Chapter 8 - ADJUVANTS

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Chapter Contents

Synopsis

An adjuvant is any compound that is added to a herbicide formulation or tank mix to facilitate the mixing, application, or effectiveness of that herbicide. Adjuvants are already included in the formulations of some herbicides available for sale (e.g. RoundUp®), or they may be purchased separately and added into a tank mix prior to use. Adjuvants are chemically and biologically active compounds, and they may improve the effectiveness of the herbicide they are added to, either increasing its desired impact and/or decreasing the total amount of formulation needed to achieve the desired impact. Some herbicides require the addition of an adjuvant to be effective. Some adjuvants enhance the penetration of herbicide into plants by ensuring adequate spray coverage and keeping the herbicide in contact with plant tissues, or by increasing rates of foliar and/or stomatal penetration.

The U.S. Environmental Protection Agency (EPA) regulates the inclusion of certain ingredients in adjuvant formulations, but it does not stringently test and regulate the manufacture and use of adjuvant products (as they do for herbicides and other pesticides). As such, there is little information on the effects of these different adjuvants, other than that provided by the manufacturer. A herbicide label may specify what types of adjuvant are appropriate or advisable to use with that herbicide, but it will not suggest specific brands. Therefore, there is no good single resource or system to help you determine which specific adjuvant product (if any) to use for each application situation. However, it is worth checking the label of any adjuvant you are considering to see if it is registered in certain states, such as California or Washington. These states regulate adjuvants and require the disclosure of their ingredients, results from efficacy trials, and data from environmental and toxicological studies. The best source of information for which adjuvant to use (if any) in each situation is usually your local agriculture or university extension agent, county weed coordinator, or herbicide company representative.

INTRODUCTION TO ADJUVANTS

An adjuvant is any compound that can be added to a herbicide formulation to facilitate the mixing, application, or effectiveness of that herbicide. Adjuvants are already included in the formulations of some herbicides available for sale (e.g. RoundUp®), or they may be purchased separately and added into a tank mix prior to use (Pringnitz 1998). Herbicides must overcome a variety of barriers to their entry into plants in order to be effective. For example, herbicides applied to foliage must remain on the leaf instead of beading up and rolling off, then get past the leaf hairs and waxes on the leaf surface, then finally penetrate through the cell walls and cell membranes (DiTomaso 1999; Hull et al. 1982). Some adjuvants alter the formulation so that they more completely and evenly cover plant surfaces thereby keeping the herbicide in contact with plant tissues rather than beading up and rolling off. Others increase the formulation's penetration through the cuticular wax, cell walls and/or stomatal openings. In some situations, an adjuvant may enhance the formulation's ability to kill the targeted species without harming other plants (i.e. enhance its selectivity; Hess & Foy 2000). Adjuvants may also improve a herbicide's efficacy so that the concentration or total amount of herbicide required to achieve a given effect is reduced, sometimes as much as five- or ten-fold (WSSA 1982). In this way adding an appropriate adjuvant can decrease the amount of herbicide applied and lower total costs for weed control (Green 2001, 1992).

Adjuvants are chemically and biologically active (NOT chemically inert) compounds. They produce pronounced effects in plants and animals, and some adjuvants have the potential to be mobile and pollute surface or groundwater sources. Be especially aware of the use of adjuvants near water, as adverse effects may occur in some aquatic species (Parr 1982). The Material Safety Data Sheets (MSDSs) of most adjuvants will list materials that are incompatible with the adjuvant, conditions in which they should not be used, and some toxicological information (LC50 or LD50s), but this information is usually not as complete as that found on herbicide labels and MSDSs.

Unfortunately, there is no good system available to help you assess which types of adjuvants (if any) to select for different situations, much less which brand will best meet your needs. Most herbicide labels specify the *type* of adjuvant to use for best control (see Box 1), but there are many different brands of most types of adjuvants to select from and few sources of good information regarding their relative performance under different conditions. The best source of information is most likely your local agriculture or university extension agent, local county weed coordinator or herbicide company representative. Local herbicide dealers may also offer suggestions, but be sure that the dealer is qualified to make recommendations (Carroll 2001).

Adjuvants may be classified in a variety of ways, such as by their function (activator or utility), chemistry (such as organosilicones), or source (vegetable or petroleum oils) (Penner 2000b). This adds to confusion about which adjuvant to select in different situations. In this chapter, we group adjuvants by their function, as either activator adjuvants or utility adjuvants (see Box 1). Activator adjuvants work to enhance the activity of the herbicide, often by increasing rates of absorption of the herbicide into the target plant(s). Utility adjuvants, sometimes called spray modifiers, work by altering the physical or chemical characteristics of the spray mixture to improve its ease of application, its ability to remain on the plant surface rather than rolling off, or its persistence in the environment (McWhorter 1982). There is much disagreement regarding how certain adjuvants should be categorized, and to complicate matters further some adjuvants perform more than one function and thus really do fit in more than one category.

Box 1: Adjuvant Types*

Activator Adjuvants

Surfactants
- Nonionic (incl. organosilicones)
- Ionic
- Amphoteric

Oil adjuvants (incl. crop oil concentrates)
- Petroleum oil concentrates
- Vegetable oils

Ammonium (nitrogen) fertilizers

Utility Adjuvants (including Spray Modifiers)
- Wetting agents (spreaders)
- Dyes
- Drift control & foaming agents
- Thickening agents
- Deposition agents (stickers)
- Water conditioners
- Compatibility agents
- pH buffers
- Humectants
- Defoaming & antifoam agents
- UV absorbents

*There are many ways to classify adjuvants. In this chapter, we divide adjuvants into two primary types (activator or utility), based on their functions. For a more complete listing of available adjuvants in the U.S., see the Compendium of Herbicide Adjuvants, available at http://www.herbicide-adjuvants.com/index.html.

Adding adjuvants allows the applicator to customize the tank formulation for each particular situation (Green 2001). In many situations, adding an adjuvant can significantly enhance a herbicide's effect (Green & Hazen 1998). However, it is important to note that in some circumstances, adding adjuvants will not significantly improve control. For example, there is no benefit to be gained from adding an activator adjuvant when applying a herbicide to broadleaf weeds with thin cuticles that are growing in high humidity and shade (Kudsk & Streibig 1993). Sometimes adjuvants can have negative effects, such as actually decreasing the killing power of the herbicide (antagonistic effects), increasing the formulation's ability to spread or persist in the environment where it is not wanted, or otherwise increasing harmful affects to non-target plants and animals (see Environmental Fates and Toxicity sections). There is no universal adjuvant that can improve the performance for all herbicides, against all weeds, or under all environmental conditions. The herbicide and adjuvant selected and the relative amounts used must be tailored to the specific conditions of each application.

SELECTING AN ADJUVANT

Choosing an appropriate and effective adjuvant can be daunting. To begin with, it is sometimes difficult to determine which adjuvants actually meet the recommendations on the herbicide label. There are hundreds of adjuvants available, and choosing the best one(s) will depend on the plant species targeted, its phenological stage, site conditions, current environmental conditions, and the method of application, etc. (see Box 2). Herbicide labels and MSDS sheets often list the *types* of adjuvants recommended (see Box 4) (e.g., a nonionic surfactant), but they cannot recommend specific adjuvant brands. A further complication is that the US EPA does not stringently regulate the manufacture and marketing of adjuvants since many compounds in adjuvants are classed as ‘inert’ compounds. Compounds in a herbicide are often referred to as ‘inert’ if they do not kill plants or regulate their growth directly (i.e. they are not the active ingredients such as glyphosate or triclopyr). These compounds however, may be (and usually are) chemically and biologically active. In contrast, adjuvant formulations that do not cause any significant biological or chemical effects, are often referred to as ‘inert’; this is closer to the meaning of the word ‘inert’ as it is used in the study of chemistry, but still not entirely the same. Another source of confusion is that adjuvant manufacturers sometimes change the chemical formulation of an adjuvant formulation from one year to the next, even though it is marketed under the same name. A factor to consider is that certain adjuvants or adjuvant mixes may sometimes be more toxic to certain non-target organisms than the herbicide itself. For example, the surfactant included in RoundUp® is more toxic to fish than the active ingredient glyphosate. For this reason it is not legal to use RoundUp® over water bodies, but glyphosate formulations sold without a surfactant (e.g. Rodeo®) are legal in aquatic situations.

Box 2: Some factors to consider when choosing an adjuvant

Environment
Site conditions (Aquatic or terrestrial? In sensitive areas?)
Current conditions (Air temperature? Windy?)
Water chemistry (Hard or soft water? Low or high pH?)

Target(s)
Species and growth form
Phenological stage
Dense or sparse growth? (Will it warrant high volumes of spray?)
Barriers to penetration (Waxy, hairy or thick leaves?)
Method of application (foliar spray, boom spray, stump paint, hack & squirt)

Other
Product interactions or compatibility issues
Order of mixing into the tank mix

How to choose an adjuvant

We recommend that once you decide which herbicide to use, you should contact your local (county or otherwise) weed coordinator, agriculture commissioner, and/or your local university weed extension agent for suggestions. Some herbicide companies, such as DuPont (2000, 2001), produce lists of brand-name adjuvants that are approved for use with their herbicides, but most companies do not. Local representatives from the herbicide companies (or their technical help phone lines), as well as your local chemical supplier or dealer, may also suggest adjuvants that enhance the effects you want from an herbicide.

California and Washington have some of the strictest state regulations for herbicides and adjuvants. In order for an adjuvant to be registered in these two states, the adjuvant company must divulge all product ingredients, list all registered components on the label, and submit efficacy data to prove the product will do what the company says it will. To see if the adjuvant that you are interested in using is labeled in these states, see:

http://www.cdpr.ca.gov/docs/label/labelque.htm#regprods
http://picol.cahe.wsu.edu/LabelTolerance.html

Box 3. Tips for adjuvant selection (from Brian Carroll of the Helena Chemical Company 2001)

- Read labels, but remember that adjuvants are not regulated on the federal-level by the U.S. EPA, and are therefore not held to any strict standards.
- Always consult your local agriculture extension agent, local weed coordinator, or local chemical dealer
- Calculate the cost of adjuvant based on % active ingredient
- Be familiar with the adjuvant company and salesperson-are they reputable?
- Look for a California or Washington registration number on the label – these states require all adjuvant products sold within the state to be registered with their state's equivalent to the U.S. EPA. To be registered, the company must divulge all product ingredients, list all registered components on the label and submit efficacy data to prove the product will do what the company says it will do
- Buy high-quality adjuvants
- It is not always necessary or desirable to add an adjuvant
- Use good application techniques and calibrate equipment often.

A complete and up-to-date listing of all currently available adjuvants, listed by name and by type, is available in the Compendium of Herbicide Adjuvants, prepared by Bryan Young (2000) of Southern Illinois University. This compendium is available hardcopy for $3.00, or can be viewed online at http://www.herbicide-adjuvants.com/index.html.

Cautions about adjuvant use

Always follow the herbicide label for mixing instructions and proportions to use. U.S. EPA-approved label directions have the full force of federal law behind them, and must be followed for lawful herbicide application. Consider how the resulting formulation (herbicide plus adjuvants) will affect populations of desirable native plants and other organisms. Will the adjuvant increase damage to the desirable plants to unacceptable levels? If the formulation is likely to do more harm than good overall, do not use it. Also consider the timing of your application. For example, plants under stress (drought, etc.) do not translocate herbicides as well as fast-growing, healthy plants and are therefore *more* difficult to kill with herbicide (Pringnitz 1998).

Adding more than one adjuvant to a tank mix adds complexity, because different products may interact and interfere with one another, and/or it may be illegal to combine them (Pringnitz 1998). Read labels of each product you intend to add to the mix to determine if there are any restrictions regarding their use. Remember that in most states, adjuvants are not regulated, so you may need to take extra care to determine whether they will perform as advertised. Compare the quantity of active ingredients in similar types of additives to help determine value. Be wary of any product that makes exaggerated claims.

Herbicide (Examples of common brands)	**Box 4. Recommended* adjuvant *types*, for the herbicides listed in this handbook**
2,4-D (many brands)	Most brands recommend adding a nonionic surfactant; may be mixed with a nitrogen fertilizer or crop oil concentrate
Clopyralid (Transline®, Stinger®)	Nonionic surfactant
Fluazifop-p-butyl (Fusilade DX®)	Nonionic surfactant or crop oil concentrate
Fosamine ammonium (Krenite S®)	Oil-based surfactant suggested
Glyphosate (RoundUp Original®)	Adjuvants already added; nonionic surfactant or ammonium sulfate may also be added
Glyphosate (RoundUp Ultra®)	Adjuvants already added; ammonium sulfate may also be added
Glyphosate (Rodeo®, Aquamaster®, Glypro®)	Nonionic surfactant
Hexazinone (Velpar L®)	No recommendations on label
Imazapic (Plateau®)	Methylated seed oil or crop oil concentrate; nonionic surfactant; silicone-based surfactant; fertilizer-surfactant blends
Imazapyr (Arsenal®)	Methylated seed oil or crop oil concentrate; nonionic surfactant; silicone-based surfactant; fertilizer-surfactant blends
Picloram (Tordon K®, Tordon 22K®)	Nonionic surfactant
Sethoxydim (Poast®, PoastPlus®)	Methylated seed oil or crop oil concentrate; urea ammonium nitrate or ammonium sulfate (not recommended in Pacific Northwest, not allowed in California)
Sethoxydim (Vantage®)	Adjuvants already added, none needed
Triclopyr (Garlon 3A®, Garlon 4®)	Nonionic surfactant

*Recommended from herbicide labels. Be sure to always follow the label instructions for specifics on choosing and mixing herbicides and adjuvants.

REGULATION OF ADJUVANTS

As of 2003, regulatory agencies in the U.S. still pay relatively little attention to the regulation of adjuvants for herbicides. In the absence of consistent labeling laws, thousands of different formulation and brands of adjuvants are marketed and sold without consistent ingredient lists or proper scientific trials (Swisher 1982). This lack of regulation is probably at least partially the result of the role of adjuvants in reducing overall rates of pesticide use in the U.S. and because adjuvants have historically been perceived as 'inert' or GRAS (generally regarded as safe) compounds.

The U.S. EPA has exempted about 2,500 chemical compounds from restrictions for use as adjuvants, and therefore, does not require that they be tested and registered. The 1996 Food Quality Protection Act (FPQA), however, is eliminating the 'inert' classification and changing how adjuvants will be regulated. FPQA requires that the U.S. EPA review all adjuvant exemptions to ensure "reasonable certainty of no harm." As of early 2003, there has been little action and resources from the U.S. EPA to begin this testing or to regulate adjuvants. A few states however, have their own laws regarding adjuvants. For instance, California and Washington both regulate adjuvants and require the disclosure of their ingredients, data from efficacy trials, and environmental and toxicological studies.

Prompted by regulations at the state-level, concern regarding product quality, and government proposals to require full disclosure of ingredients, the adjuvant industry has started to self-regulate (Green 2001; Underwood 2000). There is currently a movement by the Chemical Producers and Distributor Association (CPDA) to require a certification process based on 17 standards for labeling and manufacturing, but this has not yet been fully implemented. These adjuvant producers also state that they intend to hold properly designed experimental trials and to make these results available to the herbicide companies as well as to consumers (Green 2001).

ENVIRONMENTAL FATES OF ADJUVANTS

The long-term fates of most adjuvants in soils and elsewhere in the environment are largely unknown, partially because of the lack of long-term monitoring data, but also because the ingredients in most adjuvants are not disclosed. Most adjuvant labels or Material Safety Data Sheets (MSDSs) include information on the adjuvant's physical properties (boiling and freezing points, specific gravity, evaporation point, etc.), fire and explosion hazard data, reactivity data, and health hazard data. Unlike herbicide labels however, most adjuvant labels or MSDSs do not include information of the compound's behavior or fates in the environment (in plants and soil). Most adjuvant labels and MSDSs also do not describe the adjuvant's mechanism of action, rates of metabolism within plants, rates of photodegradation or microbial degradation, persistence (half-life) in the environment, potential for volatilization, or potential mobility in soil or water.

It is known that many surfactants adsorb to soil particles (Bayer & Foy 1982). Because of this, surfactants tend to be less toxic to plants in soil than to plants growing in water or other aqueous solutions or in nutrient culture alone (Bayer & Foy 1982). Adjuvants from different chemical groups have different effects and toxicities in different soil types. For instance, when applied directly to soils (as in pre-emergence herbicide formulations), ester adjuvants tend to have greater impacts in sandy soils while ether adjuvants are most effective on clay soils. Adjuvants that are alcohols are most effective in soils with high levels of organic matter.

TOXICITY OF ADJUVANTS

Although adjuvants are typically categorized as “inert” or “essentially non-phytotoxic” (i.e. not toxic to plants) compounds, many can produce wide ranging effects on physiological and metabolic processes within plants, animals, and/or microorganisms (Norris 1982; Parr & Norman 1965). Almost all of these effects can occur at low concentrations or doses. Some adjuvants can have pronounced effects on biochemical processes, including enzyme activity. Some can disrupt or otherwise alter biological membranes, which affect the quantity and rate of uptake and movement of nutrients and other materials within plants. Some adjuvants may create changes in cell membrane permeability or enzyme activity. Some can deter seedling germination, but the level of impact varies among plant species. Adjuvants can enter plants through their leaves, stems or roots. Plant roots tend to be extremely sensitive to adjuvants in nutrient solutions since their fine roots have no waxy cuticle layer to prevent absorption, unlike leaves and stems.

The effects of some adjuvants are subtle and transitory, but the impacts of others can be long lasting (Parr & Norman 1965). Parr (1982) reports that some surfactants produce either stimulatory or inhibitory effects on the growth and metabolic processes of biological systems, depending on the plant species, and the chemistry, concentration, and dose of the surfactant. There is typically a dose response when adjuvants are used, meaning that an adjuvant may have no effect at relatively low concentrations, be stimulating at intermediate concentrations, and toxic at high levels (Norris 1982). For instance, most surfactants work to decrease surface tension at the spray droplet-leaf cuticle interface, and this reduction is typically maximized at concentrations ranging from 0.01 to 0.1%. However, pronounced toxic effects in plants can be found once surfactant concentrations become greater than 0.1%. Some plants are stimulated to grow by nonionic surfactants when applied up to 0.001%, but these same compounds have phytotoxic effects at a mere 0.005%. Cationic surfactants repressed algal growth at concentrations of only 0.0005%, but after 2 weeks, growth was stimulated, indicating that these effects can be transitory depending on the surfactant used (Parr 1982).

Some adjuvants can have adverse effects on aquatic species, and certain types can be extremely toxic to fish and shellfish. Some adjuvants (such as the surfactant MONO818® in RoundUp®) are toxic to fish and also interfere with cutaneous respiration in frogs and gill respiration in tadpoles (Tyler 1997 a,b; Folmar et al. 1979). Parr (1982) reports that some adjuvants caused noticeable alterations in fish gill tissue, and that the toxicity of these adjuvants increased as exposure time increased. Other adjuvants can inhibit bacteria by disrupting their cell membranes (Norris 1982). Earthworms incubated in soil with a cationic surfactant, however, showed no detrimental effects even after a 90-day exposure (Bayer & Foy 1982). “Normal” environmental exposure levels of surfactants and emulsifiers to humans, however, would appear to be negligible based on the extremely high dosages that are typically necessary to cause toxic responses in mammals (Parr 1982).

TYPES OF ADJUVANTS

There are many ways to classify adjuvants, and there is currently no standard system used by all adjuvant or herbicide manufacturers. A good review of different adjuvant terms and definitions can be found in Hazen (2000) or in Van Valkenburg (1982). In this chapter, we divide adjuvants into two primary types based on their functions: activator adjuvants and utility adjuvants (Hess

1999; Kirkwood 1994). Activator adjuvants enhance the activity of the herbicide, often by increasing rates of absorption of the herbicide into the target plant(s). Utility adjuvants, which are sometimes called spray modifiers, alter the physical or chemical characteristics of the spray mixture making it easier to apply, increasing its adherence to plant surface so that it is less likely to roll off, or increasing its persistence in the environment.

When deciding which type of adjuvant to use, remember to always read and follow the directions on the herbicide label.

Activator Adjuvants

Activator adjuvants are compounds that when added to the spray tank, enhance herbicide activity (Penner 2000a). Activator adjuvants include surfactants, oil carriers such as phytobland (not harmful to plants) oils, crop oils, crop oil concentrates (COCs), vegetable oils, methylated seed oils (MSOs), petroleum oils, and silicone derivatives, as well as nitrogen fertilizers. Some brands of herbicide formulations already include activator adjuvants (e.g. RoundUp Ultra® contains the herbicide glyphosate and a surfactant, and Pathfinder II® which contains the herbicide triclopyr, an oil carrier which is an activator, and a dye which is a utility adjuvant).

Oils are sometimes used alone as contact herbicides and in other situations as adjuvant carriers for synthetic herbicides. Salts may also be used as activator adjuvants, often to fertilize and enhance the growth of the target plant in the short-term, which can increase the uptake and effect of the herbicide in the slightly longer term. Salt adjuvants of this type are used extensively in crop agriculture and in some rangelands, but are rarely appropriate in wildlands.

Surfactants

Surfactants are the most widely used and probably the most important of all adjuvants (Miller & Westra 1998). The name is derived from **surf**ace **act**ive age**nts** and these compounds facilitate or enhance the emulsifying, dispersing, spreading, sticking or wetting properties of the herbicide tank mix (includes spray modifiers). Surfactants reduce surface tension (see Box 5) in the spray droplet, which ensures that the formulation spreads out and covers plants with a thin film rather than beading up. This facilitates herbicide absorption into the plant. Surfactants can also directly influence the absorption of herbicides by changing the viscosity and crystalline structure of waxes on leaf and stem surfaces, so that they are more easily penetrated by the herbicide (Kirkwood 1999; Coret et al. 1993).

Some herbicide formulations come with a surfactant already added, but most require the addition of a surfactant for good control results. Surfactants are generally not added to pre-emergent herbicides that are applied directly to soil (Miller & Westra 1998).

Box 5: Surface Tension

All fluid surfaces exhibit a phenomenon called "surface tension." Surface tension results because molecules in a pure fluid are attracted strongly to each other, but molecules on the surface of a fluid are not completely surrounded by other fluid molecules and so have unmatched forces. These unmatched forces contain potential energy. Nature strives to disperse energies, and in this case works by minimizing the surface area of the fluid surface, which in turn minimizes the number of unmatched molecules and therefore minimizes potential energy. The unmatched molecular forces on the surface of the liquid also tend to form a barrier between the volume of fluid and its surroundings, much like an elastic skin.

It is surface tension that makes droplets become spherical in shape, and makes water bead up on glass. A sphere has the minimum possible surface area for a given volume of liquid. Surface tension influences the sizes of droplets in a spray, rates of evaporation, the likelihood that droplets will roll off leaves, etc. Static or equilibrium surface tension (EST) is the surface tension strength of well-established surfaces, while dynamic surface tension (DST) is the surface tension strength of new or highly disturbed surfaces, such as the surface of a newly formed spray droplet, or the surface of a droplet striking a leaf surface.

Increasing the concentration of a surfactant in a tank mix generally decreases DST, which in turn increases the probability that a droplet will adhere to a leaf and spread onto its surface, thus improving penetration of the herbicide through leaf cuticle. Adding too much surfactant, however, can sometimes negatively affect this wetting and spreading ability. For instance, some surfactants work by increasing droplet size to decrease DST, and are thus less prone to drift. If too much surfactant is added however, these larger spray droplets may roll or fall off, therefore being less likely to adhere to a leaf surface. Hence, more adjuvant does *not* necessarily translate into better control results.

Surfactants work by improving contact between spray droplets and plant surfaces, and enhance absorption by:

1. Making the spray solution spread more uniformly on the plant
2. Increasing retention (or 'sticking') of spray droplets on the plant
3. Increasing penetration through hairs, scales, or other leaf surface structures
4. Preventing crystallization of spray deposits
5. Slowing drying and increasing water retention in the spray droplets

The effectiveness of a surfactant is determined by environmental conditions, characteristics of the target plant, and by interactions between the surfactant and the herbicide. Surfactants contain varying amounts of fatty acids, which are compounds capable of binding to two types of surfaces, such as oil and water. It is important that the degree of solubility of the surfactant in oil or water match the solubility of the herbicide. The Hydrophilic –Lipophilic Balance (HLB) is a measure of the balance between hydrophilic (water-soluble) and lipophilic (oil-soluble) components in fatty acids (see Box 6). A surfactant's HLB can therefore indicate the conditions under which the surfactant will perform best.

<u>Box 6: Hydrophilic-Lipophilic Balance (HLB)</u>

Surfactants contain both hydrophilic and lipophilic components (this is called amphiphatic). The hydrophilic-lipophilic balance (HLB) is a measure of the molecular balance of the hydrophilic and lipophilic portions of the compound. Many herbicides have an optimum surfactant HLB, and surfactants that most closely match a particular herbicide's optimum HLB will optimize the formulation's spread on and penetration into plants. <u>Unfortunately, information about the HLB of most surfactant products is not available</u> or hard to find, and so matching them appropriately is difficult (Green 2001).

For nonionic surfactants, the optimum surfactant HLB for a herbicide can be predicted based on the solubility of the herbicide in water (Griffen 1954 *in* Green 2001). For ionic surfactants, the HLB can be estimated by observing their dispersablity in water (with no dispersion = 1 to 3; poor dispersion = 3 to 6; unstable milky dispersion = 6 to 8; stable milky dispersion = 8 to 10; translucent to clear dispersion = 10 to 13; and clear solution = 13+).

Typically, low HLB surfactants work best with water insoluble herbicides, while high (>12) HLB surfactants work best for water-soluble herbicides. For example, surfactants with a high HLB are more active with the hydrophilic herbicide glyphosate, while more lipophilic, low HLB surfactants are more active with the lipophilic quizalofop-P ester. Surfactants with intermediate HLB values are the most active with intermediately soluble nicosulfuron. Additionally, low HLB surfactants permit the formation of invert emulsions (water-in-oil). Mid- and upper-range HLB may be wetting agents or for oil-in-water emulsions, and high HLB surfactants are often used as detergents or solubilizers. One the other hand, a surfactant that is incorrectly matched may even deactivate a herbicide (Gaskin & Holloway 1992)

Nonionic Surfactants

Nonionic surfactants are the most commonly recommended and used adjuvants. Labels for most post-emergent herbicides used in wildlands that do not already contain a non-ionic surfactant often recommend the addition of one. Nonionic surfactants have no ionic charge and are hydrophilic (water-loving). They are generally biodegradable and are compatible with many fertilizer solutions. Some nonionic surfactants are waxy solids and require the addition of a cosolvent (such as alcohol or glycol) to solubilize into liquids. Glycol cosolvents are generally preferred over alcohols, as the latter are flammable, evaporate quickly, and may increase the number of fine spray droplets (making the formulation likely to drift when sprayed). The adjuvant label or MSDS should specify the active ingredient (alcohol, glycol, ether, etc.) of the adjuvant product.

<u>Organosilicone and silicone surfactants</u> are two types of nonionic surfactants. Organosilicone surfactants drastically reduce surface tension to the point where the herbicide droplets thin and coalesce to form a thin layer on the leaf surface (known as "superspreading"). They can even reduce surface tension to the point that some of the formulation may be able to slide through the microscopic stomatal openings on leaf surfaces. Once through the stomates however, the herbicide formulation must still penetrate the thin cuticle and cell membranes of the cells that line the cavity below the stomates.

Silicone surfactants also decrease surface tension and may allow spray solutions to penetrate the stomates. They can also make the formulation nearly impossible to wash off (rainfast) even if it rains shortly after they are applied (Green 2001; Roggenbuck et al. 1993). Silicone surfactants can also influence the amount/rate of herbicide that is absorbed through the cuticle.

Ionic Surfactants

Ionic surfactants possess either a positive (cation) or a negative (anion) charge, and can pair readily with oppositely charged herbicides, increasing the solubility of polar herbicides in water. Ionic surfactants may complex with other compounds in the mix (including contaminants in the water) in unexpected ways, and this can interfere with their function. For this reason, nonionic surfactants are more commonly recommended.

Ionic surfactants are not often used in wildland settings, but are frequently used in agriculture. The most common cationic surfactants used in agriculture may be the tallow amine ethoxylates, which are often used with glyphosate. The most common anionic surfactants are sulfates, carboxylates, and phosphates attached to lipophilic hydrocarbons.

Amphoteric Surfactants

Amphoteric surfactants contain both a positive and negative charge and typically function similarly to nonionic surfactants. A commonly used amphoteric surfactant is lecithin (phosphatidylcholine), which is derived from soybeans. There is little published research on the use and efficacy of amphoteric surfactants.

Oil Adjuvants

Oil adjuvants can increase the penetration of oil-soluble herbicides into plants, and are commonly used when conditions are hot and dry, and/or when leaf cuticles are thick. They are derived from either refined petroleum (mineral) oils or from vegetable oils (including seed oils), and do not readily mix with water. Therefore, when an oil adjuvant is combined with water in a spray tank, a surfactant emulsifier must also be added, which distributes the oil droplets (micelles) uniformly throughout the mix. These “emulsifiable oil” adjuvant combinations typically contain both a non-phytotoxic oil (typically ranging 80 to 99%) and a surfactant (1 to 20%), and are added to the spray tank usually as just 1% of the total spray volume (Hess 1999).

Emulsifiable oil adjuvant blends can enhance the absorption of an oil-soluble herbicide into the plant more than an oil adjuvant by itself. Adding a surfactant to the mixture not only emulsifies the oil in the water-based spray solution, but also lowers the surface tension of the spray solution. These adjuvants can also increase herbicide absorption through the plant cuticle, increase spray retention on leaf surfaces, and reduce the time needed for the herbicide formulation to become rainfast (Pringnitz 1998; Miller & Westra 1996). The exact mode of action of these oils is unknown, but they enhance the spread of droplets on plant surfaces (Gauvit and Cabanne 1993 *in* Green 2001). They may also split open the cuticle and increase both the fluidity of cuticular components and herbicide diffusion rates (Santier & Chamel 1996 *in* Green 2001).

Two types of emulsifiable oil adjuvants are “crop oils” and “crop oil concentrates” (COC). Crop oils contain up to 5% surfactant and COCs may contain up to 20% surfactant (Hess 1999). COCs enhance spreading and penetration and are used primarily with grass-specific herbicides (Miller & Westra 1996). Crop oils and COCs do not necessarily contain oil derived from crop plants (although some do), but are so named because they are intended for application to crops (Pringnitz 1998).

Petroleum oils

Petroleum oils or petroleum oil concentrates are highly refined oils, which are often used as carriers of oil-soluble herbicides. They are typically used in low quantities (generally 0.25 to 1 gallon/acre), and when used as carriers, can reduce surface tension, increase wetting and spreading, give quicker absorption, improve rainfastness, and reduce loss of carrier during and after application (Bohannan & Jordan 1995 *in* Green 2001).

Petroleum oil concentrates may include paraffinic and napthalenic oils. Paraffinic oil can smooth epicuticular wax, or cause cracks in the cuticle, allowing increased herbicide penetration (Foy & Smith 1969 *in* Green 2001). Paraffinic oils are sometimes referred to as dissolving waxes, but in fact, paraffinic oils are poor solvents and only soften wax.

Vegetable oils

Vegetable-derived oils (from soybeans, cottonseeds, etc.) also decrease surface tension, but they are not as effective as other surfactants at increasing spreading, sticking, or penetration (Miller & Westra 1996). Vegetable oils are generally of two types: triglycerides or methylated oils. Triglycerides are essentially oil-surfactant hybrids, and are generally called "seed oils." These seed soils are extracted from plants by pressing or solvent extraction, and tend to have higher viscosities than methylated oils. Triglyceride oils usually contain only 5 to 7% surfactant emulsifier, while methylated seed oils contain 10 to 20% surfactant.

Methylated seed oils (MSO) are better solvents than petroleum-based oils, but their role as a solvent of cuticular waxes is controversial. The composition of these oils varies depending on the seed source and can influence efficacy (Nalewaja 1994). Esterified seed oils are vegetable-seed oils with a surfactant or an emulsifier already added. They have good spreading and penetration properties, but tend to be more expensive than other oil adjuvants.

Ammonium (Nitrogen) Fertilizers

Ammonium, or nitrogen, fertilizers are often added to herbicide mixes in range and row-crop agriculture situations, where the addition of fertilizer works to both enhance herbicidal effects as well as to stimulate the growth of desirable crop or forage plants. Ammonium fertilizers can function as utility adjuvants, because they help prevent the formation of precipitates in the tank mix or on the leaf surface. They also decrease surface tension, increase spreading of the herbicide on the leaf surface, neutralize ionic charges, and increase herbicide penetration into the leaf (Nalewaja & Matysiak 2000). Ammonium fertilizers are used primarily with broadleaf-specific herbicides (Miller & Westra 1996; Wanamarta et al. 1993).

Ammonium fertilizers used as adjuvants include urea-ammonium nitrates (UAN), ammonium sulfates, ammonium nitrates and ammonium polyphosphates. Although their exact mode of action in herbicide control is unknown, they are often used to enhance the postemergence activity of weakly acidic herbicides, primarily by increasing herbicide absorption. The activity of ammonium fertilizers is strongly herbicide- and species-specific, and is probably dependent on several mechanisms.

Ammonium sulfates are also used to reduce antagonism by hard water ions in spray solutions. Iron, zinc, magnesium, sodium, potassium and calcium ions can react with certain herbicides (such as 2,4-D and glyphosate) to form precipitates or herbicide salts, decreasing the efficacy of those herbicides (Nalewaja and Matysiak 1993). Ammonium sulfate prevents the formation of the calcium salt of glyphosate (Thelen et al. 1995), and is recommended in most areas with hard water (Hartzler 2001).

Utility Adjuvants (including Spray Modifiers)

Utility adjuvants are added to improve the application of the formulation to the target plants. By themselves, they do not directly enhance herbicidal activity (McMullan 2000). Instead, they change the physical or chemical properties of the tank mix in ways that make it easier to apply to the target plant(s), minimize unwanted effects, and broaden the range of conditions under which a given herbicide formulation can be effective.

Most utility adjuvants are typically not used in wildland situations, since herbicides applied in wildlands are generally not applied aerially, with large booms, or in tank mixtures with several herbicides and other additives. Examples of the different types of functions that different utility adjuvants have are listed below. There is some overlap of these functional categories. Some activator adjuvants are also utility adjuvants and some even have herbicidal effects of their own.

Wetting or Spreading Agents

Wetting agents or spreading agents lower surface tension in the spray droplet, and allow the herbicide formulation to form a large, thin layer on the leaves and stems of the target plant. Since these agents are typically nonionic surfactants diluted with water, alcohol, or glycols (Hazen 2000), they may also function as activator adjuvants (surfactants). However, some wetting or spreading agents affect only the physical properties of the spray droplets, and do not affect the behavior of the formulation once it is in contact with plants.

Dyes

Dyes are commonly used for spot or boom spraying. We recommend the use of a dye for most herbicide treatments in wildlands even if applied with small handheld sprayers or wicks because the presence of a dye makes it far easier to see where the herbicide has been applied and where it has dripped, spilled or leaked. Dyes make it easier to detect missed spots and to avoid spraying a plant or area twice. It is never appropriate to use food coloring or any other substances that have not been approved or labeled by the U.S. EPA for use as herbicide adjuvants.

Drift Control & Foaming Agents

Drift control agents are designed to reduce spray drift, which most often results when fine (< 150 μm diameter) spray droplets are carried away from the target area by breezes, including those caused by the aircraft or vehicle carrying the spray equipment (Downer et al. 1998). Drift control agents alter the viscoelastic properties of the spray solution, yielding a coarser spray with greater mean droplet sizes and weights, and minimizing the number of small, easily-windborne droplets (Hewitt 1998). These agents are typically composed of large polymers such as polyacrylamides, and polysaccharides, and certain types of gums.

Foaming agents also act as drift control agents. When used with specialized nozzles, these agents create foams with different degrees of stability (Witt 2001). These foams can be placed more precisely than standard liquid sprays, and are sometimes used to mark the edge of spray applications. Foams ensure complete coverage without over-spraying. Foaming agents are usually added in quantities of 0.1 to 4.0% of the entire spray mixture (McWhorter 1982).

Thickening Agents

Thickening agents can modify the viscosity of spray solutions and are used to reduce drift, particularly for aerial applications (Witt 2001). They are used primarily in agriculture. Thickening agents may include water swellable polymers that can produce a "particulated solution," hydroxyethyl celluloses, and/or polysaccharide gums. Viscosity can also be increased by making invert emulsions (follow directions on individual herbicide labels) of the spray solution. The compatibility of the thickening agent with the tank mix can be influenced by the order of mixing, pH, temperature, and/or the salt content of the tank solution. Thickening agents are typically used in areas where sensitive populations or crops are growing close to treated areas (McWhorter 1982).

Deposition Agents (Stickers)

Deposition agents, or stickers, are used to reduce losses of formulation from the target plants due to the droplets evaporating from the target surface, or beading-up and falling off. Spray retention on difficult-to-wet leaf surfaces is regulated by the degree of surface tension and energy dissipation during the spray process. Deposition agents such as guar gum can reduce surface tension while increasing the viscoelasticity of the droplets (Bergeron et al. 2000). Stickers keep the herbicide in contact with plant tissues by remaining viscous, and therefore resist being washed-off by rain or knocked off by physical contact. Stickers are generally the most useful with dry wettable powder and granule formulations (Hazen 2000).

Film-forming vegetable gels, emulsifiable resins, emulsifiable mineral oils, vegetable oils, waxes, and water-soluble polymers can all be used as stickers (Witt 2001). Fatty acids (technically anionic surfactants) are frequently used as stickers, and although they are "naturally derived" and are typically considered safe, they may have considerable contact activity. Certain oils may also function as stickers, but only if they have a low degree of volatility (Hazen 2000).

Water Conditioners
Water conditioners are frequently added when the water used in the formulation is high in salts in order to minimize or prevent reactions between ions in the spray solution and the herbicide, which would result in the formation of precipitates or salts. When there are many cations present, as in hard water, they can react with the herbicide, decreasing the uptake and effect of the herbicide. For instance, high levels of calcium in water (hard water) reduce the control efficacy of glyphosate (Nalewaja & Matysiak 1993). Similarly, sodium bicarbonate reduces the efficacy of sethoxydim (Matysiak & Nalewaja 1999). A water conditioner, such as ammonium sulfate (which also happens to be a nitrogen fertilizer), can negate this effect for both glyphosate and sethoxydim (McMullan 2000).

Compatibility Agents
Compatibility agents prevent chemical and/or physical interactions between different herbicides and fertilizers that could lead to non-homogeneous or unsprayable mixtures when these compounds are combined. For instance, if the herbicides bentazon and sethoxydim are mixed, they may react to form precipitates, resulting in reduced rates of sethoxydim penetration (Wanamarta et al. 1993). In most cases, the herbicide label will state which herbicides may or may not be mixed together.

Some herbicides are applied with fertilizers or fertilizer solutions, especially in agricultural settings. Compatibility agents are used to keep these herbicides in suspension, and are generally added with a liquid fertilizer (Witt 2001). Most herbicides can be applied in nitrogen solutions without any compatibility problems, but compatibility may be poor when the water contains high levels of various salts (hard water), or when the water is unusually cool. When 2,4-D is applied with liquid-nitrogen fertilizers the solution may separate even if mixed vigorously unless a compatability agent is added to the mix.

pH Buffers
pH plays a large role in herbicide efficacy. The pH of the tank mix affects the half-life solubility and efficacy of the herbicide, and may determine whether or not precipitates form (McMullan 2000). Being able to buffer or otherwise control changes of pH in the tank mix can be important in preventing herbicides from being degraded by acid or base hydrolysis in aqueous solutions. Some herbicides are sold with a pH buffer already included. Adjuvants that adjust or buffer pH can also improve the herbicide's dispersion or solubilization in the mix, control its ionic state, and increase tank-mixture compatibility. pH buffers are most beneficial when used in extremely alkaline or acid water, which could otherwise have detrimental effects on the herbicide's performance (McWhorter 1982).

Humectants
Humectants, like stickers, increase the amount of time that the herbicide is on the leaf, in a form available for uptake (Hazen 2000). When water evaporates from the spray droplet and the herbicide becomes a crystalline residue, it is no longer available for uptake into the leaf. Humectants keep the spray deposit moist and in true solution, and therefore extend the time that it is available for absorption (Hess 1999). They are generally water-soluble and increase the water content of spray deposits by slowing the drying time or by drawing moisture from the environment. Commonly used humectants include glycerol, propylene glycol, diethylene glycol,

polyethylene glycol, urea, and ammonium sulfate. Even glucose and molasses were used as humectants in the past, but they are not labeled for such use and should not be added to any herbicide formulation.

Defoaming and Antifoam Agents
Defoaming and antifoam agents reduce or suppress the formation of foam in spray tanks (Witt 2001). Many spray mixtures have a tendency to foam excessively, especially when mixed with soft water, which can cause problems during mixing (foam overfill) or when rinsing the sprayer (McMullan 2000). Most defoamer agents are dimethopolysiloxane-based, but silica, alcohol, and oils have also been used for this purpose. Defoaming agents can reduce surface tension, physically burst the air bubbles, and/or otherwise weaken the foam structure. In general, it is easier to prevent foam formation than to eliminate foam after it forms (Green 2001). Antifoam agents are usually dispensed from aerosol cans or plastic-squeeze bottles, and are added directly to the mix at the onset of foam formation. The highest concentration needed for eliminating foam is typically about 0.1% of the entire tank. Some applicators in agricultural settings even use kerosene or diesel fuel at about 0.1% for eliminating foam in spray tanks, but this is not recommended in natural areas.

UV Absorbents
Natural sunlight, especially ultraviolet light, may degrade some herbicides (Green 2001). A few adjuvants that protect herbicides from the deleterious effect(s) of sunlight are available. They may do this by either physical or chemical processes, such as by increasing the rate of herbicide uptake into the cuticle, or by absorbing the UV-light themselves.

A FEW EXAMPLES OF COMMONLY USED HERBICIDES AND ADJUVANTS IN NATURAL AREAS

The choice of herbicide and adjuvant to be used will depend on the target weed, site and environmental conditions, cost of chemicals, and in some cases, on state regulations. The herbicides and adjuvants listed below are not necessarily examples of the best combinations to use, but these mixes have been used in a few natural areas with some success. Examples are given only for glyphosate and triclopyr, and contact information for the mentioned land managers follow these examples.

GLYPHOSATE

RoundUp Pro®
Andropogon virginicus (broomsedge), *Paspalum conjugatum* (buffalograss), *Melinis minutiflora* (molasses grass) and *Setaria palmifolia* (palmgrass)
Pat Bily (TNC-Hawaii) used a 2% solution of RoundUp Pro® with water-soluble packets of blue Turfmark® dye for foliar applications in Hawaii. A surfactant was already included in the RoundUp Pro® formulation so there was no need to add any other adjuvants.

Panicum repens (torpedo grass) and *Urochloa distichya* (Tropical signalgrass)
Mike Renda and Jovan Dodson (TNC-Florida) used a 2% solution of RoundUp Pro® with SunEnergy® surfactant (applied at 1oz/gallon) for foliar applications.

Rodeo®
Phragmites australis (common reed) and *Rosa multiflora* (multiflora rose)

Curtis Hutto (Virginia Dept. of Cons. & Rec.) reports a 90% kill rate for common reed and multiflora rose using a 2% solution of Rodeo® with 0.5% TL-90® non-ionic surfactant, applied with a backpack or ATV-mounted sprayer. Curtis adds that it will take 2 successive fall applications to multiflora rose to achieve a 90% mortality rate. It takes 2 or 3 applications to get a 90% kill rate on common reed.

Mimosa pigra (catclaw mimosa), *Lygodium japonicum* (Japanese climbing fern), *Panicum repens* (torpedo grass), *Paederia foetida* (skunkvine), *Lantana camara* (lantana), *Solanum viarum* (tropical soda apple) and *Imperata cylindrica* (cogon grass)
Michael Jenkins (Florida Park Service) reports excellent control (>95% kill) results with a 4% solution of Rodeo® plus a 0.3% solution of either Silken® or Kinetic® organosilicone surfactant to catclaw mimosa foliage. He also reports excellent control on Japanese climbing fern, torpedo grass, skunkvine, lantana, and tropical soda apple with a 2.5% solution of Rodeo® plus a 0.3% solution of Silken® or Kinetic®. He has also controlled cogon grass using a 1% solution of Rodeo® with 0.3% solution of Silken® or Kinetic®, applying it on foliage in late fall.

Phalaris arundinacea (reed canarygrass)
Mandy Tu (TNC-Oregon) reports good control of reed canarygrass by first mowing in late spring-early summer at the onset of flowering, then applying a foliar spray of Rodeo® in a 2% solution with either 0.5% Bio-88® or R-11® nonionic surfactant in fall, before the first frost. The formulation can be applied with a backpack sprayer or an ATV with a boom attachment.

Typha spp. (cattails)
Russ McClain (TNC-West Virginia) reports near 100% kill of cattails in West Virginia by combining 2.5 gallons Rodeo®, 1 quart Surf-Ac 820® nonionic surfactant plus Blazon® blue turf dye and 7.25 gallons of water to make 10 gallons of tank mix. Since cattails often grow in sensitive wetland areas, Russ recommends applying the formulation using the "bloody glove" or "glove of death" (herbicide soaked cotton gloves worn over rubber or nitrile gloves, and stroked over the target weed leaf surfaces) technique for minimal off-target effect.

Accord®
Hypericum perforatum (St. Johnswort), *Lythrum salicaria* (purple loosestrife), and *Phalaris arundinacea* (reed canarygrass)
Jack McGowan-Stinski (TNC-Michigan) uses Accord® herbicide in a 2.5% a.i. with Hi-Light Dye® tablets (1 tablet per gallon mix) for the control of St. Johnswort. He applies the formulation to St. Johnswort foliage by either wicking using a modified exterior sponge PVC adapted to a Solo® backpack sprayer, or by using a backpack sprayer. For purple loosestrife and reed canarygrass, he first cuts the stems then applies Accord® in a 5% a.i. solution with the Hi-Light Dye®, and applies the mix using either a backpack sprayer or a sponge wicking applicator to the stem and cut surface. Jack adds that the sponge wicking applicator gives extremely targeted applications with minimal off-target effects (see Appendix 1 for details on how to construct one of these applicators).

Rhamnus frangula (glossy buckthorn)
Jack McGowan-Stinski (TNC-Michigan) controls buckthorn shrubs using a cut-stump herbicide treatment. He first cuts each stem 6 inches above the ground surface, and within at most 5 minutes, applies Accord® in a 14% a.i. mix directly to that cut surface using a sponge-tipped applicator (see Appendix 1 for more details). He has also controlled buckthorn by wicking a 5% a.i. Accord® mix to the foliage with a specially made PVC tube tipped with a sponge applicator and connected to a Solo® backpack sprayer. Accord® can also be sprayed onto foliage using a 2% a.i. mix.

TRICLOPYR

Garlon 3A®
Polygonum cuspidatum (Japanese knotweed)
Jonathan Soll (TNC-Oregon) reports near 100% kill of knotweed using a 3 to 5% solution of Garlon 3A® with 1 oz/gallon Hasten® ethylated seed oil. For treatments near water, he uses a 3-5% solution of Garlon 3A® with 1 oz/gallon of R-11® nonionic surfactant. Jonathan recommends first cutting the stems in spring, then foliar spray the regrowth with a backpack sprayer in fall.

Foeniculum vulgare (fennel)

Bob Brenton and Rob Klinger (UC Davis) report near 95% kill of fennel in California by using 1 lb a.i./acre of Garlon 3A® with a 0.25% solution of Pro-Spreader® activator nonionic surfactant. They recommend using a backpack sprayer to apply to foliage in early spring.

Dioscorea bulbifera (air potato)
Michael Jenkins (Florida Park Service) reports good control of air potato with a 2.5% solution of Garlon 3A® plus a 0.3% solution of either Kinetic® or Silken® surfactant, applied as a foliar spray onto leaves.

Rosa multiflora (multiflora rose), *Elaeagnus umbellata* (autumn olive) and *Ailanthus altissima* (tree of heaven)
Curtis Hutto (Virginia Dept. of Cons. & Rec.) applied undiluted Garlon 3A® with no additional adjuvant, to cut stems of multiflora rose and autumn olive and achieved 100% mortality for those species. He found that the season of application did not matter for these species. He has also used undiluted Garlon 3A® with no adjuvant on tree of heaven, using a girdle and squirt (cut into bark with a girdling knife, squirt in herbicide using a spray bottle) technique which caused about 95% mortality.

Wedelia trilobata (trailing daisy)
Mike Renda and Jovan Dodson (TNC-Florida) report moderate control of trailing daisy using repeated treatments of a 2% solution of Garlon 3A® with1 oz/gallon CideKick II® surfactant. They also add TurfMark® dye (1 to 2 oz/gallon) for these foliar treatments.

Tibouchina herbacea (glorybush) and *Ulex europaea* (gorse)
Pat Bily (TNC-Hawaii) controls these two invasive species in Hawaii using a 2% solution of Garlon 3A® combined with a 0.2% solution of Breakthru® organosilicone surfactactant as a foliar spray. Pat adds that he obtains similar success by using either Sylwet L-77® or Sylgard® surfactants, applied using the same concentrations.

Garlon 3A® or Garlon 4®
Senna pendula (climbing cassia), *Colubrina asiatica* (Asiatic colubrina), *Schinus terebinthifolius* (Brazilian peppertree), *Casuarina equisetifolia* (Australian pine), and *Cupaniopsis anacardioides* (Carrotwood)
Mike Renda and Jovan Dodson (TNC-Florida) have also had excellent control of these woody invaders by using either a cut-stump treatment with a 50% solution of Garlon 3A® (in water), or a basal bark treatment with 10% Garlon 4® mixed with 90% JLB® oil solution. For both types of treatments, no other surfactants were used, but Turfmark® dye was added at a rate of 1 to 2 oz/gallon tank mix.

Garlon 4®
Rhamnus cathartica (common buckthorn)
Bill Kleiman (TNC-Illinois) reports good control results on common buckthorn with a solution of 20% Garlon 4® and 80% mineral oil using the basal bark application technique. He also adds Basal Red® dye at 3 oz/15 gallons to the tank mix.

Garth Fuller & Colin McGuigan (TNC-Minnesota) also report good control of buckthorn, but they use a cut-stump treatment using a solution of 25% Garlon 4® with 75% Diluent Blue®.

Tamarisk spp. (salt cedar, tamarisk)
Ian Torrence (National Park Service- Utah) reports good kill rates for salt cedar by using two different treatments and concentrations of Garlon 4®. He reports a 90 to 95% kill rate for a basal bark spray of 20% Garlon 4 in 80% JLB Oil Improved Plus® applied with a low-volume backpack sprayer. He reports a 80 to 85% kill rate using a cut-stump treatment with 25% Garlon 4® to 75% JLB Oil Improved Plus®. Ian reports good control with trees up to 6 inches in diameter using the basal bark method. For larger trees with thicker bark, Ian recommends the cut-stump method, where the tree is first cut at its base and herbicide immediate applied to the cut surface (using squirt bottles or brushes), especially to the outer cambium layer. Ian adds that JLB Oil Improved Plus® oil comes with a red dye already mixed in.

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ADJUVANT FAQs and TIPS:

Q: Are adjuvants necessary for good control results?
Adjuvants are necessary for best control results in most herbicide applications. Some brands of herbicide already include adjuvants and no others are needed.

Q: If adding adjuvants or surfactants at labeled rates can lead to increased rates of control efficacy…should I add more to get even better performance?
No! Do not add any more adjuvant than amounts specified on the label. Adding more adjuvant may lead to antagonistic effects between the adjuvant and the herbicide, rendering the mix useless. Using adjuvants above label rates may also cause unwanted damage to non-target plants, soils, and to surface or groundwater sources.

Q: Where do I find relevant information about herbicide and adjuvant compatibility?
The herbicide label or MSDS will specify the best type of adjuvant to use with that herbicide. It will also specify whether that herbicide can be mixed with any other herbicides and which ones.

Q: Are surfactants ok to use in wetland or aquatic situations?
Some surfactants (such as those included in RoundUp®) are toxic to fish, shellfish, and/or other aquatic invertebrates. When applying herbicides to areas over or adjacent to water (including wetlands), be sure to use only those herbicides and surfactants (and other adjuvants) specifically approved for aquatic use. In general, adjuvants (particularly surfactants) will not improve herbicide effectiveness against submerged aquatic weeds, but they may be important for use on emergent aquatic and riparian plants.

Q: Are surfactants necessary in cut-stump applications?
It is probably not necessary to use a surfactant in most cut-stump applications. This may be, in part, because there is no waxy cuticle layer on a cut stump.. Jack McGowan-Stinski (TNC-Michigan) has had success using herbicides without surfactant (e.g., Rodeo® instead of RoundUp®) and stresses the importance of applying the herbicide to the stump a short time after it is cut; best if no more than 5 minutes. Jonathan Soll (TNC-Oregon) notes that whether you need to add a surfactant depends on what you are trying to kill. In most cases, a general nonionic surfactant will suffice if the herbicide beads-up on the surface of the stem. If the cut stumps of the plant you are treating exude an oily substance, use an oil-type of surfactant for good control.

Q: Is it OK to add impure water into the tank mix? Can I use pond water, salt water, or water from a well for making the tank mix?
Wherever possible, use pure, clean, moderate-temperature water in your tank mix. Pond water may contain soil particles that may adsorb to and render some herbicides or adjuvants useless, and water that is too cold may cause the herbicide to precipitate out of solution. Good quality well water may be used, but if it contains high concentrations of ions (hard water - calcium, magnesium, etc.) or salts, try to find purer water (unless a buffering adjuvant is also used). Well water can be tested locally for impurities. Do not use salt water because the salts and ions it contains may create antagonistic effects with the herbicide, the adjuvants, or both, rendering the mix worthless.

Q: Can I use food coloring instead of a registered dye?
No! Food colorings are not registered for use with herbicides, and therefore should not be used as a dye in herbicide mixes.

Q: Will the adjuvant decrease in effectiveness if I don't use it up right away?
In general, if adjuvants (as well as most herbicides) are stored under appropriate conditions (as specified on the label), they are relatively stable compounds and can be stored and used successfully for some time. For instance, the herbicide hexazinone is stable for at least two years, and glyphosate can be stored for at least five years. Most adjuvants do not include shelf-life information on the label, but may have use-by dates on the container.

REFERENCES

Bayer, D.E. and C.L. Foy. 1982. Action and fate of adjuvants in soils. *In:* Adjuvants for Herbicides, WSSA, Champaign, IL. Pp. 84-92.

Bergeron, V., Bonn, D., Martin, J.-Y. and L. Vovelle. 2000. Controlling droplet deposition with polymer additives. Nature 405: 772-775.

Carroll, B. 2001. Selecting the right adjuvant. Helena Chemical Company's Guide to Adjuvants. http://www.helenachemical.com/proprietary/products/adjuvants/introduction.htm#

Coret, J., Bambonnet, B., Brabet, F. and A. Chamel. 1993. Diffusion of three ethoxylated octylphenols across isolated plant cuticles. Pesticide Science 38: 201-209.

DiTomaso, J.M. 1999. Barriers to foliar penetration and uptake of herbicides. Proceedings of the California Weed Science Society 51: 150-155.

Downer, R.A., Mack, R.E., Hall, R.F. and A.K. Underwood. 1998. RoundUp Ultra with drift management adjuvants. In: McMullan, P.M. (ed.) Adjuvants for Agrochemicals: Challenges and Opportunities. Proceedings of the Fifth International Symposium on Adjuvants for Agrochemicals, Chemical Producers Distributors Association, Memphis, TN. Pp. 468-474.

DuPont. 2000. Guidelines to qualify adjuvant for use with DuPont row crop and cereal herbicides. DuPont Agricultural Bulletin H-87285.

DuPont. 2001. 2001 Approved adjuvant list for use with DuPont row crop and cereal herbicides. DuPont Agricultural Bulletin H-91222.

Folmar, L.C., H.O. Sanders, and A.M. Julin. 1979. Toxicity of the herbicide glyphosate and several of its formulations to fish and aquatic invertebrates. Arch. Environ. Contam. Toxicol. 8:269-278.

Gaskin, R.E. and P. Holloway. 1992. Some physicochemical factors influencing foliar uptake enhancement of glyphosate-mono(isopropylaminonium) by polyoxyethylene surfactants. Pesticide Science 34: 195-206.

Gaskin, R.E. and P.J.G. Stevens. 1993. Antagonism of the foliar uptake of glyphosate into grasses by organosilicone surfactants. Pesticide Science 38: 185-200.

Green, J.M. 2001. Herbicide adjuvants. *In:* UC Davis WRIC Weed Science School, September 26-28, 2001, Woodland, CA.

Green, J.M. 1992. Increasing efficiency with adjuvants and herbicide mixtures. Proceedings of the First International Weed Control Congress, Melbourne, AU. Pp. 187-192.

Green, J.M. 2000. Adjuvant outlook for pesticides. Pesticide Outlook. October: 196-199

Green, J.M. and J.L. Hazen. 1998. Understanding and using adjuvants properties to enhance pesticide activity. *In:* McMullan, P.M. (ed.) Adjuvants for Agrochemicals: Challenges and

Opportunities. Proceedings of the Fifth International Symposium on Adjuvants for Agrochemicals, Chemical Producers Distributors Association, Memphis, TN. Pp. 25-36.

Hartzler, B. 2001. Role of AMS with glyphosate products. Iowa State University Extension Agronomy. http://www.weeds.iastate.edu/mgmt/2001/ams.htm

Hazen, J.L. 2000. Adjuvants - Terminology, classification, and chemistry. Weed Technology 14: 773-784.

Hess, F.D. 1999. Surfactants and additives. Proceedings of the California Weed Science Society 51: 156-172.

Hess, F.D. and C.L. Foy. 2000. Interaction of surfactants with plant cuticles. Weed Technology 14: 807-813.

Hewitt, A.J. 1998. The effect of tank mix and adjuvants on spray drift. *In:* McMullan, P.M. (ed.) Adjuvants for Agrochemicals: Challenges and Opportunities. Proceedings of the Fifth International Symposium on Adjuvants for Agrochemicals, Chemical Producers Distributors Association, Memphis, TN. Pp. 451-462.

Hull, H.M., Davis, D.G. and G.E. Stolzenberg. 1982. Action of adjuvants on plant surfaces. *In:* Adjuvants for Herbicides, WSSA, Champaign, IL. Pgs. 26-67.

Kirkwood, R.C. 1999. Recent developments in our understanding of the plant cuticle as a barrier to the foliar uptake of pesticides. Pesticide Science 55: 69-77.

Kudsk, P. and J.C. Streibig. 1993. Formulation and adjuvants. *In:* Strigib, J.C. and P. Kudsk (eds.) Herbicide Bioassays. CRC Press, Boca Raton, FL. Pp. 99-116.

Matysiak, R. and J.D. Nalewaja. 1999. Temperature, adjuvants, and UV light affect sethoxydim phytotoxicity. Weed Technology 13: 94-99.

McMullan, P.M. 2000. Utility adjuvants. Weed Technology 14: 792-797.

McWhorter, C.G. 1982. The use of adjuvants. *In:* Adjuvants for Herbicides, WSSA, Champaign, IL. Pgs. 10-25.

Miller, P. and P. Westra. 1996. Herbicide surfactants and adjuvants, no. 0.559. Colorado State University Cooperative Extension, Production Crop Series.

Miller, P. and P. Westra. 1998. How surfactants work, no. 0.564. Colorado State University Cooperative Extension, Crop Fact Sheet. http://www.ext.colostate.edu/pubs/crops/00564.html

Nalewaja, J.D. 1994. Esterified seed oil adjuvants. North Central Weed Science Society Proceedings 49: 149-156.

Nalewaja, J.D. and R. Matysiak. 1993. Optimizing adjuvants to overcome glyphosate antagonistic salts. Weed Technology 7: 337-342.

Nalewaja, J.D. and R. Matysiak. 2000. Spray deposits from nicosulfuron with salts that affect efficacy. Weed Technology 14: 740-749.

Norris, R.F. 1982. Action and fate of adjuvants in plants. *In:* Adjuvants for Herbicides, WSSA, Champaign, IL. Pgs. 68-83.

Parr, J.F. 1982. Toxicology of adjuvants. *In:* Adjuvants for Herbicides, WSSA, Champaign, IL. Pgs. 93-114.

Parr, J.F. and A.G. Norman. 1965. Considerations in the use of surfactants in plant systems: A review. Botanical Gazette 126(2): 86-96.

Penner, D. 2000a. Activator adjuvants. Weed Technology 14: 785-791.

Penner, D. 2000b. Introductory statement on adjuvants. *In:* Young, B. Compendium of Herbicide Adjuvants, 5th edition. Southern Illinois University, Carbondale.

Pringnitz, B. 1998. Clearing up confusion on adjuvants and additives. Iowa State University Extension Agronomy. http://www.weeds/iastate.edu/mgmt/qtr98-2/cropoils.htm

Roggenbuck, F.S., Penner, D., Burow, R.F. and B. Thomas. 1993. Study of the enhancement of herbicide activity and rainfastness by an organosilicone adjuvant utilizing radiolabelled herbicide and adjuvant. Pesticide Science 37: 121-125.

Swisher, E.M. 1982. Adjuvant regulation and registration. *In:* Adjuvants for Herbicides, WSSA, Champaign, IL. Pgs. 115-118.

Thelen, K.D., Jackson, E.P. and D. Penner. 1995. The basis for the hard-water antagonism of glyphosate activity. Weed Science 43: 541-548.

Tyler, M.J. 1997a. Herbicides kill frogs. Newsletter of the declining amphibians population task force #21.

Tyler, M.J. 1997b. Environmentally friendly: A false sense of security? Species. Newsletter of the Species Survival Commission, IUCN, The World Conservation Union. 29:20-21.

Underwood, A.K. 2000. Adjuvant trends for the new millennium. Weed Technology 14: 765-772.

Van Valkenburg, J.W. 1982. Terminology, classification, and chemistry. In: Adjuvants for Herbicides, WSSA, Champaign. Pgs. 1-9.

Wanamarta, G., Kells, J.J. and D. Penner. 1993. Overcoming antagonistic effects of sodium bentazon on sethoxydim absorption. Weed Technology 7: 322-325.

Witt, W.W. 2001. Adjuvants. University of Kentucky College of Agriculture, Agripedia. http://www.ca.uky.edu/agripedia/pls404/adjuvant.htm

WSSA. 1982. Adjuvants for Herbicides. Weed Science Society of America, Champaign. 144 pgs.

Young, B. 2000. Compendium of herbicide adjuvants. Southern Illinois University, Carbondale. 66 pgs.

Zollinger, R.K. 2000. Extension perspective on grower confusion in adjuvant selection. Weed Technology 14: 814-818.

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