the spray deposit is retained in a semi-liquid state by increasing the period of uptake, so adjuvants that delay the drying of spray deposits often improve control.

Lipophilic pesticides (for example many contact insecticides, Group F & G herbicides and herbicides formulated as esters) will find it easier/faster to enter through the waxy cuticle via diffusion.

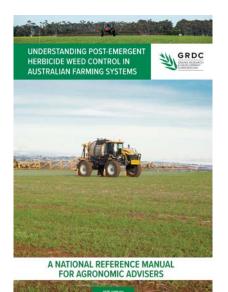
Certain adjuvants (in particular oils and 'penetrating' surfactants) may also increase the uptake of pesticides across a plant or insect cuticle, by physically disrupting or dissolving the waxy surface. For enhanced pesticide entry via this pathway the pesticide needs to be soluble in the adjuvant. Correspondingly, a lipophilic adjuvant will work best with a lipophilic pesticide and a hydrophilic adjuvant will assist a hydrophilic pesticide.

This cuticle-disrupting property of some adjuvants may heighten the injury to the target crop. Faster entry, or greater total volume of pesticide entering the leaf, may result in higher quantities of pesticide requiring metabolism by the crop. If this process cannot occur fast enough, crop damage may be seen in some situations. In addition, the disruption to cell membranes associated with certain crop oils when exposed to heat or ultra-violet light on leaf surfaces, can result in phytotoxicity to some crops, even in the absence of any pesticide.



**Figure 1g:** Cross section of a leaf surface with spray droplet on surface. The waxy surface acts as a barrier to water droplet penetration (Source: Rochecouste, 2004). Once inside the leaf, uptake across the cell wall and plasmalemma (cell membrane) may occur via diffusion, ion transfer or be facilitated by an electrochemical transport system, depending upon the pesticide involved. Ammonium-based spray adjuvants have been shown to assist in ion transfer when used with some weak acid herbicides e.g. glyphosate.

For more information on herbicide entry through the plant cuticle refer to the GRDC publication 'Understanding post-emergent herbicide weed control in Australian farming systems' chapter 4.3.2. https://grdc.com.au/understanding-postemergent-herbicide-weed-control



#### TO SUM UP

- Adjuvants are products added to a spray solution that enhance or modify the action of a pesticide.
- Adjuvants can be classified according to their function or chemical grouping.
- Adjuvants can have a variety of functions such as spreading, wetting and/or modifying leaf surface, droplet formation or droplet behaviour.
- While there are many types of spray adjuvants, they can be conveniently categorised as surfactants, oils, acidifiers/ buffers and fertiliser adjuvants.

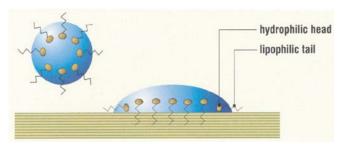


## 2. MAJOR ADJUVANT GROUPS

#### **Surfactants**

Surfactants make up by far the largest group of spray adjuvants.

The primary role of surfactants is to act at the surface of a droplet to reduce surface tension. This assists dispersal of many pesticides in the spray tank, while also aiding the droplet to spread over the leaf surface. Surfactants are made up of two functional parts – a hydrophilic polar group or 'water loving' structure (head) attached to a lipophilic long chain hydrocarbon group or 'fat loving' component (tail) (Figure 2a).



## **Figure 2a:** Interaction of hydrophilic and lipophilic parts of a surfactant to reduce surface tension and spread the droplet (Source: Hall et al, 1999).

Surfactants are often classified on the basis of the electrical charge carried by the hydrophilic group (Table 2a). Surfactants may be anionic (negative charge), cationic (positive charge), amphoteric (carry both positive and negative charge) or non-ionic (no charge).

The lipophilic tail is derived from natural or petrochemical feedstocks. Lipophilic groups include:

- Alkylbenzenes
- Linear alkyls
- Branched alkyls
- Linear alkyls, e.g. derived from plant and animal fats
- Alkylphenyls, e.g. Nonylphenol
- Polyoxypropylenes
- Polysiloxanes

Non-ionic (having no net electrical charge) surfactants (NIS) are widely used in agricultural applications, either added to the pesticide formulation, supplied as a stand-alone adjuvant or included in an adjuvant blend. Traditionally, these non-ionic agricultural surfactants have a non-ionic head with a

## Table 2a: Surfactant types according to electrical charge on thehydrophilic group.

Surfactant type	Charge on hydrophilic group	Hydrophilic group examples		
		Sulphate		
		Sulphonate		
		Ether sulphate		
Anionic	Negative	Ether phosphate		
		examples Sulphate Sulphonate Ether sulphate		
		examples Sulphate Sulphonate Ether sulphate Ether sulphate Ether sulfosuccinate Ether carboxylate Carboxylate Carboxylate Primary ammonium Secondary ammonium Secondary ammonium Guaternary ammonium Amine oxide Betaine Amino carboxylate Polyoxyethylene (ethoxylate) Acetylenic Monoethanolamine		
		Carboxylate		
		Primary ammonium		
Cationic	Positive	Secondary ammonium		
Cationic		Tertiary ammonium		
		Quaternary ammonium		
		Amine oxide		
Amphoteric	Positive and negative Betaine			
		Amino carboxylate		
		Polyoxyethylene (ethoxylate)		
		Acetylenic		
Non ionic	No charge	Monoethanolamine		
		Diethanolamine		
		Polyglucoside		

hydrocarbon base comprising the lipophilic component of fatty alcohols, alkylphenols, fatty amine or sorbitan esters attached to an ethylene oxide (EO) or ethylene + propylene (PO) chain of varying length. Increasing the number of EO or PO units increases the polarity (hydrophilicity) of the surfactant.

In recent years, surfactants based on a trisiloxane-backbone (organosilicones) have been developed with agricultural applications.

Organo-silicones	Fatty amine (tallow amine)	Alcohol alkoxylates	Alkylaryl	ethoxylates	di-1-p menthene	Soyal phospholipids
	ethoxylates	,, <b>,</b> , <b></b>	Nonyl phenol	Octyl phenol		
e.g. Freeway Maxx® Organo-silicone plus	e.g. Deluge® Gly Wetter plus	Many of the wetter 1000 type products e.g. BS1000® Surewet 1000	Wetter 600 type products e.g. Agral Shirwet® 600	Wetter 1040 or TX type products e.g. Trilogy Wetter 1040 TX	Spreader/stickers e.g. Nu-Film Tru-Film 905	e.g. Liberate®
alcohol ethoxylate e.g. Bond		Many combination	formulations.			
Organo-silicone plus latex e.g. Designer®		alcohol ethoxylate ormulations exist.				

A number of dry formulations utilise anionic surfactants (net negative electrical charge) built into the formulation to assist in dispersibility when added to the spray tank. Another group occasionally represented as agricultural surfactants are cationic surfactants (with a net positive electrical charge).

#### Oils

Historically, oils were used for insect and weed control as well as anti-microbial agents before the development of synthetic pesticides.

As adjuvants, oils are used to:

- Enhance the penetration of systemic pesticides into plants and insects;
- Reduce evaporation of spray droplets after they leave the sprayer;
- Extend the active life of certain herbicides, insecticides and fungicides on plant surfaces, by reducing the speed of droplet drying.

Oils can also be used as carriers/bulking agents for ultra-low volume (ULV) spray applications in certain situations.

Oils can be categorised on the basis of their origin (i.e. vegetable or petroleum base) and their formulation.

Petroleum based oils can be subdivided into those with low (1-3%), medium (5%) and high (>15%) levels of added surfactant/emulsifier (often referred to as petroleum spray oils, petroleum oil/surfactant blends and petroleum spray oil concentrates respectively).

The type and amount of surfactant used in a petroleum spray oil product can have a major effect on performance.

Petroleum oils also vary in base oil composition, paraffin content and the amount of unsulfonatable residue. These properties influence viscosity and phytotoxicity.

Some petroleum spray oils, e.g. Canopy®, contain additional UV stabilisers which provide a degree of UV protection for pesticides.

Vegetable oils are usually emulsified and may be categorised according to their crop origin. In addition, plant-based oils

## Table 2c: Examples of oil-based adjuvants and oil-surfactant blends commonly used in agricultural applications by the amount and type of emulsifier added.

Petroleum spray oils (1–3% emulsifier)	Petroleum spray oil plus surfactant (5% emulsifier) Petroleum spray oil concentr (>15% emulsifier)			Multipurpose petroleum oil adjuvants providing additional functions	
e.g. Ad-Here® (970 mL/L) Empower® (861 g/L) AntiEvap® (859 g/L)	e.g. D-C-Tron® Cotton (827 g/L) Cropshield® (838 g/L)	e.g. In-bound® (653 g/L + 217 g/L non-ionic fatty acid ethoxylates) Uptake® (582 g/L + 240 g/L alkoxylated alcohol NIS)		e.g. Hot-Up® (190 g/L mineral oil + 340 g/L NIS + 140 g/L AMS) Dead Sure® (358 g/L paraffinic oil + 47 g/L guar gum)	
Vegetable oils (emulsified)	Vegetable oils (esterified and emulsified)		Multipurpose vegetable oil adjuvants providing additional functions		
e.g. Codacide® (860 g/L) Nexus® (865 g/L) X-Seed® (85 5g/L)	, , ,	rs of canola oil fatty acids) nethyl esters of canola oil + 196 g/L NIS) methyl esters of canola oil + 196 g/L NIS)		/L vegetable oil ester + 334 g/L NIS blend + 300 g/L AMS) vegetable oil ester + 105 g/L NIS + 572 g/L AMS)	

NIS = non-ionic surfactant (unspecified)

AMS = ammonium sulphate

Oil adjuvants grouped in the various categories in the Table may not be necessarily identical in their composition or performance. Differences in qualities of the feedstock used (e.g. hydrocarbon chain length); types of emulsifiers used and combination with other minor ingredients for example, can give rise to differences in performance. Where pesticide labels specify a particular brand of adjuvant for use, the specified product should be used.



may be esterified as well as emulsified (see Table 2c) to give a much lower viscosity than the parent oil. As with petroleum oils, the types of emulsifiers used can affect the properties of the formulated product and its phytotoxicity.

Herbicides vary significantly in their response to various oil adjuvants depending on their relative solubility in water or oil. For example, glyphosate is hydrophilic and water soluble and the addition of crop oils sometimes reduces its effectiveness. In contrast, herbicides such as atrazine or clethodim and most ester formulations are more lipophilic and are generally enhanced by the addition of oil adjuvants.

#### **Acidifiers and buffers**

Acidifiers are usually based on proprietary mixes of acids (primarily propionic but also phosphoric, carboxylic and others) or phosphate ester derivatives (Table 2d). Many acidifying adjuvants are formulated with a non-ionic surfactant blend or plant-derived lipids (e.g. LI-700®).

Certain weak acid herbicides applied in the salt form, especially those with a dissociation constant (pKa) in the range of 3-5, may benefit from being applied in an acidic spray solution i.e. spray tank pH in the range of 4.5-6. For example, the absorption and translocation of 2,4-D was greatly increased in some experimental studies (Ashton & Crafts, 1973) when applied at a pH below 6. This principle has led to many users wanting to acidify the spray tank before adding many weak acid herbicides. However, acidification of the spray solution may result from adding certain of these acidic pesticides to the water, without any acidifying adjuvant. For example, gluphosate is an effective acidifier in its own right when added to water of neutral or alkaline pH and can normally reduce pH to around 5 (the optimal pH for glyphosate activity) without the addition of any acidifying adjuvant, depending on the dilution rate.

Alkaline hydrolysis (degradation under alkaline conditions) of certain insecticides, particularly organophosphates, is also sometimes the basis for the use of acidifiers and buffers with these products. But much of the data showing extremely short half-lives for active ingredients under alkaline conditions is for the technical material rather than for the formulated product. Buffering capacity built into formulated products may significantly reduce the effects of alkaline hydrolysis.

Currently, no Australian insecticide product labels specify the use of buffering or acidifying agents to ensure product efficacy, although recommendations for buffering spray solution to pH 7 or below are found on US product labels for dimethoate and carbaryl.

Acidification of spray solutions may not always be helpful to the activity of pesticides. Some products, for example some 2,4-D amine formulations, may 'salt out' or 'gel' at low pH. Accelerated degradation of many sulfonylurea herbicides will also commence as the spray solution reduces below pH 5.

#### Fertiliser adjuvants

Some ammonium-based fertiliser products have been investigated as adjuvants with various herbicides. Rates are generally 2% volume to volume (v/v) for liquid products or 1-2% weight to volume (w/v) for solid formulations.

Ammonium sulphate (AMS) has been shown to enhance effectiveness of certain salt-based formulations of herbicides (e.g. glyphosate, 2,4-D, MCPA, picloram, bentazone, imazethapyr), however, only limited products such as glyphosate, imazethapyr and pyrasulfotole (when formulated as Precept®) have recommendations for the addition of ammonium sulphate on manufacturers' product labels. But ammonium sulphate is often used with clethodim, imidazolinone and phenoxy herbicides more generally.

Liquid ammonium sulphate formulations are typically 417 to 425 g/L formulations whereas spray-grade formulations are 980g/kg formulations, milled to a particle size that enhances quick dissolving in the spray tank. Prilled ammonium sulphate is unsuitable as an adjuvant with glyphosate products because the aluminium used in the prilling process is antagonistic to glyphosate.

In recent years, combination adjuvants that contain AMS in a liquid form along with a surfactant or oil + surfactant blends are becoming more popular as multi-purpose adjuvants.

Conditioning the spray water with AMS can enhance performance by:

- i) reducing antagonism between certain products (e.g. when mixing atrazine and glyphosate)
- reducing the formation of insoluble salts of some herbicides (see "Conditioning 'hard' water withAMS" on the following page), and
- iii) free ammonium may assist weak acid herbicides cross the plasma membrane surrounding the cell (via a process known as ion-trapping).

Table 2d: Examples of acidifiers or buffers commonly used in agricultural applications.					
Propionic acid-based adjuvants	e.g. LI-700® (350 g/L propionic acid + 350 g/L soyal phospholipids) Buff-It (383 g/L propionic acid + 545 g/L non-ionic fatty acid ethoxylates + 192 g/L triethanolamine)				
Phosphoric acid-based adjuvants	e.g. Primabuff® (375.1 g/L phosphoric acid derivatives + 266.2 g/L nonoxinol-9) Quatrabuff (375.1 g/L phosphoric acid derivatives + 266.2 g/L nonyl phenol ethoxylate)				
Carboxylic acid-based adjuvants	e.g. Ag-buffer 550 (350 g/l aliphatic carboxylic acid + 200 g/L NIS) Kombo 950 (150 g/kg carboxylic acid + 800 g/kg AMS)				
Phosphate ester-based adjuvants	e.g. Agri-Buffa® (430 g/L phosphate esters of polyalkylene oxide derivative + 100 g/L polyalkylene oxide derived of synthetic alcohols) Triad (290 g/L phosphate esters of alcohol ethoxylate + 550 g/L alcohol ethoxylate)				

NIS = non-ionic surfactant (unspecified) AMS = ammonium sulphate US research has shown that reduction in efficacy of clethodim by sodium bicarbonate in spray solution is effectively overcome by the addition of a crop oil concentrate plus ammonium sulphate (McMullan, 1994).

## Conditioning 'hard' water with AMS

The most common use of AMS is to pre-condition 'hard' water to make it more suitable for herbicide use, in particular with glyphosate formulations. By definition, hard water contains elevated levels of cations. Often this is due to high levels of calcium carbonate (CaCo<sub>3</sub>), however, other positively charged ions such as sodium, manganese, aluminum or iron may also contribute to 'hardness' of the water.

Glyphosate acid is the form of glyphosate that is herbicidally active. However, glyphosate acid has very low solubility and poor ability to penetrate the waxy cuticle, hence is formulated as a salt (e.g. isoproplyamine (IPA), potassium (K) or monoammonium salts are common). Glyphosate, in these salt forms, will have increased solubility and leaf penetration as the spray droplet is drying.

Using elevated levels of calcium carbonate as an example of hard water, if one of these glyphosate salt formulations is added to a water source high in calcium, some of the glyphosate molecules will disassociate from their formulated salt and preferentially recombine with the calcium cation to form a glyphosate-calcium salt. Solubility of glyphosate-calcium salt is very low, reducing solubility in the spray tank, with entry through the leaf cuticle also severely reduced.

Adding AMS to the spray water **before** adding the glyphosate formulation results in calcium sulphate forming, removing available calcium from the spray water. This then results in less glyphosate dissociation after the glyphosate is added.

It is extremely important that spray-grade AMS is fully dissolved, and that the AMS has had time to precondition the water, before adding glyphosate to the spray tank. Using a liquid formulation of AMS can speed the tank filling operation, as the liquid AMS does not need to be dissolved first.

Other fertiliser products claimed to be of benefit as adjuvants with glyphosate include urea and certain liquid fertiliser preparations which also contain nitrogen in the ammonium form, e.g. urea ammonium nitrate (UAN). UAN will not assist in reducing antagonism or alleviating the effects of hard water.

The addition of an organic acid such as food grade citric acid may also be effective in removing hard water ions from the water source. Some organic acids are effective because the conjugate base (negative portion) of the acid binds to and removes positively charged cations (such as calcium) from solution.

#### TO SUM UP

- Surfactants and oils make up the two largest groups of spray adjuvants.
- Surfactants (surface acting agents) are made up of 'water loving' (hydrophilic) and 'fat loving' (lipophilic) parts.
- Surfactants may be cationic (having a positive charge), anionic (having a negative charge) or non-ionic (having no charge). Surfactants recommended as spray adjuvants are most commonly non-ionic.
- The most common surfactant types include alcohol alkoxylates e.g. BS1000®; alkylaryl ethoxylates e.g. Agral®, Wetter 1040 TX; fatty amine ethoxylates e.g. Deluge®, organosilicones e.g. Freeway or soyal phospholipids e.g. Liberate®.
- There are a range of other common adjuvant blends e.g. LI-700<sup>®</sup> (soyal phospholipids + propionic acid), Hot-up (ammonium sulphate + non-ionic surfactant + oil), and specialised sticking and 'filming' agents e.g. Bond, Nu-Film<sup>®</sup>-17.
- Spray oils are petroleum (mineral) or vegetable (plant) based.
- Many oils (particularly petroleum based) have pesticidal properties in their own right.
- Petroleum based oils vary according to the base oil composition and the amount and type of surfactant/ emulsifier used in the formulation.
- Vegetable oils vary according to the plant oil source, method and degree of processing.
- Esterified vegetable oils are reacted with short chain alcohols to produce final products of lower viscosity than the parent oil.
- Most oil adjuvants contain emulsifiers/surfactants to allow them to mix readily in water.
- Acidifiers and buffers reduce the pH of alkaline solutions to minimise the effects of alkaline hydrolysis that occurs with certain pesticides.
- Formulated acidifying and buffering agents usually contain a surfactant component to provide a dual purpose role.
- Acidification of spray solutions may not always be helpful to the activity of pesticides. Some products may 'salt out' or 'gel out' or degrade at low pH.
- Fertiliser adjuvants are most widely used with the herbicide glyphosate and are usually based on ammonium sulphate.
   Some other products that contain free ammonium ions may also have a beneficial effect.



## **3. ADJUVANTS FOR HERBICIDES**

#### ACCase inhibitors (Group A)

Group A herbicides include products belonging to the aryloxyphenoxypropionate (or 'fops'), cyclohexanediones (or 'dims') or phenylpyrazole (or 'dens') class of herbicides that inhibit the enzyme, acetyl CoA carboxylase (ACCase). ACCase is important for cell wall production in new growth.

Group A herbicides are typically used for post-emergent grass weed control in a range of cereals and broadleaf crops.

#### Use of adjuvants with Group A

The use of adjuvants with these products is extensive. For example, the original Group A herbicide Hoegrass® (diclofop-methyl) was shown to benefit from a range of surfactants (principally non-ionic surfactants such as the ethoxylated alkyl alcohol types, including BS1000®) and petroleum spray oils (such as D-C-Tron® Cotton and D-C-Trate®). As more Group A herbicides were developed, crop oil concentrates (including those with a much higher proportion of surfactants than the original petroleum spray oils) and esterified vegetable oil adjuvants became more widely recommended with Group A herbicides.

There are four broad groups of adjuvants that may be recommended for use with Group A herbicides:

- i) Petroleum spray oils, e.g. D-C-Tron® Cotton, Cropshield
- Petroleum spray oil concentrates, e.g. Uptake<sup>®</sup>, In-bound<sup>®</sup> (these 'oils' incorporate a relatively high loading of surfactant, in addition to a refined petroleum oil)
- iii) Non ionic surfactants (NIS) generally either linear alcohol ethoxylates or alkoxylated alcohol types
- iv) Esterified vegetable oils that include a surfactant to facilitate emulsification with aqueous solutions and enhance uptake e.g. Hasten®, Kwickin®

Of these groups, the use of petroleum spray oil concentrates or the esterified vegetable oils are the most common with Group A herbicides.

The addition of a NIS in the adjuvant formulation can increase the coverage and droplet retention on the leaf. This can be significant when targeting small grass weeds which are difficult to contact, especially where larger droplets are being used for drift management. Oil concentrate adjuvants with higher NIS load may also be beneficial where these Group A herbicides are tank mixed with more hydrophilic tank mix partners.

Clethodim, pinoxaden and most 'fop' herbicides are relatively lipophilic in their applied form and will therefore be best matched with a lipophilic (oil-based) adjuvant which will increase leaf penetration. Due to the rapid leaf entry of these herbicides in combination with oil-based adjuvants, rainfast periods are usually relatively short.

The addition of oil-based adjuvants used with these Group A herbicides may also increase the speed of leaf entry of some broadleaf herbicide tank-mixed partners, which can result in additional crop injury in certain broadleaf crops. For example, clethodim labels recommend not to mix with the broadleaf herbicides diflufenican (e.g. Brodal®), bentazone (e.g. Basagran®) or acifluorfen (e.g. Blazer®), while the haloxyfop label recommends not to mix with broadleaf herbicides in winter crops but does support mixtures with bentazone or acifluorfen in summer broadleaf crops, provided that a NIS is used in place of an oil-based adjuvant.

The 'dim' herbicides butroxydim (e.g. Factor®) and tralkoxydim (e.g. Achieve®) are less lipophilic, and therefore likely to respond better to an adjuvant with a more balanced hydrophilic-lipophilic (HLB) value. Spray oil concentrates with a higher NIS load are generally preferred. The use of Supercharge® Elite is the preferred adjuvant for tralkoxydim and butroxydim herbicides.

Results from other studies with different adjuvant types sometimes indicate little difference in herbicide performance at label rates on susceptible weeds and under favourable growing conditions. Differences may become apparent when marginal application rates for the prevailing conditions are used, or conditions are sub-optimal. In these situations, there may be differences in performance of certain adjuvant types.

#### ALS inhibitors (Group B)

Group B herbicides include three main subclasses used in grain production: sulfonylureas (e.g. chlorsulfuron, metsulfuron, triasulfuron, sulfosulfuron and many others), imidazolinones (e.g. imazamox, imazapic, imazapyr, imazethapyr), and sulfonamides (e.g. florasulam, flumetsulam, metosulam, pyroxsulam).

These products control weeds by inhibiting the acetolactate synthase (ALS) enzyme, thus preventing the formation of certain plant amino acids, resulting in eventual plant death.

#### Use of adjuvants with Group B

Imidazolinone formulations may be available as either aqueous concentrates (e.g. Spinnaker®) or water-soluble granules (e.g. OnDuty®). Sulfonylureas and sulfonamides are often formulated as either dry flowable (DF), wettable granule (WG) or water dispersible granule (WDG) formulations.

For dry formulations, surfactants are generally included during formulation to aid in the binding during granule production and dispersal in the spray tank. Some sulfonylureas are subject to degradation in the spray tank under acidic conditions, i.e. pH <5. To address this, quality formulations may contain a pH buffer designed to prevent spray tank pH falling too low. Acidifying agents typically should not be used in combination with sulfonylurea herbicides due to the effect of low pH increasing acid hydrolysis. Once mixed in the spray tank, Group B herbicides should be applied as soon as possible.

Most Group B herbicides have intermediate lipophilicity and generally can enter the leaf and translocate throughout the plant without difficulty when applied under good environmental conditions. For this reason, tank mixed adjuvants designed to modify performance on the leaf surface may be less important than is the case for many other herbicides.

Non-ionic surfactants usually enhance performance by assisting with droplet capture and leaf spread and are often recommended. The most common surfactant group recommended are the alkoxylated alcohol types e.g. BS1000<sup>®</sup>.

Adjuvants that increase cuticle penetration (i.e. oils) are generally not recommended for most in-crop uses. Adjuvants that increase penetration are likely to increase the speed of leaf entry which can be associated with increased crop phytotoxicity where full selectivity is not present. Oil plus surfactant adjuvant blends are recommended for some products (e.g. Atlantis<sup>®</sup>, Crusader<sup>®</sup>, Monza<sup>®</sup>, OnDuty<sup>®</sup>), specifically for early post-emergent applications and particularly when targeting difficult to contact small grass weeds. Careful consideration should be given to the choice of adjuvant in situations where a partner herbicide may recommend an oil-based adjuvant.

Only Spinnaker® (imazethapyr) and Raptor (imazamox) identify the use of ammonium sulphate as being beneficial, particularly under adverse growing conditions. Addition of ammonium ions in the form of ammonium sulphate or a UAN (urea ammonium nitrate) solution has been shown to enhance the activity of imidazolinone herbicides, including imazethapyr, on certain species of *Ipomoea*.

#### **PSII** inhibitors (Group C)

Group C herbicides include a diverse group of products that inhibit photosynthesis at photosystem II (PSII). Group C herbicides used in broadacre grains and cotton production include:

- Triazines atrazine, cyanazine, prometryn, simazine, terbuthylazine, terbutryn;
- Triazinones metribuzin;
- Benzothiadiazinones bentazone;
- Ureas diuron, fluometuron;
- Nitriles bromoxynil.

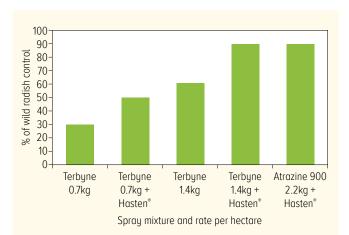
#### Use of adjuvants with Group C

**Triazines and ureas.** Most triazines and ureas are typically most effective when applied to the soil and are taken up by roots, with transportation in the xylem to the leaves where they inhibit photosynthesis. As solubility of these herbicides is generally low, they require good soil moisture for effective root uptake.

Some herbicides within these sub-groups have little postemergent activity (e.g. simazine), while others (e.g. atrazine, terbuthylazine, diuron) can also enter via the leaf and move to the chloroplasts within the cells. When applied post-emergent, there is minimal movement out of the treated leaf, so they should be treated more like a contact herbicide, ensuring good coverage and targeting small weeds. The addition of a surfactant may assist in leaf coverage and droplet retention under certain situations, especially where droplet retention or coverage is sub-optimal.

As herbicides within these sub-groups tend towards the lipophilic end of the spectrum, oil-based adjuvants are likely to result in improved leaf penetration. The addition of an oil-based adjuvant can often increase post-emergent weed control in susceptible species, although this may also increase crop injury where full crop selectivity is not present. Refer to individual directions on the label with regard to situations where the use of oil-based adjuvants can be supported.

Trials conducted in Young, NSW, in 2007 showed good responses to the addition of Hasten® (an esterified seed oil adjuvant) to the Group C herbicide Terbyne, for wild radish control in TT canola (Figure 3a).



**Figure 3a:** Effect of addition of Hasten® spray adjuvant on post emergent activity of Terbyne (terbuthylazine) on **4–8 leaf wild radish in TT canola** Source: Sipcam Pacific Australia Pty Ltd. Trials conducted Young, NSW 2007.

Physical compatibility problems may occur between some glyphosate and triazine formulations. Pre-conditioning the spray water with AMS may help to reduce incompatibility.

**Metribuzin.** The triazinone herbicide metribuzin is less lipophilic and substantially more soluble than the triazines and ureas and hence is more mobile within the plant. Foliar uptake occurs where applied post-emergent, although root uptake is the preferred method of plant entry. When used early post-emergent, herbicide overspray onto the soil is also likely to contribute to weed control via root uptake, with labelled application rates reflecting soil type interactions.

Many of the post-emergent uses on Australian metribuzin labels have marginal selectivity to the crop. As such, adjuvants that increase herbicide entry are generally not advised.

**Bentazone** has good leaf uptake when applied as a post emergent application. As with most other Group C herbicides,



any overspray reaching the soil can also enter the plant via root uptake. Bentazone is not lipophilic so typically the choice of adjuvant will be a NIS (or an adjuvant blend with a high NIS component).

**Bromoxynil.** The nitrile herbicide bromoxynil is used extensively in grain production, sometimes as a standalone herbicide but more commonly as a tank mix partner or pre-formulated with herbicides from other modes of action. Bromoxynil is somewhat different to most other Group C herbicides in that it is well absorbed through the leaf. When applied in the ester form, it will quickly enter the leaf and move to the target site within the chloroplast inside the cells.

Many labelled crops do not have complete selectivity to bromoxynil, with certain label statements recommending avoiding applications when temperature exceeds 20°C, as speed of activity will be increased and the crop will have less time to metabolise the herbicide before injury occurs. There are certain situations on the label where a NIS may be recommended.

The addition of a penetrating surfactant, such as an oil, would further increase speed of activity, and hence is generally not recommended for bromoxynil. The main exception is where bromoxynil is pre-formulated with a post-emergent Group H herbicide. Talinor® recommends the addition of Adigor® or Hasten® while Velocity® supports the addition of Hasten®, Supercharge® or Uptake®. It should be noted that both of these herbicides have a crop safener built into the formulation.

## Microtubule assembly inhibitors (Group D)

Group D herbicides disrupt the microtubule assembly in germinating seedlings.

The main herbicides from this mode of action used in grain production include the dinitroaniline (DNA) herbicides trifluralin and pendimethalin and the benzamide herbicide propyzamide.

#### Use of adjuvants with Group D

Trifluralin, pendimethalin and propyzamide are pre-emergent herbicides, with no recommendation for adjuvants.

#### PDS inhibitors (Group F)

Group F herbicides inhibit carotenoid biosynthesis at the phytoene desaturase step (PDS inhibitors), causing characteristic bleaching and yellowing of leaf tissue.

The herbicides diflufenican and picolinafen are used in grain production systems, often in mixtures with other modes of action.

#### Use of adjuvants with Group F

Diflufenican and picolinafen are lipophilic herbicides. Labels recommend **not to apply with an oil-based adjuvant** (even when tank mixing with partner herbicides that recommend an oil-based adjuvant), due to the possibility of increased levels of crop injury.

Some picolinafen labels also recommend avoiding adding any adjuvant when tank mixing with other products. If the partner product requires an adjuvant for efficacy, then the products should be applied as separate applications, ideally at least 10 days apart.

Diflufenican + MCPA formulations also recommend against adding any surfactant when mixing with metsulfuron.

#### PPO inhibitors (Group G)

Group G herbicides are inhibitors of enzyme protoporphyrinogen oxidase (PPO). Inhibition of this enzyme interferes with the chlorophyll biosynthetic pathway leading to cell membrane disruption.

Within this mode of action there are a number of herbicide sub-classes used in grain production, including:

- diphenylethers (oxyfluorfen, acifluorfen);
- n-phenylphthalimides (flumioxazin);
- phenylpyrazoles (pyraflufen);
- pyrimidindiones (butafenacil, saflufenacil); and
- triazolinones (carfentrazone).

#### Use of adjuvants with Group G

Most PPO inhibitors tend towards being lipophilic in nature, suggesting that an oil-based adjuvant will lead to increased leaf penetration. Many of these herbicides are used in fallow situations, or prior to planting, so when used in a 'non-crop' situation, an oil-based adjuvant will usually be advantageous in increasing control of weeds targeted by these herbicides. However, care needs to be taken, as many of these fallow/ non-crop applications will be in mixtures with a non-selective herbicide, particularly glyphosate. Interaction between glyphosate, oil-based adjuvants and high rates of some Group G herbicides is known to occur and can negatively impact on the performance of glyphosate, particularly on some summer germinating grass weeds.

Some products have label claims for post-emergent applications in certain crops. In these situations, the choice of adjuvant should be carefully considered in order to ensure crop acceptable crop selectivity:

**Acifluorfen** – oil-based adjuvants are not generally recommended, as increased crop damage typically occurs. Acifluorfen does have a specific recommendation for the addition of Hasten<sup>®</sup> in mungbeans only, however, the herbicide rate is reduced.

**Carfentrazone** products – where registered for in-crop application in cereals there is a label statement not to use any adjuvants, due to increased crop damage. Labels include a warning to ensure booms are also clean of any adjuvants used for previous spray applications.

**Pyraflufen** products – where registered for in-crop use, oilbased adjuvants are generally not recommended. The use of non-ionic surfactants varies by crop. Refer to the label.

#### HPPD inhibitors (Group H)

These herbicides work by inhibiting 4-hydroxyphenylpyruvate dioxygenase (HPPD) which is a critical step in plastoquinone synthesis, leading to disruption of the photosynthetic and carotenoid pathways. Without carotenoids, cells are not protected from photooxidation, and hence the typical bleaching symptoms associated with Group H herbicides are observed. Group H herbicides include the pyrazole sub-class (benzofenap and pyrasulfotole), triketones (bicyclopyrone) and isoxazoles (isoxaflutole). In Australian grain production, post-emergent Group H herbicides are currently limited to bicyclopyrone, formulated in a mixture with bromoxynil (e.g. Talinor<sup>®</sup>), and pyrasulfotole formulated in a mixture with bromoxynil (e.g. Velocity<sup>®</sup>) or with MCPA (e.g. Precept<sup>®</sup>). Isoxaflutole products (e.g. Balance<sup>®</sup>) are primarily applied as pre-emergent applications.

#### Use of adjuvants with Group H

Pyrasulfotole and bicyclopyrone are somewhat hydrophilic herbicides, suggesting they are likely to be enhanced by a non-ionic surfactant type adjuvant. However, these herbicides are formulated with lipophilic partners (bromoxynil or MCPA ester) which will also respond to an oil-based adjuvant. Therefore, an oil concentrate adjuvant with a high surfactant load is normally preferred. The recommended adjuvant for Velocity® or Precept® is Hasten®, Supercharge® or Uptake®; while the Talinor® label recommends the use of Adigor® or Hasten®.

Velocity<sup>®</sup> and Precept<sup>®</sup> provide specific recommendations when tank mixing with grass selective herbicides. The preferred adjuvant in these situations typically aligns with the recommendation for the partner product (refer to labels for details).

For Precept<sup>®</sup> (pyrasulfotole + MCPA), the use of AMS instead of a crop oil adjuvant is supported. Velocity<sup>®</sup> or Talinor<sup>®</sup>

should not be mixed with AMS, as reduced efficacy may result.

Talinor<sup>®</sup> recommends not to mix urea ammonium nitrate (UAN), as unacceptable crop injury can occur.

Non-ionic surfactants, including soyal-lipid based adjuvants in the case of Talinor<sup>®</sup>, should generally not be used due to reduced efficacy.

Isoxaflutole products are generally applied as a pre-emergent application to weed-free soil, therefore do not benefit from the addition of an adjuvant.

#### Synthetic auxins (Group I)

Group I herbicides include a wide range of products with auxin like activity, including phenoxys (2,4–D, MCPA), arylpicolinates (halauxifen), benzoic acids (dicamba) and pyridines (aminopyralid, picloram, triclopyr, fluroxypyr, clopyralid). These all act by the disruption of plant cell growth and division with accumulation in the growing points of the plant, leading to plant death.

#### Use of adjuvants with Group I

For selective in-crop applications, adjuvants are seldom recommended (and often specifically excluded in label directions) chiefly because these herbicides are reasonably efficient at entering the leaf without the need for additional adjuvants and crop selectivity often is associated with

2,4-D amine	<ul> <li>Additional surfactant is generally not recommended, except in certain situations.</li> <li>When used in conservation tillage situations:</li> <li>When mixing with glyphosate, follow adjuvant advice for the glyphosate partner.</li> <li>A soyal phospholipid acidifying adjuvant (e.g. LI-700<sup>®</sup>) can be used when tank mixing certain insecticides that are prone to alkaline hydrolysis; when faster weed brownout is required or for assistance in droplet size management.</li> <li>However, acidic spray water can be a significant contributing factor for incompatibility between certain 2,4-D amine and glyphosate formulations.</li> </ul>
MCPA amine	The addition of an acidifying adjuvant (e.g. Spraybuff <sup>®</sup> , LI-700 <sup>®</sup> ) is recommended when tank mixing certain insecticides that are prone to alkaline hydrolysis.
halauxifen	Pixxaro® (halauxifen + fluroxypyr) is compatible with Uptake®, BS1000®, Chem-wett 1000 and Spreadwet 1000. Add Uptake® when using in winter cereals. When mixing with glyphosate in fallow, follow the glyphosate adjuvant recommendations for grass weed control. Paradigm (halauxifen + florasulam) – Uptake® is the preferred adjuvant, however, BS1000® or Chem-wett 1000 may also be used. Only use BS1000® or Chem-wett 1000 if tank mixing with metsulfuron. Rexade (halauxifen + pyroxsulam) – add BS1000® or Chem-wett 1000
dicamba	For WG formulations – add a NIS when used alone or when mixing with metsulfuron. Add Uptake® or D-C-Tron® when mixing with metosulam.
aminopyralid	<ul> <li>Hotshot® (aminopyralid + fluroxypyr) is compatible with</li> <li>BS1000® or equivalent when mixed with metsulfuron</li> <li>Uptake® when mixed with clodinafop or pinoxaden</li> <li>Adigor® when mixed with pinoxaden</li> <li>Stinger® (aminopyralid + metsulfuron) – Add BS1000® or alternative when used for post-emergent weed control in winter cereals.</li> </ul>
clopyralid	For WG formulations – add a NIS when used alone or follow the adjuvant recommendation for the partner herbicide. Liquid and WG formulations are compatible with spray oils and NIS, where required for partner herbicides.
fluroxypyr	Winter cereals – when used alone in winter cereals, add Uptake <sup>®</sup> or a NIS. When mixed with clodinafop, add Uptake <sup>®</sup> . Winter fallow – when used alone add Uptake <sup>®</sup> . When mixed with metsulfuron add Uptake <sup>®</sup> or a NIS. Summer fallow – When used alone for control of pigweed, <i>Polymeria, Rhynchosia,</i> marshmallow, thornapple, <i>Sesbania,</i> perennial ground cherry, silverleaf nightshade or volunteer sunflowers add Uptake <sup>®</sup> . When mixing with glyphosate, follow the glyphosate adjuvant recommendations for grass weed control. Sorghum, maize and sweet corn – When used post-emergent with atrazine, add a NIS but do not add an oil.
picloram	<ul> <li>A range of different formulations and mixtures exist, with different use patterns. Always follow individual labels.</li> <li>In general, for broadacre uses, an adjuvant is generally not recommended.</li> <li>Where picloram products are tank mixed with metsulfuron, a NIS may be required.</li> <li>Where picloram products are tank mixed with atrazine, a crop oil or wetter may be recommended in maize, or a wetter only in sorghum.</li> <li>Acidifying adjuvants should not be used as these may lead to the precipitation of picloram at low pH.</li> </ul>
triclopyr	The addition of a crop oil is recommended for control of melons in fallow. However, do not add a crop oil when mixing with glyphosate. Follow the glyphosat label recommendations for grass weed control. Do not add a spray oil when using in sorghum, as increased crop injury is likely.



the speed of metabolism upon leaf entry. Adjuvants that significantly increase speed of leaf entry may result in the possibility of increased phytotoxicity to the crop under certain situations.

There are some herbicides and situations where the addition of spray adjuvants is specifically recommended. (see Table 3a above).

#### Lipid synthesis inhibitors (Group J)

Group J herbicides have the inhibitor of fat synthesis mode of action.

The main herbicides from this mode of action used in grain production include the thiocarbamate herbicides prosulfocarb and triallate.

#### Use of adjuvants with Group J

Prosulfocarb and triallate are typically applied as preemergent herbicides, with no recommendation for adjuvants.

#### VLCFA inhibitors (Group K)

Group K herbicides inhibit very long chain fatty acid (VLCFA) synthesis, preventing cell expansion in germinating seedlings.

Herbicides from this mode of action group used in grain production include the acetamide herbicide napropamide, chloroacetamides (dimethenamid-P, metazachlor and metolachlor/s-metolachlor) and the isoxazoline herbicide pyroxasulfone.

#### Use of adjuvants with Group K

These herbicides are typically applied as pre-emergent herbicides, with no recommendation for adjuvants.

#### PSI inhibitors (bipyridyls) (Group L)

Paraquat (e.g. Gramoxone<sup>®</sup>) and diquat (e.g. Reglone<sup>®</sup>) are bipyridyl herbicides that cause the inhibition of photosynthesis at photosystem I.

These products are quickly absorbed by leaf tissue, causing rapid destruction of plant cells adjacent to the point of contact.

#### Use of adjuvants with Group L

As the bipyridyl herbicides rely strongly on foliar contact, good coverage of leaf surfaces is essential for optimum performance. Bipyridyl herbicides are hydrophilic, and hence respond best to a hydrophilic adjuvant e.g. a non-ionic surfactant.

Diquat formulations typically require a non-ionic surfactant. Always check the product label.

Many formulated paraquat products include non-ionic surfactants to optimise droplet spread and leaf retention which is adequate for most situations. Additional NIS may be recommended under certain situations, e.g. additional non-ionic surfactant may be required when the herbicide dilution is less than 400mL product per 100L spray volume, or for some hard to wet weeds (for example the Spray.Seed® 250 label recommends additional BS1000® or Agral® when targeting silvergrass (*Vulpia* spp.).

Some high load paraquat formulations are now available that do not contain surfactants built into the formulation. These formulations require a tank mixed surfactant.

While spray oils are unlikely to assist leaf entry of bipyridyl herbicides, they may provide some advantage as an 'antievaporant' under hot, dry conditions. This use appears to be supported by trial data, particularly for control of summer broadleaf weeds such as white heliotrope.

#### Glyphosate (Group M)

Glyphosate is the only member of Group M. Glyphosate works in the plant by inhibiting the 5-enolpyruvyl shikimate-3 phosphate (EPSP) synthase enzyme in the shikimic acid pathway, preventing the production of certain amino acids essential for the production of proteins, and a range of other products required for carbon fixation and other processes.

Glyphosate is a highly polar molecule. It is hydrophilic, meaning that movement across the lipophilic leaf cuticle will be constrained. Activity relies upon getting the maximum amount of herbicide into the leaf before the spray has dried.

Under favourable conditions, some of the applied glyphosate is rapidly absorbed by plant foliage immediately after application. Initial fast entry is followed by a longer phase of slower uptake. Under fast droplet drying conditions (e.g. summer applications under hot conditions with low humidity) it is typical to apply higher rates of glyphosate. This will result in higher levels of glyphosate entering the plant in the first few hours after application.

Diffusion is the primary process for transport across the leaf cuticle. Plant cuticles vary in their permeability to glyphosate. The mode and extent of glyphosate uptake depends on several factors, including:

- Properties of leaf cuticle;
- Species;
- Plant age;
- Moisture status of the plant;
- Light;
- Temperature;
- Concentration of glyphosate;
- Adjuvants; and
- Method of application.

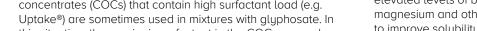
#### Use of adjuvants with glyphosate

Adjuvants that keep the glyphosate in a liquid phase on the leaf surface for longer may result in improved performance, particularly for applications under hot/low humidity conditions.

#### Effect of surfactants on absorption

At low concentrations (0.01 to 0.1% v/v), surfactants improve wetting and spreading. Leaf wetting can be very important for some species, especially those leaf surfaces which are covered in hairs or trichomes. Increased spreading across the leaf surface allows for a larger area of droplet contact and therefore more area for herbicide diffusion.

However, where droplets are spread thinly, they evaporate faster (especially for summer applications), resulting in less time for the glyphosate to diffuse across the leaf cuticle.



For this reason, glyphosate tends to work best in summer conditions when applied as a large droplet (e.g. very coarse or larger), with a high concentration of herbicide within the droplet and the correct amount of surfactant to achieve some, but not too much, droplet spread. This preferred spray set up for summer applications of glyphosate (large concentrated droplets, with not too much spreading) may also be appropriate for other fully translocated herbicides such as 2,4-D, however, is less suitable for other potential tank mix partners (i.e. herbicides from mode of action groups A, C, F, G) that require higher levels of leaf coverage for optimal results.

It is common practice to add a non-ionic surfactant or a LI-700<sup>®</sup> type product (which contains soyal phospholipid surfactant) to many glyphosate formulations. Premium, 'fully loaded' glyphosate formulations typically have adequate surfactant built into the formulation, so additional tank mixed wetters are not generally recommended in most situations with 'fully loaded' formulations. An exception may be where the glyphosate concentration is low (applied at low dose rates and/or high water volumes) and hence in-built surfactant load is also low, in which case topping up with additional adjuvant may be recommended.

At higher concentrations some surfactants may also aid foliar entru:

- The choice of in-built surfactant in the formulation can be important. Ethoxylated amine types are often considered better for glyphosate formulations. Higher levels of ethoxylation (more ethylene oxide) may provide better efficacy.
- Humectants, that keep the gluphosate in a semi-liquid state for longer on the leaf surface, may be included in some formulations.
- Organosilicon surfactants provide very low surface tension which can potentially allow for increased stomatal entry in some weed species, However, stomatal entry is generally not a primary entry pathway into the leaf of most cropping weeds. In addition, the use of organosilicon surfactants may result in thinly spread droplets which will be subject to fast evaporation under hot conditions. Further, organosilicons perform optimally at a neutral pH, whereas glyphosate in the spray mixture will create an acidic environment. For these reasons, organosilicon surfactants are only recommended in certain situations, i.e. some brushweed applications.

Several different surfactant types are included in commercial formulations. Early formulations, and many existing products, include a tallow amine ethoxylate product (tertiary amine). Subsequently, a desire to use surfactants that have lower toxicity or improved environmental profile, along with the push toward higher glyphosate loadings, has led to the introduction of alternate surfactants and blends. These include guaternary amines (used in formulations with aquatic use approvals), betaines and polyglucosides.

#### Petroleum oil adjuvants

Petroleum spray oil adjuvants are not routinely used with glyphosate. As glyphosate is hydrophilic it will not dissolve well in lipophilic surfactants such as oils. However, crop oil concentrates (COCs) that contain high surfactant load (e.g. evaporation of the spray droplet during application. The

addition of the oil may also assist a more lipophilic partner herbicide that may be tank-mixed for some broadleaf weeds.

In summer rainfall areas, responses to the addition of oils are inconsistent, sometimes leading to reduced performance (particularly on summer grasses such as awnless barnyard grass) and are often avoided where possible.

#### Vegetable oil adjuvants

Vegetable oil products (including esterified canola oils such as Hasten® and Kwickin®) are used occasionally with glyphosate.

In some trials it would appear these products are comparable in their effectiveness to surfactants, though this has not been demonstrated in a wide range of situations.

#### Buffers and acidifiers

The pH of the environment surrounding cells within a leaf is around pH 5 to 5.5. Glyphosate will be in its optimum state for entry into the cell at this pH. This often leads to many spray operators seeking to reduce the pH of the spray water by adding an acidifying adjuvant.

However, gluphosate is an acid herbicide that will significantly reduce the pH of neutral and alkaline water, in the absence of acidifying adjuvants. Unless spray water is extremely alkaline to begin with, there is normally no need to add acidifying adjuvants to the spray water. To understand if spray water requires acidification check the pH of the spray solution after adding the glyphosate (without the acidifying adjuvant). Typically, the pH of the spray solution after adding glyphosate will be in the range of 5 to 5.5, which is acceptable for glyphosate application.

Water that is highly alkaline is often 'hard water' - that is water that contains high levels of ions such as calcium, magnesium and bicarbonate. Presence of these ions ARE antagonistic to the performance of gluphosate and are usually the reason for reduced performance, not the associated high pH. Spray water containing high levels of these cations should be conditioned before glyphosate is added to the spray tank (see ammonium sulphate below).

Some acids, such as hydrochloric (pool acid), nitric and acetic acid, will reduce pH, however, they are not particularly effective in overcoming the effects of calcium, magnesium and sodium bicarbonate. These cannot be expected to assist in potential loss of performance of glyphosate where 'hard water' is used.

Many of the commercially available 'buffering agents' are based on derivatives of phosphoric acid. While phosphoric acid will reduce pH, it may also have some usefulness in assisting to sequester calcium and magnesium.

#### Ammonium sulphate

Ammonium sulphate, or more correctly diammonium sulphate, has a range of potential benefits when used as an adjuvant in combination with glyphosate.

Ammonium sulphate can maintain the performance of aluphosate in the presence of 'hard water' (water containing elevated levels of bicarbonates or cations such as calcium, magnesium and others). Glyphosate is formulated as a salt to improve solubility and leaf penetration. For example, isopropylamine (IPA) (often marketed as CT formulations), potassium (K) and monoammonium salts are commonly sold. Where the formulated glyphosate is added to 'hard water' (without preconditioning with ammonium sulphate or a similar water conditioning agent) the glyphosate salt formulation can disassociate (break apart) and recombine with the cations in the water. For example, 'hard water' often contains elevated levels of calcium carbonate. When glyphosate is added to this water, without pre-treating with ammonium sulphate, a calcium salt of glyphosate will form. The calcium salt of glyphosate has both poor solubility and poor leaf penetration abilities.

Pretreating 'hard water' with ammonium sulphate, before the glyphosate is added to the spray tank, results in formation of sulphates of these available cations, rendering them unavailable. When glyphosate is then subsequently added to the tank, it remains as the formulated salt, maintaining its solubility and leaf penetration properties.

In softer water (relatively free of antagonistic cations), the addition of ammonium sulphate may also enhance uptake and control on a number of annual grasses (but not ryegrass or barnyard grass), some broadleaf weeds (e.g. climbing buckwheat) and perennials such as couch and nutgrass. The mechanism for this effect is unclear, though it has been suggested that ammonium sulphate modifies the permeability of the leaf cuticle and cell membranes facilitating more rapid and complete uptake of glyphosate. Additionally, free ammonium present in the apoplast (intercellular spaces) can assist with a process known as ion trapping which helps weak acid herbicides to enter the cells.

Ammonium sulphate is specifically recommended as a 'compatibility agent' where glyphosate is combined with triazine herbicides, in particular atrazine. The addition of ammonium sulphate does not completely restore performance, particularly on perennial grasses, broadleaf weeds and some annual grasses (including barnyard grass and milk thistle).

Combinations of certain glyphosate formulations and amine salts of 2,4-D may result in physical incompatibility, causing blocked spray systems. Incompatibility problems are likely to be exacerbated where a combination of the following occur:

- Low volume of spray water, concentrating the herbicides;
- Unmatched salts of glyphosate and 2,4-D amine (the potassium (K) salt of glyphosate and the dimethylamine (DMA) salt of 2,4-D can be particularly problematic);
- Cold water;
- Hard water;
- pH below 5.

Fully dissolved ammonium sulphate can assist in reducing compatibility issues by addressing 'hard water', although should undissolved ammonium sulphate come into contact with glyphosate and 2,4-D amine mixtures, severe antagonism can result. Always ensure AMS is fully dissolved before adding herbicide.

#### Others

Urea ammonium nitrate (UAN) – As UAN does not contain a sulphate component it is not able to be used as a replacement for ammonium sulphate to address 'hard water' caused by high levels of cations. UAN can provide a source of ammonium which may assist with glyphosate cellular entry.

- Foliar fertilisers Several proprietary foliar fertilisers have been marketed as useful adjuvants for combination with glyphosate. Often these have an ammonium component. Claimed improvements in performance, while possible, have not been extensively investigated in all instances. Foliar fertilisers that provide available cations (e.g. calcium, magnesium, sodium, iron) are likely to be antagonistic, with effects similar to using 'hard water'.
- Drift control agents are designed to reduce droplet breakup on atomisation and therefore reduce the number of 'driftable' fines produced during application (relative to glyphosate alone or with a non-ionic surfactant). The specialist drift reduction adjuvant Dead Sure<sup>®</sup> may result in a significant reduction in driftable fine droplets with certain nozzle types.

#### **Glufosinate (Group N)**

The phosphinic acid herbicide glufosinate inhibits glutamine synthetase. Glufosinate is a non-selective, hydrophilic herbicide that provides broad-spectrum, contact activity, being particularly strong on a range of broadleaf weeds.

Being hydrophilic, glufosinate is slow to penetrate the waxy cuticle. Application conditions that result in slower droplet evaporation, i.e. warm (but not hot) conditions with high relative humidity, will allow for higher levels of herbicide entry into the leaf and will result in best control.

Glufosinate is a contact herbicide with rapid speed of activity and minimal translocation once inside the leaf. Excellent leaf coverage is critical for high levels of weed control.

#### Use of adjuvants with Group N

Commercially available glufosinate formulations normally contain surfactant. In most situations, no additional adjuvants are recommended. However, some product labels advise that benefit may be obtained when a wetting agent is added for the control of hard-to-wet plants.

#### Flamprop-m-methyl (Group Z)

Group Z herbicides, under the Australian mode of action classification system, are reserved for those herbicides with unknown or diverse sites of herbicidal activity.

Flamprop-m-methyl is the primary Group Z herbicide used in grain production.

#### Use of adjuvants with Group Z

Being applied as an ester, flamprop is somewhat lipophilic and would be expected to respond to oil-based adjuvants.

Labels recommend not to add any additional wetting agent when applied at earlier in-crop application timing targeting vegetative wild oats (3 leaf to Z30 growth stages) at the higher application rates. When used as a spray topping application (up to Z40 crop growth stage and Z30 to Z40 wild oat growth stage) a lower herbicide rate is recommended, with the addition of Uptake<sup>®</sup> spraying oil.

## **4. ADJUVANTS FOR INSECTICIDES**

Many insecticides do not require additional adjuvant. When adjuvants are important for improved efficacy, they are often built into the formulation.

Adding aggressive penetrating adjuvants, or some spraying oils, may be potentially damaging to some crops. Petroleumbased spray oils in particular may be phytotoxic to plants due to the effects of heat and UV radiation causing cell wall damage. Their use is not recommended unless crop safety is assured. Always follow label advice to minimise the chance of phytotoxicity.

When applying to difficult-to-wet surfaces (for example brassicas such as canola) some insecticides recommend a non-ionic surfactant (NIS) or a similar wetting agent. The use of non-ionic surfactants is more common with wettable granule (WG), wettable powder (WP) or dry flowable (DF) formulations.

In specific situations, a crop oil concentrate with a high surfactant load (e.g. Uptake® type products) may be recommended. In these situations, the crop oil concentrate provides leaf wetting similar to a NIS, with the oil component providing increased cuticle penetration for lipophilic insecticides.

Some emulsifiable concentrate (EC) formulations can be applied as ultra-low volume (ULV) applications at less than 5L/ha, using an oil as the spray carrier. High boiling point petroleum spray oils or vegetable oils used as carriers generally improve target retention of these low rate ULV sprays. Oils used for ULV application do not need emulsifiers in the formulation, in contrast to those spray oils used as adjuvants where a water carrier is used.

It is important to realise that some spray adjuvants, particularly the phytobland oils and derivatives, have insecticidal activity in their own right. Insect control in this instance relies on direct control of the insect pest, so spray coverage is critical with these products. Pests controlled by petroleum spray oils include scale insects, two-spotted mites, *Helicoverpa spp.*, thrips, mirids and aphids in both horticultural and field crop applications.

#### Carbamates (Group 1A)

Carbamate insecticides used in grains include methomyl, thiodicarb and pirimicarb. Group 1 insecticides are effective either by ingestion or by direct contact. After entering the insect pest, cholinesterase is inhibited leading to rapid disruption of the nervous system.

#### Use of adjuvants with Group 1A

These insecticides are often used in crops with leaf surfaces that are difficult to wet, and hence a non-ionic surfactant is

typically recommended when applied using water as the carrier. The pirimicarb label recommends the addition of a spray oil under low humidity situations in some crops.

#### Organophosphates (Group 1B)

Organophosphate (OP) insecticides are also cholinesterase inhibitors (similar mode of action to carbamates). As such, they have rapid speed of activity following either ingestion or direct contract.

Organophosphates are a large family of insecticides. The main OP insecticides used in grains include chlorpyrifos, dimethoate and omethoate. Chlorpyrifos-methyl and fenitrothion are also used for protection of grain in storage.

#### Use of adjuvants with Group 1B

Broadacre use patterns for organophosphates typically do not require the addition of an adjuvant.

Some organophosphates are known to undergo hydrolysis under alkaline conditions. For example, dimethoate in the technical active ingredient form is subject to rapid hydrolysis at a pH of 9, though it is likely that the formulated product is not hydrolysed to the same degree as the technical material.

On US product labels the addition of a buffering or acidifying agent is recommended, however this is not suggested on product labels for dimethoate products marketed in Australia. However, the use of acidifying agents such as LI-700® has been widely adopted with dimethoate.

#### Phenylpyrazoles (Group 2B)

Group 2 insecticides are GABA-gated chlorine channel blockers, which act on the nervous system of susceptible insects. Group 2A was assigned to the organochlorine insecticides, which are no longer registered for any crop uses.

Group 2B includes the insecticide fipronil. In broadacre crops, fipronil is used as a foliar application in sorghum, cotton or as a seed treatment.

#### Use of adjuvants with Group 2B

No specific adjuvants are recommended for suspension concentrate formulations used for foliar application in sorghum and cotton.



#### Synthetic pyrethroids (Group 3A)

Synthetic pyrethroids are contact and ingestion toxins. They bind to the sodium channel protein in the nervous system, resulting in continuous nerve stimulation and rapid insect death.

Many pyrethroids are registered in Australia. The main insecticides used in grains include alpha-cypermethrin, bifenthrin, cypermethrin (mostly used as a seed treatment to protect planting seed), gamma-cyhalothrin and lambdacyhalothrin.

#### Use of adjuvants with Group 3A

Most product labels do not recommend specific adjuvants for use in broadacre crops when using water as a carrier, however, some labels do recommend the addition of a nonionic surfactant for difficult to wet surfaces, such as brassica vegetables.

Trojan<sup>®</sup> (gamma-cyhalothrin), lambda-cyhalothrin products and some emulsifiable concentrate (EC) formulations of alphacypermethrin can also be applied as ultra-low volume (ULV) applications diluted in a spray oil.

#### **Neonicotinoids (Group 4A)**

Neonicotinoids are systemic insecticides with contact and ingestion activity, acting on the central nervous system of susceptible insects by causing irreversible blockage of acetylcholine receptors.

Imidacloprid or thiamethoxam-based seed treatments are an important mode of action used to prevent damage from many establishment pests in Australian grain crops. Foliar applications are made in cotton.

#### Use of adjuvants with Group 4A

Adjuvants are not required when applied as seed treatments in Australian grain crops.

Where used as a foliar application in cotton, an organosilicon surfactant is generally recommended.

#### Sulfoximines (Group 4C)

Sulfoxaflor is the only currently available insecticide from the novel sulfoximine class of insecticides, which acts through the interaction with the nicotinic acetycholine receptors in insects. Sulfoxaflor has translaminar, contact and ingestion activity to give knockdown control of several piercing and sucking pests in a range of crops.

#### Use of adjuvants with Group 4C

An adjuvant that enhances leaf wetting is recommended for application of Transform<sup>®</sup> (sulfoxaflor) for control of pests in canola or when applied under less than ideal application conditions. Suitable products recommended are Uptake<sup>®</sup>, Agral<sup>®</sup>, Spreadwet 1000 or Chem-wett 1000.

#### Spinosyns (Group 5)

Group 5 insecticides have a unique mode of action that affects nicotinic acetylcholine receptors on target insects, although at a different location to Group 4 insecticides. Spinosyns are particularly effective on a range of caterpillar pests along with some beetle and thrips species. Spinetoram (Success<sup>®</sup> Neo) is used for control of certain caterpillar pests in canola, pulses and cotton, while spinosad (Conserve<sup>®</sup>) is used as a grain protectant.

#### Use of adjuvants with Group 5

The addition of Uptake® or a non-ionic wetting agent is recommended with Success® Neo for difficult to wet crops such as canola.

#### **Avermectins (Group 6)**

Avermectins act as chloride channel activators on susceptible insects, in particular a range of mite pests and selected caterpillars. They are quickly absorbed, with translaminar movement across the leaf, although they are not systemic within the plant.

Emamectin is effective against diamondback moth in canola, selected caterpillar pests in pulses and cotton and suppression of green mirid in cotton. Check labels, as individual claims vary by product. Abamectin is primarily used as a miticide, although some labels claim a registration for *Helicoverpa* control in cotton or soybeans.

#### Use of adjuvants with Group 6

A non-ionic wetter is normally recommended for emamectin formulations. No adjuvants are typically recommended for use with abamectin products in cotton or broadacre grains.

#### Pymetrozine (Group 9B)

Pymetrozine is a pyridine-azomethine insecticide with activity against sucking pests such as aphids and whitefly. Soon after ingestion, aphids withdraw their stylet and stop feeding, however, resulting death via starvation may take many days. Pymetrozine has good translaminar and xylem mobility, with useful levels of systemic translocation.

Registered uses in broadacre crops are limited to aphid and whitefly control in cotton. Although permits exist for aphid control in faba beans (PER 85363, expires 31/8/2021) and lupins (PER85365, expires 31/12/2023).

#### Use of adjuvants with Group 9B

Pymetrozine products are available as WG or WP formulations. Permits for pulse crops recommend the addition of a suitable wetting agent at recommended rates. When used in cotton, an organosilicon surfactant is normally recommended, while a non-ionic surfactant is typically recommended for use in horticultural crops.

#### Biological insecticides (Group 11A & 11B)

Group 11 insecticides are microbial disrupters of the insect mid-gut membrane and include various Bt *(Bacillus thuringiensis)* products. Activity is limited to certain caterpillar pests only, and hence they are well suited to integrated pest management (IPM) programs that seek to maintain beneficial predators and parasitoids within the crop.

Bt insecticides must be ingested by the caterpillar pests, and hence may take days before full mortality is achieved. These insecticides are more effective on very small instars, so application is best timed just after hatching. As larval size increases, generally insecticide performance declines. Bt insecticides are not systemic within the leaf and hence good spray coverage is required. Any new growth will not be protected. They are subject to wash off following rainfall and are also subject to moderately fast UV degradation on the leaf surface, which often results in only short periods of residual control for foliar applications.

#### Use of adjuvants with Group 11s

A non-ionic surfactant is often recommended when treating crops which are difficult to wet, especially for WG or DF formulations.

Some labels recommend adding a buffer to reduce the pH of alkaline water, or to avoid mixing with highly alkaline tank mix partners.

Common practice often sees UV protected petroleum spray oils used in mixtures to provide some protection of conventional Bt products from degradation by UV light, and so increase their efficacy (Table 4a).

#### Table 4a: Mortality of *Helicoverpa* larvae with Bt alone and in mixtures with petroleum spray oil (Caltex) near Gunnedah 1999–2000

(Source: Mensah et al., 2002).

Treatment	Percent mortality <sup>1</sup>					
neutinent	Day 1	Day 2	Day 3	Day 4		
Bt	50.0	12.5	3.0	0.0		
Bt + PSO 5399	61.1	42.9	21.4	4.4		
NPV	41.7	14.3	4.4	0.0		
NPV + PSO 5399	58.2	32.0	21.1	4.4		

<sup>1</sup>Treatments applied to cotton plants. Leaves collected were fed to neonate larvae for 24 hours which were then removed and placed on artificial diets. Percent mortality was measured for four days following placement on artificial diets.

#### **Disruptors of ATP formation** (Group 12A)

Group 12 contains a number of products that are primarily miticides. Most insecticides from this mode of action group have been used in horticultural or cotton applications in Australia.

In addition to mite control, diafenthiuron (Pegasus®) also provides useful levels of insecticide activity against sucking pests such as aphids and whitefly in cotton and has recently been registered for control of redlegged earth mite and suppression of lucerne flea in canola.

Diafenthiuron rapidly penetrates the cuticle of treated plants, however, is not a systemic insecticide, so good coverage is essential and new growth after application is unlikely to be protected. It is not effective as an application to bare earth.

Insecticidal activity comes from feeding on treated leaves or via direct contact of the insect pest. Diafenthiuron is a proinsecticide, becoming insecticidally active after metabolism within the pest, therefore it often takes a few days before mortality is observed. Under warm temperatures, and after row closure, vapour movement within the canopy can be important for insecticide distribution in cotton, but this will not occur during early winter applications in canola.

#### Use of adjuvants with Group 12A

No adjuvants are recommended for use with diafenthiuron.

#### Oxadiazines (Group 22A)

Group 22 insecticides are disruptors of the insect nervous system, blocking the voltage-dependent sodium channel.

Certain indoxacarb (Group 22A) products are registered for use in cotton and pulse crops for control of Helicoverpa and mirids, along with soybean looper in soybean.

Indoxacarb rapidly enters the leaf, although is not systemic within the plant. Insect control comes from direct contact or ingestion of treated leaf material.

#### Use of adjuvants with Group 22A

EC and WG formulations of indoxacarb are available. Different formulations contain different crop use patterns and different adjuvant recommendations. Always follow specific advice from the individual product label.

Typically, EC formulations are preferred for pulse crops and cotton, with no requirement for additional adjuvants. The label also advises not to apply EC formulations via ULV application.

When targeting mirids, labels typically advise to add salt to the spray mix. Salt increases mirid feeding, resulting in increased efficacy.

#### Diamides (Group 28)

The diamide insecticides affect nerve and muscle action of insect pests via unregulated activation of ryanodine receptor channels which impairs regulation of muscle contraction, ultimately resulting in lethargy and muscle paralysis in insects and eventual death.

This group is highly effective on many caterpillar pests, especially Helicoverpa, with activity coming from either direct contact or ingestion of treated plant material.

Cyantraniliprole has translaminar movement and some local translocation within the leaf, with insecticide moving from the point of leaf entry towards the leaf tip (DuPont 2015). As a result, cyantraniliprole also has activity on certain sucking pests such as aphid and whitefly in cotton.

#### Use of adjuvants with Group 28

In pulses and cotton, the WG formulation of chlorantraniliprole (Altacor®) requires the addition of a non-ionic surfactant unless in mixtures with a product that already contains a surfactant, or recommends against use of surfactant, or where liquid fertilisers are mixed. It is not compatible with ULV formulations.

The oil-in-water cyantraniliprole cotton insecticide (Exirel®) recommends using an ethylated seed oil (e.g. Hasten®) except where a surfactant is already contained in a companion product, where the companion product advises against additional adjuvant, or where a liquid fertiliser is added. If the spray solution remains above pH 8 after all products have been added, it is recommended to add a buffering agent to lower the pH to below 8.



## Nuclear polyhedrosis virus (not grouped)

Nuclear polyhedrosis virus (NPV) is a commercial preparation of virus from *Helicoverpa*, and as such is not an insecticide so is not given an insecticide mode of action group.

Gemstar<sup>®</sup> and Vivus<sup>®</sup> Max are registered for a range of cereals, pulses, oilseeds, sorghum and cotton for the control of *Helicoverpa*. After application, the virus infests larvae and will continue to spread under suitable environmental conditions. Speed of control depends on environmental conditions and may be relatively slow compared to many conventional insecticides.

For ULV application, add Canopy®, D-C-Tron® or equivalent at recommended label rates.

Feeding attractants are useful additives when using NPV. Milk powder is recommended for Gemstar® treatments applied in chickpea, while Optimol® is recommended for Vivus® Max use in sorghum, cotton and pulses. The Vivus® Max label recommends the addition of a pH buffer or acidifier if the spray tank pH is above 8.

## **5. ADJUVANTS FOR FUNGICIDES**

Activity of contact 'protectant' fungicides is strongly influenced by coverage of the active ingredient on the leaf and stem surface. These protectant fungicides provide a barrier to the establishment of the fungal pathogen on the host plant, hence adjuvants that provide improved wetting, spreading and adhesion are likely to play an important role in improved performance.

The activity of 'systemic' foliar fungicides may also be improved by the correct choice of adjuvants. Several studies have shown that improvements can result from changes to factors such as droplet formation, surface contact and behaviour of spray deposit, penetration into the leaf, transport within the plant and interaction within the fungal cell itself.

However, adjuvants that increase penetration may increase the risk of crop damage under some circumstances with some fungicides.

For these reasons, the careful selection of adjuvants and adherence to label directions is very important.

#### Benzimidazoles (Group 1)

Group 1 fungicides (benzimidazoles) are systemic fungicides with curative and protectant action. Carbendazim is registered for the control of chocolate spot and grey mould in chickpeas, faba beans, lentils and vetch.

#### Use of adjuvants with Group 1

The addition of a non-ionic surfactant is recommended in certain situations to improve spray coverage on difficult to wet surfaces.

#### Dicarboximides (Group 2)

Dicarboxamide fungicides include iprodione and procymidone that provide both protective and curative control for a range of fungal pathogens in various crops.

In grain crops, iprodione is registered for use in soybeans and peanuts, with some formulations also registered for use in canola.

Procymidone foliar applications in grain crops includes uses in navy beans, faba beans, with some labels also supporting use in canola and lentils or as a seed treatment.

#### Use of adjuvants with Group 2

Iprodione requires good coverage for effective control. Most labels do not support mixtures with surfactants, spray oils or foliar fertilisers, as increased crop damage may ensue. Alkaline spray water should be buffered to below pH 7 to increase spray tank stability. Similarly, procymidone formulations should not be mixed with alkaline water. A non-ionic surfactant is normally recommended for foliar applications of procymidone.

#### **Demethylation inhibitors (Group 3)**

Demethylation inhibitors (DMIs) are a large, diverse group of fungicides that are widely used in many crops. Most DMI fungicides have foliar activity with protective, curative and/or eradicant action.

Many fungicides developed for grain crop use in Australia are based on fungicides from the triazole sub-class of DMIs. These are available as either a stand-alone fungicide, or commonly pre-formulated with other triazoles or different fungicide modes of action (Table 5a). Triazole mixtures can broaden the spectrum of activity, while mixtures with other

## Table 5a: Common foliar applied triazole fungicides (and mixtures) used in Australian grain production.

Combination triazoles	Straight triazoles	Mixtures with a strobilurin (Group 11)	Mixtures with a SDHI (Group 7)
Cyproconazole + propiconazole e.q. Tilt® Xtra	Cyproconazole e.g. Alto®	Cyproconazole + azoxystrobin e.g. Amistar® Xtra	
Propiconazole +	Propiconazole e.g. Tilt®		
e.g. Cogito®	Tebuconazole various	Tebuconazole + azoxystrobin e.g. Veritas®	
priothioconazole e.g. Prosaro®	Priothioconazole e.g. Brumby®		Priothioconazole + bixafen e.g. Aviator® Xpro
		Epoxiconazole + azoxystrobin e.g. Radial®	
	Epoxiconazole e.g. Opus®	Epoxiconazole + pyraclostrobin e.g. Opera®	
		Epoxiconazole + tebuconazole + azoxystrobin e.g. AC Triaxe	
	Flutriafol		

Some triazole fungicides, e.g. difenoconazole, fluquinconazole, flutriafol, ipconazole, prothioconazole, triticonazole also have applications as seed dressings.



modes of action may broaden the spectrum of activity and/or provide an additional mode of action for resistance management.

#### Use of adjuvants with Group 3

Triazole fungicides are somewhat lipophilic and the inclusion of an oil-based surfactant is likely to increase leaf entry. Although this may not always be desirable, as it may lead to increased phytotoxicity in some situations. Many foliar applied triazole fungicides, in particular EC formulations, do not recommend additional adjuvants when used in grain crops.

Suspension concentrate (SC) formulations of tebuconazole require the addition of Agridex® spray oil/surfactant in peanuts and recommend that a mineral spray oil may improve performance in wheat.

Labels for epoxiconazole, epoxiconazole + azoxystrobin and epoxiconazole + pyraclostrobin fungicides differ with regard to their adjuvant recommendations. Always follow the label advice on individual drums. Some formulations do not recommend any additional adjuvant, others suggest that a non-ionic surfactant may assist in providing better coverage under certain environmental conditions or when using lower total application volumes, while some other labels recommend the addition of a non-ionic surfactant in all situations.

Tazer® Xpert® (epoxiconazole + azoxystrobin) recommends the addition of Banjo® (methoxylated canola oil + non-ionic surfactant blend) for use in cereals.

Cyproconazole + azoxystrobin is often formulated as a SC. The addition of Adigor® spray adjuvant is recommended to improve disease control in barley.

Detailed adjuvant instructions are provided on the prothioconazole + tebuconazole label. The choice of no adjuvant, a non-ionic surfactant or a crop oil concentrate depends upon the crop, disease being targeted and application rate. See label for details.

When applied as a foliar application, flutriafol SC formulations recommend the addition of a non-ionic surfactant.

Table 5b shows the improved control of leaf disease in wheat when the surfactant/acidifier LI-700® was added to flutriafol.

#### Table 5b: Effect of surfactant addition on activity of foliar application of flutriafol (250 g/L) against septoria leaf spot in wheat (Source: Nufarm).

Flutriafol rate/ha	% control				
Thatharon rate/fia	No adjuvant	+ LI-700® @ 0.5 %v/v			
200 mL	10	26			
400 mL	30	41			
700 mL	41	70			
1000 mL	62	78			
1500 mL	66	81			
2000 mL	79	88			

% v/v = Percent of adjuvant, in terms of volume (e.g. ml/L), in the final spray mix.

#### Spiroxamine (Group 5)

Spiroxamine (Prosper®) is a unique powdery mildew fungicide, registered for use in barley and grapes.

There is no recommendation for additional tank mix adjuvants with the EC formulation of Prosper.

## Succinate dehydrogenase inhibitors (Group 7)

Succinate dehydrogenase inhibitors (SDHIs) are fungicides effective against a range of diseases. There are several fungicide sub-classes within this mode of action.

Foliar fungicides used in grains include fungicide mixtures based on bixafen (Aviator® Xpro) which is registered for use in barley, wheat, canola and certain pulses and the pydiflumetofen fungicide (Miravis®) used in canola.

Carboxin (Vitaflo<sup>®</sup>), sedaxane (Vibrance<sup>®</sup>), penflufen (Evergol<sup>®</sup>) and fluxapyroxad (Systiva<sup>®</sup>) based products are used as seed treatments in cereals. Certain mixtures containing penflufen (Evergol<sup>®</sup> Xtend) can be used as a seed treatment in canola. Vibrance<sup>®</sup> CST, containing sedaxane, is a seed treatment for cotton.

#### Use of adjuvants with Group 7

Aviator® Pro is an emulsifiable concentrate formulation which may cause temporary leaf damage to broadleaf crops. No additional adjuvants are recommended. When a tank mix partner requires the addition of an adjuvant significant crop effects can occur, hence these mixtures should be avoided. Don't mix with foliar fertilisers in canola.

Pydiflumetofen (Miravis®) is a suspension concentrate formulation, with no requirement for additional adjuvant when used in canola.

Adjuvants are not required for seed treatment uses.

#### **Strobilurins (Group 11)**

Strobilurins are highly effective protective fungicides, with little curative activity once an infection is established.

Strobilurins are often co-formulated with another fungicide from a different mode of action that may have some early curative activity (e.g. commonly Group 3 fungicides). Mixing with a curative fungicide is especially important when using in crops where a single application is only likely to be applied and some infection may have already occurred before application.

Most strobilurins are somewhat lipophilic, which assists in partitioning fungicide in the cuticle and prevents spore germination. There is generally minimal movement away from the site of application. For this reason, thorough coverage of all foliage is critical. Azoxystrobin has the best chemical properties within this class for translocation and may provide some acropetal (upwards/outwards) movement in the xylem.

Azoxystrobin (co-formulated with either cyproconazole, tebuconazole or epoxiconazole) and pyraclostrobin (coformulated with epoxiconazole) are the main strobilurins used for foliar applications in cereals in Australia.

Veritas® (azoxystrobin + tebuconazole) is registered for use in certain pulses and peanuts. Some azoxystrobin + cyproconazole products are also registered for peanuts.

Azoxystrobin is also a component in several seed treatments.

#### Use of adjuvants with Group 11

Most azoxystrobin + epoxiconazole labels do not recommend additional adjuvant use, however Tazer® Xpert® (azoxystrobin + epoxiconazole) recommends the addition of Banjo® (methoxylated canola oil + non-ionic surfactant blend) for use in cereals.

Azoxystrobin + cyproconazole products are often formulated as a suspension concentrate. The addition of Adigor® spray adjuvant is recommended to improve disease control in barley.

Pyraclostrobin + epoxiconazole formulations are typically suspo-emulsions (SE) and state that the addition of a non-ionic surfactant may provide better coverage of treated surfaces.

Adjuvants are not required for seed treatment uses.

#### Quinoxyfen (Group 13)

Aza-napthalenes are a small group of fungicides that provide protection from certain species of powdery mildew.

In broadacre situations, quinoxyfen (Legend®) is registered against powdery mildew in barley. It provides protection from new infections and will not provide curative activity of existing infections.

#### Use of adjuvants with Group 13

Fungicides from this mode of action group are lipophilic and will partition into the waxy cuticle. Legend® (quinoxyfen) is rapidly absorbed into the cuticle, being rainfast within one hour of application. No specific adjuvant recommendations are made on the label.

#### Multi-site fungicides (Group M)

Group M fungicides are classified as a group having multiple sites of activity. These comprise a wide range of chemical groupings including inorganics (M1, M2), dithiocarbamate (M3), phthalimide (M4), chloronitriles (M5), sulfamides (M6), guanidine (M7) and quinones (M9). This group represents predominantly protectant fungicides with contact activity.

The main multi-site fungicides that are foliar applied in grain cropping include the M3 fungicides mancozeb (pulses, peanuts, soybeans) and metiram (pulses) and the M5 fungicide chlorothalonil (faba beans and peanuts, while some labels also include use in chickpea, lentils and field peas).

Thiram (M3) can also be used as a seed treatment in chickpeas, lupins and sorghum.

#### Use of adjuvants with Group M fungicides

When applied as a foliar application, these fungicides do not penetrate the leaf, remaining on the treated surface – hence they can be subject to wash off after rainfall. Some mancozeb and chlorothalonil products contain stickers in the formulation which helps to reduce wash off after rainfall.

Mancozeb and metiram labels recommend including a surfactant for improved coverage when used in pulses. Some mancozeb labels recommend a sticker/wetter e.g. Bond® adjuvant.

Chlorothalonil labels specifically recommend not to add any additional adjuvants. Surfactants have been shown not to assist performance, and in some situations may cause crop

injury. Spraying oils should not be tank mixed, and spray oils should only be used 10 days before, or after, chlorothalonil applications. Other oil-based pesticides should not be mixed.



## 6. ADJUVANTS FOR DEFOLIANTS AND GROWTH REGULATORS

#### Defoliants

Herbicides such as glyphosate, diquat, paraquat or saflufenacil are used to defoliate certain grain crops in preparation for harvest. Ensure the use pattern is covered on the label of the product you are intending to use. Using unregistered herbicides for defoliation may either damage the marketable produce and/or result in crop residues exceeding established maximum residues levels. GRDC has produced a fact sheet addressing pre-harvest application of herbicides. https://grdc.com.au/GRDC-FS-PreHarvestHerbicide



In cotton, defoliation is undertaken by products which have either a growth regulator mode of action e.g. thidiazuron (Dropp®) or desiccant activity (e.g. sodium chlorate, carfentrazone-ethyl, pyraflufen-ethyl).

#### Use of adjuvants with defoliants

Thidiazuron-based cotton defoliants are applied with petroleum spray oils (e.g. D-C-Tron® Cotton).

Refer to Chapter 3 for adjuvant advice for herbicides used as defoliants.

#### Plant growth regulators

In broadacre grains, the main growth regulators include chlormequat chloride (e.g. Cycocel®) and trinexapac-ethyl (Moddus®), while ethephon (Prep®) and mepiquat chloride (Reward®) are regularly used in cotton.

#### Use of adjuvants with growth regulators

Non-ionic surfactants are recommended with the plant growth regulator chlormequat chloride and for some uses with ethephon. No adjuvant is required with mepiquat chloride or trinexapac-ethyl.

## 7. ADJUVANTS FOR FOLIAR NUTRIENTS

The application of foliar nutrients is becoming regular practice in some broadacre crops and regions.

Nutrients that may be applied as foliar sprays include manganese, zinc, potassium, iron, nitrogen, sulfur, calcium, boron and copper. The use of foliar nutrients allows farmers to supplement the use of soil-applied nutrients on an 'as needs' basis, as well as to respond to deficiencies later in the crop.

Foliar nutrients need to pass through the cuticle and enter the plant to be effective. Spray adjuvants therefore have potential to enhance spread and uptake of foliar nutrients.

Formulations of foliar fertilisers vary greatly. Some manufacturers include surfactants in the formulation while sometimes the addition of a non-ionic surfactant is recommended to improve uptake, particularly on hard-to-wet leaf surfaces.

Caution: When added to the spray tank, foliar nutrient products that contain available cations (e.g. calcium, magnesium, iron in particular) may increase the 'hardness' of the water. These available cations are likely to contribute to disassociation of herbicides such as glyphosate and other amine formulations which is likely to result in reduced herbicide performance.

Incitec has produced an excellent summary of foliar fertilisers, including their physical and biological interactions with other products. (Incitec. 2016. Foliar Fertilisers.) https://www. incitecpivotfertilisers.com.au/~/media/Files/IPF/Documents/ Agritopics/52%20Foliar%20Fertilisers%20Agritopic.pdf

#### Use of adjuvants with foliar nutrients

Trials in the UK, US and Australia have indicated that buffering surfactants (such as LI-700<sup>®</sup> and others) may improve uptake of foliar-applied nutrients and this often leads to improvements in yield and quality. Trials have been conducted on a range of crops including wheat (see Tables 7a and 7b), cotton, soybeans and certain other crops. Responses to adjuvants have been most marked with foliar manganese, zinc, nitrogen, potassium and calcium.

Some foliar fertilisers can be phytotoxic (damaging plants) if the solution becomes alkaline (e.g. potassium nitrate). The addition of an acidifying or buffering adjuvant may reduce the potential for phytotoxic effects on foliage.

## Table 7a: Effect of foliar nutrient and adjuvant on wheat (Janz) yield – Naracoorte SA 1999 (Source: Nufarm 2000).

Treatment	Rate	Yield – t/ha
Manganese Sulphate	2.5 kg/ha	1.30
Manganese Sulphate + LI-700®	2.5 kg/ha + 0.3% v/v	2.01
Zinc Sulphate + Manganese Sulphate	1.5 + 2.5 kg/ha	1.49
Zinc Sulphate + Manganese Sulphate + LI-700®	1.5 + 2.5 kg/ha + 0.3% v/v	1.89

% v/v = Per cent of adjuvant, in terms of volume (e.g. ml/L), in the final spray mix.

#### Table 7b: Effect of foliar nutrient and adjuvant on wheat (Hartog) yield – Pittsworth Qld 1999 (Source: Nufarm 2000).

Treatment	Rate	Yield – t/ha
Nil	-	3.16
Zinctrac + Super N-32	350 mL/ha + 2% v/v	3.30
Zinctrac + Super N-32 + 11-700®	350 ml /ha + 2% v/v + 0.2% v/v	3.48

% v/v = Per cent of adjuvant, in terms of volume (e.g. ml/L), in the final spray mix.



## 8. MORE INFORMATION – SPRAYING AND MIXING

#### **Pesticide application**

GRDC has developed an extensive Spray Application resource which provides more information on aspects of spray application and sprayer set-up. It can be accessed at https://grdc.com.au/spray-application-manual

Maximising spray efficiency https://www.youtube.com/watch?v=qcj8ZpuA2Ww&list=PL2PndQdkNRHHKINyS-3v04o46SA1g0V2ND&index=6

## Best practice spray drift management

Growers who use best practice spray application are keeping themselves, their farms and their neighbours as safe as possible. Practices such as not spraying during inversion conditions, not spraying when the wind is blowing towards sensitive areas or when the wind speed is too low or too excessive will minimise impacts on the environment outside the target crop.

Correct nozzle selection and application set-up is important to maximise product efficacy, while also minimising the amount of driftable fine droplets produced. The choice of adjuvants can also have a positive or negative effect on the composition of the spray and fines that are created (see Chapter 1).

The GRDC has been supporting new spray-drift reduction research through the National Working Party on Pesticide Applications, to improve knowledge of drift-reduction technologies for growers.

Additional information on managing spray drift can be found at https://grdc.com.au/spray-drift



# SPRAY WATER QUALITY



NATIONAL UPDATED JULY 2019

## Water Quality for Spraying Operations





#### **KEY POINTS**

- Poor water quality can adversely affect many products. Always consult product labels and the manufacturer's technical information about water quality requirements.
- Water testing should be done on a regular basis when using bore water, water from streams and rivers, reticulated (piped) water sourced from ground water, and water stored in unlined dams or concrete tanks.
- Water tests should analyse the following to be useful: pH, total hardness (including a measure of bi-carbonate levels) and total dissolved salts (TDS) or salinity (electrical conductivity).

#### Why test water quality?

The quality of the water used for spraying operations can be critical to ensuring the best spray results for many farm chemicals. Many products can be affected by poor water quality.

When considering if the water quality is suitable for a particular product, you need to have accurate information about what may be present in the water that could affect the products you intend using.

The starting point should always be an accurate water test from a reputable laboratory and a thorough check of the product label and technical information from the manufacturer.

#### What should tests measure?

Water quality test strips can be used to assess pH and

water hardness in the field.

Water tests for spraying operations should include:

- ∎ pH;
- total hardness;
- bicarbonate levels; and

either total dissolved salts (TDS) or salinity (EC or electrical conductivity). While pH levels and total hardness can be assessed in the field using water test strips or simple titrations (jar tests), other measurements will typically require laboratory analysis.

If using test strips it may be useful to compare laboratory results to test strip results by setting aside water collected for analysis to check the accuracy of the strips. The strips can then be used to assess if significant changes in water quality have occurred and when another laboratory test may be required.

Commonly available water test strips include those supplied by Hach Pty Ltd (ranging from simple pool test strips to more accurate individual test strips and titration kits) or individual pH and hardness test strips supplied by Rowe Scientific Pty Ltd.

Typically, these will be able to measure hardness or pH at varying levels of precision depending on the type of strips purchased. It is worth researching which may best suit your situation after receiving results from a laboratory.



## Collecting water samples for testing

Use a clean container of at least 500mL size. Rinse the bottle a minimum of four times with the sample water (emptying it away from the sample site).

Collect the water (see Table 1). Fill the bottle to the top, leaving little or no air space, and seal tightly.

Label the bottle accurately with where the sample was taken, the date and intended use. Wrap the sample in aluminium foil to prevent UV light from degrading the sample.

#### Water pH

pH is a measure of the hydrogen ion concentration (H<sup>+</sup>), which indicates how acidic or alkaline the water may be on a 1 to 14 scale, **where seven is considered neutral**. Values below seven are **acidic**, values above seven are **alkaline**.

Alkaline water (pH values typically

#### TABLE 1 Sample timing and location

A new bore or well Sample after pumping for several hours

An operating bore Sample after running the pump for 30 minutes, collect as close as possible to the head of

*A stream* Sample main stream flow

#### A dam or lake

the bore.

Sample away from the edge and near the suction inlet to the pump. Ensure water is well mixed and filtered, or sample various depths. above eight) can cause several problems. These include alkaline hydrolysis and increased dissociation (breakdown of the product), poor droplet contact with the target and reduced performance or stability from some formulations and adjuvants.

If considering reducing the pH of water to be used for spraying, a buffering agent or buffering surfactant will generally be simpler to use than straight acid. A buffering agent will reduce pH to a set point and hold it there, whereas straight acids tend to continue to reduce pH as you add more. Commercial adjuvants such as LI700 can reduce pH and have buffering capacity.

Acidic water (pH values typically below 5) can affect tank mix stability and lead to gelling of some saltbased products such as 2,4-D amines, particularly in tank mixes with some other salt-based and flowable products.

#### Water hardness

Total hardness is a measure of the amount of cations (positive ions) such as calcium, magnesium, sodium, iron and bicarbonates in the water, usually expressed in parts per million (ppm) or mg/L as calcium carbonate equivalents (e.g. CaCO<sub>3</sub> mg/L). See Table 2 for examples of products affected by water quality.

Cations such as calcium and magnesium in the water can bind with negatively charged products such as the weak acid herbicides (e.g. glyphosate), so that they lose their activity in the target plant.

Typically, water hardness above 250ppm (CaCO<sub>3</sub> equivalents) should be treated before using seveal herbicides, particularly where pH is above seven.

Bicarbonates can also affect some products. Bicarbonate levels as low as 175ppm (mg/L) have been

#### TABLE 2 Herbicide tolerances to water qualities

	Water quality				
Active constituent (example product)	Muddy	Saline	Hard	Alkaline (> pH 8)	Acidic (< pH 5)
Carfentrazone-Ethyl (Affinity®)	✓	✓	✓	Х	NR
Chlorsulfuron (Lusta®)	✓	✓	✓	Marginal	Х
Clopyralid (Lontrel™)	~	✓	Х	Х	
Dicamba	✓	~	NR	NR	
Diclofop-methyl (Rhino®)	~	✓	✓	NR	✓
Diflufenican (Brodal®)	✓	✓	Х		
Diquat + Paraquat (Spray.Seed®)	Х	✓	✓	✓	✓
Diuron	✓	Test	✓	✓	
Diuron + 2,4–D amine	~	Test	Х	NR	
Diuron + MCPA amine	✓	Test	Х	NR	
Fluazifop-P (Fusilade®)	✓	✓	~	NR	Х
Glyphosate	Х	✓	Х	✓	
Haloxyfop (Verdict®)	✓	✓	✓	NR	✓
Metsulfuron-methyl (Ally®)	~	✓	✓	Marginal	Х
Quizalofop-p-ethyl (Leopard®)	✓	✓	✓	✓	✓
Sethoxydim (Sertin®)	✓	✓	✓	✓	✓
Simazine	~	Х	✓	NR	
Diflufenican + MCPA ester (Tigrex®)	✓	Х	Х	NR	
Triasulfuron (Logran®)	✓	✓	✓	Marginal	Х
Trifluralin	✓	~	~	✓	
2,4-DB		Х	NR		
2,4–D or MCPA amine	~	✓	Х	NR	
2,4–D or MCPA ester	✓	Test	Test	✓	✓

Key:  $\checkmark$  = OK; X = Do not use; NR = Not recommended but use quickly if there is no alternative; Test = Mix herbicides and water in proportion and observe any instability; Marginal = Not ideal, but acceptable

SOURCE: WEED CONTROL IN WINTER CROPS, 2011 - NSW DPI

reported to reduce the efficacy of some Group A herbicides and 2,4-D amine. Often it is useful to have the level of bicarbonates identified as a separate measurement in a water quality test.

Ammonium sulfate (known as AMS) can assist with water hardness. Ammonium sulfate-based products (such as Liase<sup>®</sup> and Liquid Boost) that are registered as adjuvants may be used with a number of products to reduce the impact of water hardness.

Ammonium sulfate is most useful when supplied as a formulated liquid (typically around 417grams/L) or in a soluble crystalline form (typically around 980gram/kg). These are often preferred by growers for their ease of mixing than the granular form.

Ammonium sulfate can assist in dealing with cations that may be present in the water, but by itself will not significantly change the pH, which

#### TABLE 3 Water hardness levels (WHL)and recommended treatment with AMS to alleviate the effects of hard water

Water hardness level Ca++ ppm	Water hardness level CaCO <sub>3</sub> ppm	Water hardness level	Liquid Boost (AMS) recom- mend mL/100L
80	200	0.69	250
120	300	0.89	375
160	400	1.18	500
200	500	1.48	625
240	600	1.78	750
280	700	2.07	875
320	800	2.37	1000
360	900	2.66	1125
400	1000	2.96	1250
500	1250	3.70	1565
750	1875	5.55	2345
1000	2500	7.40	3125
Calcium	Calcium carbonate	1 WHL = 342 parts per million (ppm)*	

\* testing kits are available in measurements of 342ppm or 1000ppm

SOURCE: SYNGENTA TECHNOTES TN08-379 NON-SELECTIVE HERBICIDES AND ADJUVANTS

TABLE 4 Examples of products affected by water quality						
Active/products	Hardness	Bicarbonates	Salinity	Muddiness	Alkalinity	
Alpha Cypermethrin (Fastac® Duo)					LI-700	
Atrazine WG	Liase®					
Chlorsulfuron (Lusta®)	Liase®		Avoid			
Clethodim (Sequence®)		Liase®				
Clopyralid (Archer®)	Liase®				LI-700	
Chlorpyrifos EC					LI-700	
Cypermethrin EC					LI-700	
Dicamba Amine (Kamba® M)	Liase®				LI-700	
Diclofop-methyl (Rhino®)					LI-700	
Diflufenican					LI-700	
Diflufenican/MCPA (Nugrex®)	Liase®				LI-700	
Dimethoate					LI-700	
Diquat/Paraquat (Revolver®)				Avoid		
Diuron	Liase®		Avoid		LI-700	
Diuron + 2,4-D amine	Liase®	Avoid			LI-700	
Diuron + MCPA amine (Agritone® 750 amine)	Liase®		Avoid		LI-700	
Glyphosate (Roundup® DST)	Liase®			Avoid	LI-700	
Glyphosate (Roundup™ Attack)	Liase®			Avoid		
Imazamox/Imazapyr (Intervix®)						
Imazamox (Raptor®)	Liase®					
MCPA ester (Agritone <sup>®</sup> LVE)	Liase®				LI 700	
MCPA amine (Agritone® 750 amine)	Liase®		Avoid			
Simazine 900 DF	Liase®		Avoid			
Tralkoxydim (Achieve®)		Liase®				
2,4–D ester (Estercide Xtra® 680)	Liase®		Avoid			
2,4—D amine (Surpass® 475)	Liase®	Avoid			LI 700	
Chart legend: Managing water quality – recommendations depend on the severity of problem						
Can be managed with Liase		Liase®	Generally no problem			
Can be managed with LI 700		LI 700	Water should be avoided		Avoid	

SOURCE: NUFARM NOZZLE CHARTS 2012 AND NUFARM SPRAYWISE SPRAY LOG

may also need to be addressed at the same time to minimise issues such as alkaline hydrolysis and stability.

The amount of ammonium sulfate required can be calculated if a suitable water test is available. As a guide to appropriate amounts of ammonium sulfate to add to hard water, see Table 3.

#### Salinity (dissolved salts)

Salinity is usually measured as the electrical conductivity (EC) of the water.

High levels of salinity (above 1000ppm sodium chloride or ECs above 500 microsiemens/cm) can result in some chemicals precipitating out of the solution and others being inactivated. It can also make it



difficult to adjust pH using buffers.

Often the only solution with highly saline water is not to use it for spraying, or to greatly dilute it with clean rain water when it is available.

## Dirty water (suspended solids)

Dirty or turbid water can adversely affect products such as Spray.Seed<sup>®</sup> and glyphosate due to the clay colloids suspended in the water. As a general rule, if a 10 cent coin cannot be seen in the bottom of a bucket of water it is too dirty for use with products affected by dirty water (see Table 4). Filtering water and settling it in a holding tank prior to use can help to reduce turbidity. If using a settling agent, such as alum, only very small quantities should be used in accordance with the manufacturer's guidelines. Often too much alum is added to dam water, which can result in high levels of aluminum in solution. This increases hardness and creates more problems for several products than the untreated dirty water may have.

#### Temperature

Increased water temperatures can accelerate the breakdown of some

#### FREQUENTLY ASKED QUESTIONS

#### Where can I get my water tested?

Check with your local department of agriculture or primary industries, or talk to your local chemical reseller about suitable laboratories in your state. Some chemical and adjuvant manufacturers also offer water testing through the reseller networks.

#### Where can I buy test strips?

Some of the basic test strips for pH and hardness are available in hardware stores or through stores that supply pool equipment. For more accurate test strips visit the manufacturer's websites to locate a local distributor (Hach.com or Rowe.com.au)

#### How often should I test my water?

If using bore water or water sourced from the ground, obtain a full laboratory test annually. If extending the interval between tests to two years, use test strips to check water quality in between. If a significant change in pH or hardness is noticed on the test strips get the water retested by a laboratory.

### What should I do before mixing a spray load if I am not sure about the water quality?

Conduct a jar test to ensure the tank mix will be stable. For susceptible products use a robust rate of product and utilise an acidifying buffer/adjuvant and ammonium sulfate where appropriate.

products when the water quality is not suitable.

Low-temperature water can lead to solubility problems and gelling in the tank (even in clean water).

#### Summary

Poor water quality can adversely affect many spray jobs, particularly where products remain in the tank for extended periods, where high water rates are used, or where low rates of product are used.

Know what your water quality is and how to treat it when using different products.

#### RESOURCES

'Adjuvants: Oils, surfactants and other additives for farm chemicals', GRDC

www.grdc.com.au/GRDC-Booklet-Adjuvants

T. Burfitt, S. Hardy and T. Somers, "Weed Control in Winter Crops, 2011" with extracts from Spray Sense Bulletin No.12, NSW DPI, 1996.

Gerard Bardell, "Water quality and spraying issues for 2007", BCG Crop and Pasture Production Manual 2006-2007.

John Moore, Vanessa Stewart & Jessica Johns, "Water quality for spraying", Department of Agriculture, Western Australia, e-weed, Edition 8, 5 June 2003.

Ground Cover Direct Free Phone: 1800 11 00 44 ground-cover-direct@canprint.com.au

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#### Acknowledgements: Bill Gordon, Graham Betts.

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## SPRAY MIXING REQUIREMENTS FACT SHEET



NATIONAL UPDATED JULY 2019

# Mixing requirements for spraying operations



Jar tests can be done in the paddock prior to mixing the chemicals. Chemicals can be measured using syringes, by substituting mL for L/ha and mixing in the same ratio and order as the actual tank mix.

## Importance of correct mixing order

Correct mixing order reduces the risk of products interacting in a way that may reduce their efficacy or affect the stability of the tank mix.

The addition of multiple products to the spray tank must take place in a specific order to ensure they can be adequately mixed through the solution, according to their solubility and formulation type.

Bringing most products into contact with each other in a concentrated form

will usually result in undesirable interactions between products.

Applicators must understand what the formulation and adjuvant type is for each of the products they intend mixing.

Information about the correct mixing order can often be found on the product label. However, for some tank mix combinations, further information may be required from the manufacturer through tech notes or product guides.

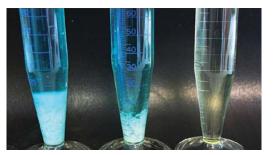
#### **KEY POINTS**

- Understand what the formulation type is for each product and adjuvant being used.
- Never bring concentrated products into contact with each other through mixing equipment or in low tank volumes.
- Know the correct mixing order for every tank mix you use.



TABLE 1 Formulation types and products.			
Formulation type	Code	Example of products	
Water dispersible granules, water-soluble granules and dry flowables	WDG	Spinnaker 700 WDG	
	WDG	Simazine 900 WG	
	DF	Penncozeb 750 DF	
Suspension concentrates	SC	Regent® 200SC	
concentrates	SC	Mancoflo 420 SC	
Emulsifiable concentrates	EC	Broadside®	
	EC	Bromicide <sup>®</sup> 200	
	EC	Triclopyr 600	
	EC	TriflurX®	
	EC	Fastac <sup>®</sup> Duo	
Soluble liquids (which include soluble concentrates and aqueous concentrates)	SL	Amicide Advance® 700	
	SL	Kamba® M	
	SL	Spray.Seed®	
Soluble liquid (containing glyphosate)	SL	Weedmaster <sup>®</sup> Argo	
	SL	Roundup <sup>®</sup> Ultramax	
	SL	Gladiator CT	

TABLE 2 Adjuvant types and products.			
Adjuvant type	Types of products	Examples	
Surfactants	Wetter 1000 products	BS 1000°	
	Organosilicones	Pulse®	
	Stickers	Bond®	
Oils	Petroleum-based oils	Uptake <sup>®</sup>	
	Vegetable oils	Hasten®	
Acidifiers and buffers	Acidifier/buffer	LI 700° or Collide°	
difu bullers	Buffer	Primabuff®	
Fertiliser adjuvants	Ammonium sulfate based	Liase®	
		Boost®	
		Free Flow Ammo®	



Three possible outcomes of the jar test: Left – layers forming, middle – sediment produced, right – well mixed. PHOTO: NUFARM LTD

TABLE	3 Basic chemical mixing order.	
Mixing order	Water – chemical – additives	Example of product
1	Water conditioners, acidifiers, etc.	Liase <sup>®</sup> , LI 700 <sup>®</sup>
2	Wettable, dispersible granules	Lusta°, Nugran°, Associate°
3	Dry, flowable (DF)	Diuron (WG), Simazine (DF)
4	Flowables (suspension concentrates)	Regent <sup>®</sup> 200SC
5	Wetter if using ECs <sup>⁺1</sup>	Activator <sup>®</sup> , BS 1000 <sup>®</sup>
6	Emulsifiable concentrate (EC)	Triflur® X™, Avadex® Xtra, Estercide Xtra 680®
7	Water soluble concentrates	Amicide Advance 700°, Gladiator CT
8	Adjuvants	Oils <sup>*2</sup> , LI 700 <sup>°*3</sup> , BS 1000°
9	Liquid UAN	Easy N

<sup>\*1</sup> Wetter to be added at stage 5 if using ECs

<sup>\*2</sup> Oils must be added last to all mixes

<sup>\*3</sup> If added at stage 1, do not add at stage 5 or 8

When adding water conditioner, fill spray tank as full as practical while adding water conditioner. Add water conditioners before adding any chemicals.

There are some exceptions to these basic guidelines:

• Glyphosate and some 2,4-D products. See mixing instructions for isopropylamine forms of 2,4-D:

1. Clean water

Mix thoroughly

- 2. Add water conditioners
- 3. Add other herbicides, insecticides, etc.
- 5. Fill the tank to around 95%
   6. Add glyphosate
   7. Add other adjuvants
   8. Add remaining water

4. Add 2,4-D product

• Glyphosate and Starane<sup>™</sup> Advanced Herbicide. Refer to the Starane<sup>™</sup> Advanced label. Glyphosate is put in the spray tank before Starane<sup>™</sup> Advanced.

SOURCE: NUFARM AND ASK GB

# FIGURE 1 A simple jar test

A guide to the suitability of water for spray applications can be quickly obtained using the following procedure:

- **1** Mix at least 500mL of correctly diluted spray in a clear glass sealed container according to the manufacturer's instructions.
- **2** Mix thoroughly and allow to stand for up to 30 minutes.

**3** If creaming (where suspended droplets of product appear to remain in a layer at the top of the jar), sedimentation or separation into layers occurs, the water may be unsuitable for mixing sprays.

- If suspected of being unsuitable, a sample of this water should be chemically analysed for salt and hardness levels.
- **5** Different brands of the same chemical may react differently because of different additives in each formulation.

# FIGURE 2 Mixing instructions for isopropylamine forms of 2,4-D

Ensure the spray tank is free of any residue of previous spray materials.

**1** Fill the spray tank with clean water to the recommended amount before introducing the products. Often this requires the tank to be around 70 per cent full before starting the agitation. Do NOT use mechanical agitators as these may cause excessive foaming when herbicides are added.

2 Add water conditioners at the required rate.

**3** Add recommended herbicide additive/insecticide to the spray tank and mix thoroughly.

4 Add isopropylamine form of 2,4-D and mix thoroughly.

**5** Top up tank to 95 per cent of desired capacity then add the glyphosate product and remaining water.

**6** When surfactant is used, add near the end of the filling process to minimise foaming.

7 Always maintain adequate agitation during application and use the tank mix promptly.

Adapted from a Nufarm label for a product that is no longer registered.

## Jar test – water volume

The easiest way to simulate actual tank-mix ratios is to divide everything by 100. For example, 70 litres per hectare (L/ha) becomes a 0.7L volume in the jar. It is a good idea to use the same water source that is going to be used to spray with. If the initial mixing takes place with 60 per cent tank capacity of water, this should be reflected in the jar test as well. For example, 60 per cent of 0.7L would amount to 0.42L (0.7 x 0.6 = 0.42) for the initial volume of water in the jar.

## Jar test - product rates

Product rates for the jar test should also use the field rate divided by 100 (see Table 4). For example: a rate of 2L/ha, or 2000 millilitres per hectare (mL/ha) becomes 20mL per test, a rate of 800mL/ ha becomes 8mL per test, and so on.

Adjuvants can be a little trickier because they are mixed at a rate per 100L. For example, 2000mL per 100L of water with a liquid AMS becomes 20mL per litre. For a tank mix to be applied at 70L/ha, the total jar test volume would be 0.7L, not a whole litre. The amount of liquid AMS to add to the total jar volume of 0.7L would be 14mL (20mL per litre x 0.7L = 14mL).

It is useful to have some syringes to measure small volumes. They are easily obtained from pharmacies or medical supply shops and come in various sizes; 3mL and 20mL should provide sufficient volume variation. Dry products require scales: a portable scale (electronic balance) should provide reasonable accuracy in the 10–20 gram range.

# Conducting the jar test

The mixing order should be the same as that used in the field. Shaking the jar after mixing will simulate agitation. When dry products are used they should be fully dissolved before the next product is introduced (this may require a separate container to dissolve dry products, if that is what you do in the field). Waiting for products to fully dissolve may take some time, (for example, when using crystalline ammonium sulfate), but this is also what will be required for the actual tank mix.

After the mixing is finished the jar should be left to stand for for at least 5 minutes, ideally up to 30 minutes.

# Possible results of the jar test

- The jar contains a homogenous solution. This is where the whole mixture appears consistent in appearance. This is the best result a jar test can produce. The mixed solution seems to be stable and suggests that the planned tank mix is physically compatible and products will be able to be mixed in the tank.
- The jar contains thick layers or banding in the profile. This indicates that the solution is not stable without agitation. If some shakes of the jar can make the solution homogenous again, and it stays this way for two minutes before layers start to form slowly again, it can be assumed that agitation should overcome the problem. However, if the banding returns within about 30 seconds, it is a strong indication that there will be a problem with the tank mix that even good agitation may not be able to overcome.
- There is sediment or precipitate on the bottom of the jar. This indicates strongly that the mix is not physically compatible or the mixing procedure was not right, e.g. adding 2,4-D before allowing sufficient time for crystalline ammonium sulfate to dissolve.

# TABLE 4 An example of field rates and the rates to be used for a jar test.

Example of volumes in a jar test (one-hundredths of a hectare rate or volume)				
Field rates		Jar volume or amount		
Total application volume	70L/ha	70 ÷ 100 =	Final jar volume 0.7L	
Initial mix – starting water volume	60% tank capacity	0.7 x 0.6 = or 0.7 x 60%	Initial jar water volume 0.42L	
Liquid AMS	2000mL per 100L	2000 ÷ 100 x 0.7 =	14mL	
2,4-D	800mL per ha	800 ÷ 100 =	8mL	
Glyphosate	2000mL per ha	2000 ÷ 100 =	20mL	

SOURCE: GRDC GROWNOTES, SPRAY APPLICATION MANUAL FOR GRAIN GROWERS



# Knowledge of formulation types is essential for mixing

Formulation type is sometimes indicated on the product label if it is incorporated into the name of the product (for example, Simazine 900DF for dry flowable, or Chlorpyrifos 500 EC for emulsifiable concentrate), but this is not always the case.

Examples of formulation types and products are shown in Table 1.

## Adjuvant types

The type of adjuvant is also important for determining the correct point during the mixing process that it should be added.

The addition of adjuvant to the tank mix can change depending on the formulation of the products actually being mixed.

Examples of adjuvant types and products are shown in Table 2.

# FREQUENTLY ASKED QUESTIONS

### When should I add adjuvants?

That will depend on the adjuvant type. Water conditioners such as ammonium sulfate should be added to the recommended amount of water before other products are introduced into the tank. Surfactants such as Wetter 1000 products are introduced at the end, unless liquid UAN is used which would go in after the wetter. If one of the products is an EC formulation the wetter would be added after the dry products, so always check the mixing order chart.

### Why do I get excessive foaming when I am mixing some products?

Often foaming results when using the Venturi system to fill the spray tank. Sometimes foaming can be reduced by having more water in the tank before introducing products or by using anti-foaming agents. Where these strategies do not work, it might require that filling be done using an external pump.

# How can I tell if products I have not used before can be mixed together?

Often there will be information about compatibility on the product labels. If specific information about the products you want to mix is not on the label, It is best to contact the manufacturer of the product before mixing takes place. If you are still in doubt conduct a jar test, which will let you know if they are physically compatible. Remember that even if they can be mixed, this will not tell you if they are biologically compatible.

### Why do some products 'gel' when mixed together?

Often this can result from a couple of factors interacting, which are water quality, mixing order and water temperature. Sometimes gelling can be accelerated if water is at a high temperature and water quality is not suitable. Other times gelling can occur with some products at low water temperatures. It is essential that water quality is considered as a part of the solution, and when using water conditioners that they be added to the water and sufficient time is allowed for them to dissolve before other products are added. Then make sure the correct mixing order is followed.

## **Mixing order**

Table 3 and Figure 2 include the suggested mixing orders for a range of situations.

# Jar tests to assess physical compatibility

If you are unsure about the ability to mix certain products it is always a good idea to contact the manufacturers for further information, and to conduct a jar test to confirm physical compatibility (see Figure 2). A jar test can only tell you if the products are physically compatible (able to be mixed). It will not tell you if there are problems with biological compatibility, where one product may interfere with the biological activity of another.

## Summary

Mixing order is critical to ensure that tank mixed products perform to their potential. Understanding formulation type and adjuvant type are an important part of getting the mixing order right. If in doubt about the compatibility of products in a tank mix, contact the manufacturers and conduct a jar test to ensure they will mix.

# RESOURCES

Graham Betts, 'Water Quality and Your Spray Product' in *Adjuvants: Oils, surfactants and other additives for farm chemicals*, revised 2014 edition.

https://grdc.com.au/AdjuvantsBooklet

# MORE INFORMATION

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#### Acknowledgements: Bill Gordon, Graham Betts.

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# **FREQUENTLY ASKED QUESTIONS**

# **Q**: Legally, can I use a spray adjuvant that is not approved for use with a pesticide?

Any product that makes a claim in relation to controlling a pest population must be approved for use by the Australian Pesticides and Veterinary Medicines Authority (APVMA) before it can be sold or used. This includes spray adjuvants that modify the performance of other pesticides.

Where a pesticide label recommends the use of an adjuvant without nominating a specific tradename (e.g., 'wetting agent' or 'non-ionic surfactant'), the user is free to choose any product that conforms to this description.

The situation is less clear where a specific product is recommended for use and several other alternative or equivalent products exist. In this instance, using a different brand of adjuvant may place the user in a difficult situation should a product performance issue arises. Some labels go as far as stating that non-specified brands are not supported.

When an adjuvant type (e.g. buffering agent) is not specifically recommended with a particular pesticide but is widely used (e.g. with certain insecticides and herbicides such as glyphosate), the absence of a reciprocal registration on a pesticide label may also place the user in a difficult situation should a product performance issue arise.

If in doubt about the use of a particular spray adjuvant, refer to the respective product labels first and then the manufacturer of the pesticide or their representative.

### Q: Are all surfactants the same?

No. Surfactants vary widely in their chemical structure and function. They all have some water loving 'hydrophilic' and fat loving 'lipophilic' components, however, the composition varies widely.

Surfactants assist dispersion in the spray tank and coverage of the leaf surface. They can be broadly classified according to their structural type, on the basis of whether they carry a net positive (cationic), negative (anionic), amphoteric or neutral (non-ionic) electrical charge. There are many surfactants/wetting agents commercially available. In addition, most other types of commercial adjuvants (spray oils, buffering agents, stickers etc.) often also contain a surfactant in their formulation.

If a specific surfactant brand product is specified on a pesticide label it is important to heed this, as it is possible that an alternative product may not give the desired effect or reduce the effectiveness of the product or lead to unacceptable levels of crop damage. Where surfactant use rates are provided on the pesticide label this is likely to be based on the surfactant type and loading.

#### Q: Are all oils the same?

No. Oils may be either petroleum or plant-based. Within these groups, spraying oils also vary according to the type and quantity of emulsifiers (surfactants) used in the formulation. In addition, certain plant-based oils are 'esterified' (combined with an alcohol to form a fatty acid ester).

Within the petroleum spray oil group, performance may vary according to the properties of the base oil from which they are refined, the degree of refinement and the presence or absence of other additives, e.g. UV stabilisers or specialised surfactants.

## Q: When should I not use a surfactant?

Certain selective herbicide labels specifically recommend not to add surfactants or crop oils. This is mostly seen with pesticides used in-crop as the addition of the surfactant may reduce the selectivity of the product. These recommendations should be heeded, even where the addition of a spray adjuvant apparently enhances control of the weed, pest or disease.

Where no specific adjuvant advice is given on the pesticide label it is likely that the formulation already contains adequate adjuvant. In these cases, adding extra adjuvant may add unnecessary cost, may lead to excessive foaming, produce more small droplets that can be subject to drift or change the droplet produced, especially when using airinduction nozzles. In some situations, it has been shown that excessive rates of surfactant may actually reduce retention on the leaf, should the extra surfactant cause droplets to run off the surface before drying. Crop damage is also a potential outcome of too much or the wrong type of adjuvant.

Some surfactants and spray adjuvants may be antagonistic. For example, organosilicone surfactants such as Pulse® may reduce weed control of many annual grasses when added to glyphosate. A similar effect may be observed with the addition of petroleum spray oil to glyphosate, leading to reduced control of some summer grasses, such as awnless barnyard grass.

# **Q:** If spray adjuvants are so important, why don't the chemical manufacturers always include them within their products?

Pesticide products are generally formulated in order to allow the consistent and effective application of one or more active ingredients to the pest or weed target. Many formulations contain components such as emulsifiers (surfactants) and other agents that enable the product to 'hold together' in storage and be dispersed effectively in a water carrier when mixed in preparation for spraying. This is particularly important for active ingredients that are not readily soluble in water.



Some formulations may also contain adjuvants specifically to facilitate the spread of spray droplets and uptake of active ingredient. Unfortunately, it is very difficult to optimise this for the widest possible range of situations, varying as it does with the rate of product being used, the volume of spray carrier and the nature of the spray target. For some products it would be physically very difficult to incorporate some adjuvants into a formulation, while maintaining a sufficiently high concentration of active ingredient to make it cost effective. A glyphosate formulation containing ammonium sulphate, for example, may have to have a third to a half of the concentration of active ingredient, compared to a regular formulation containing surfactant only. The relative cost and effectiveness of a 'fully loaded' product may affect its market acceptability, even if it were to be a superior product in respect of its performance.

# **Q:** What effect do spray adjuvants have on nozzle performance?

Relative to water, many conventional surfactant products (in particular non-ionic surfactants) will increase the proportion of small droplets produced by a hydraulic nozzle (i.e. they reduce average droplet size and create more 'driftable fines'). This is because the reduction in surface tension produced by the addition of a surfactant leads to greater disintegration of a spray sheet as it emerges from a spray nozzle. But there can be big differences in this effect depending on the type and concentration of surfactant, the pesticide it is being mixed with and the type of nozzle.

The addition of an oil may increase the average droplet size, however, many commercial spray oil formulations also contain a significant concentration of surfactant that may negate this effect.

Adding oils at high rates (around 20 per cent or more of the sprayable volume) may lead to reduced evaporation of droplets, following release from the nozzle.

### Q: How toxic are surfactants?

Relative to the active constituents of some pesticide formulations, toxicity of surfactants is not particularly high. This is not surprising considering the universal application of surfactant technology to many household items including cleaning agents, foods, cosmetics and pharmaceuticals.

By their nature, surfactants reduce surface tension of water and may lead to skin or eye irritation.

Surfactant products are regulated in the same way as pesticides and data must be submitted as to the acute effects of surfactants, either as components of a spray formulation or as products for use as spray adjuvants.

Long-term effects of many surfactants is not as well known and this has led to some concern that certain surfactants may be detrimental to the environment e.g. in waste streams from urban and industrial areas. However, surfactants do not generally persist in the environment and, in normal agricultural applications, are rarely present in sufficient concentration to be detrimental.

# **Q:** I seem to have too many surfactant products in the chemical shed. Can we rationalise our use of products?

While there will always be some need for specialised spray adjuvant products, it is possible to rationalise the use of surfactants.

Many pesticide products simply call for the addition of a non-ionic surfactant (nearly all agricultural surfactants are non-ionic) or a spreader or wetter (all surfactants perform this function to a greater or lesser extent).

Of the base line surfactants, the choice often comes down to either an alkoxylated alcohol (e.g. BS1000®) or an alkyl phenol ethoxylate (e.g. Agral®). Many alkoxylated alcohols are 1000g/L formulations, while many alkyl phenol ethoxylates are 600g/L formulations, so there will often be a difference in required use rate.

Many pH buffering adjuvants, organosilicons and spray oil products also contain a non-ionic surfactant or other similar wetter, so normally an additional surfactant/wetter is not required when using these products. Always check the adjuvant label, as the level of surfactant varies considerably between different adjuvants.

pH reducing buffers are widely used in Australia. However, there are limited situations where benefit is achieved purely from reducing spray tank pH. It is usually more important to address the underlying reason for high pH, which is often associated with 'hard water'. Most buffers contain an acid (to reduce pH) and a surfactant. Often the benefit achieved from the addition of the 'buffer' is coming largely from the surfactant component, so in these situations pre-conditioning the water and replacing the buffer with a simple surfactant may be appropriate.

Where the source of spray water is 'hard' (> 250 ppm CaCo<sub>3</sub> equivalent), pre-treatment with ammonium sulphate (or a surfactant blend containing ammonium sulphate) will be beneficial when using glyphosate and many other amine/salt herbicides.

Some products specifically recommend the use of a petroleum spray oil (e.g. Cropshield), petroleum spray oil concentrate (e.g. Uptake®), vegetable oil (Codacide®) or an esterified vegetable oil (e.g. Hasten®). Pesticides recommending these oil-based adjuvants will typically be more lipophilic. Oils generally do not assist in penetration with hydrophilic pesticides.

Beyond this there are a range of more specialised adjuvants that should only be used where they are specifically recommended on specific product labels.

# **GLOSSARY OF TERMS**

To help understand the terms used in describing the types and functions of spray adjuvants, a glossary of terms and definitions is included here, based on standard terminology relating to agricultural tank mix adjuvants developed by the American Society for Testing of Materials (Berger et. al. 1993).

Acidifier: An acid that can be added to spray mixtures to lower the pH. Strong acids (e.g. sulphuric, nitric or hydrochloric acids) will continue to reduce solution pH progressively as concentration of acid continues to increase. Weak acids (e.g. citric or propionic acids) will acidify the water where the pH is above the acids pKa value, however the acidifying effect reduces as the pH falls to around the pKa value of the acid (see buffering agents below). A number of pH reducing adjuvant blends are also available (e.g. LI-700<sup>®</sup> type products or products sold as 'buffers') which also have other adjuvant functions in addition to simply lowering pH.

**Activator:** A term to include any substance that increases the biological effectiveness of a pesticide. These may include a variety of substances including surfactants, spray oils and fertilisers such as ammonium sulphate.

**Alkaline hydrolysis:** Degradation of a pesticide when in an alkaline environment.

**Anionic surfactant:** A surface active agent (surfactant) in which the active portion of the molecule containing the hydrophilic ('water loving') segment forms a negative ion (anion) when in solution with water.

**Antifoaming agent:** A material used to inhibit or prevent the formation of foam. Foaming characteristics of adjuvants may be modified by the incorporation of a small quantity of an anti-foaming agent in the formulation.

**Attractant:** A material that attracts specific pests. These may include substances such as pheromones or feeding stimulants (e.g. salt, milk powder or molasses-based products may be used for certain pests).

**Buffering agent:** A compound or mixture that, when contained in solution, causes the pH of the solution to move to a particular level and then hold around this level, even when more buffering agent is added. Most buffering agents used in agriculture typically contain a weak acid. For example, Buff-it® or LI-700® type products contain propionic acid. Propionic acid has a pKa value of 4.87, When added to neutral or alkaline water, the propionic acid will reduce the pH. As the pH reaches the pKa value, additional propionic acid will not continue to reduce the pH.

**Cationic surfactant:** A surface active agent (surfactant) in which the active portion of the molecule containing the hydrophilic ('water loving') segment forms a positive ion (cation) when in solution with water.

**Crop oil concentrate:** An emulsifiable petroleum-based phytobland oil containing 15 to 20% w/w (or more) surfactant.

**Crop oil:** An emulsifiable petroleum-oil based product containing up to 5% w/w surfactant and the remainder being a phytobland oil.

**Dissociation constant (pKa):** pKa is a measurement of the strength of an acid. A lower pKa value indicates a stronger acid. Acids with lower pKa values will dissociate more fully (give off H+) when in water.

**Extender:** A material that increases the effective life of a pesticide after application. This is a claimed function for the product di-1-p-menthene (e.g. Nu-Film®-17).

**Humectant:** A material that reduces the drying time of an aqueous spray deposit.

**Hydrophilic-lipophilic balance (HLB):** A measure of the relative contribution of the hydrophilic and lipophilic component of an adjuvant. Both the type and size of the hydrophilic (water soluble) and lipophilic (oil soluble) properties of a surfactant may influence droplet spread, droplet bounce, evaporation and pesticide absorption.

**Modified vegetable oil:** Oil extracted from oilseeds that have been chemically modified (for example, ethylated).

**Non-ionic surfactant:** A surface active agent that has no ionisable polar end-groups but is made up of hydrophilic ('water loving') and lipophilic ('fat loving') segments.

**Penetrant:** A material that enhances the ability of a pesticide to penetrate the surface (cuticle) of a plant.

**Pesticide:** Pesticide is a broad term that comprises all chemical substances used to control insects, diseases, weeds, fungi and other 'pests' on plants, fruits, vegetables, animals and in buildings. Fungicides, herbicides, sanitisers, growth regulators, rodenticides, soil fumigants and insecticides fall under the category of pesticides or crop protection chemicals.

**Petroleum oil:** Oil derived from petroleum that contains a mixture of hydrocarbons broadly classified as paraffins, napthenes, aromatics or other unsaturates.

**Phytobland oil:** A highly refined paraffinic material with a minimum unsulphonated residue of 92% v/v.

**Surface active agent (surfactant):** A material that, when added to a liquid, modifies the properties of the liquid – such as spray droplets – at the leaf surface.

**Spreader:** A material that increases the area that a droplet of a given volume of spray mixture will cover on a target.

**Sticker:** A material that assists a spray deposit to adhere or stick to a target and resist removal by wind, water, mechanical or chemical action.



**Vegetable oil:** Oil extracted from oilseeds, including canola, corn, cotton, soybean or sunflower.

**Vegetable oil concentrate:** An emulsifiable vegetable oil product containing 5 to 20% w/w surfactant and a minimum of 80% w/w vegetable oil.

% v/v (% Volume per Volume): Percent of volume of adjuvant, in terms of volume of the final spray mix.

Wetting agent: See spreader.



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# Links to associated information:

http://www.hcpsl.com/wp/wp-content/uploads/2018/04/ Nufarm-Tank-Mixing-Guide-1.pdf

https://www.dpi.nsw.gov.au/agriculture/broadacre-crops/guides/publications/weed-control-winter-crops

http://www.pestgenie.com.au

http://portal.apvma.gov.au

https://grdc.com.au/understanding-post-emergentherbicide-weed-control

https://grdc.com.au/GRDC-FS-PreHarvestHerbicide





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