

# Surfactants and Additives

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## Adjuvants for postemergence herbicide applications

An adjuvant is any material added to a herbicide spray solution to enhance or modify the performance of the solution. Adjuvants can be divided into two general categories: spray modifiers and activators (Kirkwood, 1994). Spray modifiers are those adjuvants that change the wetting, spreading or sticking characteristics of the spray solution. This is primarily accomplished by a modification in the surface tension of the spray solution. Activator adjuvants primarily influence the absorption of the herbicide by a direct interaction with the plant cuticle. The most common types of adjuvants are surfactants (surface active agents). Surfactants can be defined as spray additives that facilitate or enhance the emulsifying, dispersing, spreading, sticking or wetting properties of liquids (spray modifiers). However, surfactants also directly influence the absorption of herbicides by changing the cuticle characteristics (activators). Surfactant types receiving significant attention in the past few years are organosilicones. Another commonly used adjuvant type is oil. In addition to oils being used as adjuvants they can also be used as contact herbicides and as carriers for synthetic herbicides. A third adjuvant type, salts commonly used as fertilizers, is rapidly gaining in popularity. A final adjuvant grouping are buffers which are used to adjust the acidity of the spray solution. The most commonly used buffers are for reducing the pH of water.

## Surfactants

Most surfactant molecules are composed of a lipophilic long chain hydrocarbon (alkyl) group and a hydrophilic polar group. The polar group can be ionic [cationic (positive charge), anionic (negative charge) or zwitterionic (having both a positive and negative charge)] or nonionic. Because adjuvants contain both lipophilic (oil-like) and hydrophilic (water-like) properties, they can interact with lipophilic plant surfaces and lipophilic herbicides as well as hydrophilic herbicides and water. The most common surfactants for agricultural use are nonionic and anionic. Common anionic surfactants are alkyl sulfates and alkylbenzene sulfonates (see diagram). Most agricultural nonionic surfactants have chains of ethylene oxide (also called oxyethylene or ethoxylate) (-CH<sub>2</sub>CH<sub>2</sub>-O-) as the polar (hydrophilic) groups. The number of ethylene oxide units in the polar portion of the nonionic surfactant is often referred to as the "number of moles of ethylene oxide (EO)." Common nonionic surfactants are alcohol, alkyl sulfates and alkylphenol ethoxylates (see diagram). Propylene oxide [- (CH<sub>2</sub>)<sub>3</sub>-O-] or butylene oxide [- (CH<sub>2</sub>)<sub>4</sub>-O-] can be built into the ethylene oxide chain to reduce its hydrophilic nature which makes the surfactant more compatible with lipophilic herbicides (Butselaar and Gonggrijp, 1993). The more EO or PO units on the surfactant the more polar the surfactant. The polarity of the surfactant can be further modified by the constituent at the end of the EO or PO chain (often called the end-cap). For example, a methoxy end-cap (-O-CH<sub>3</sub>) is less polar than a hydroxy end-cap (-OH).

Amine surfactants (e.g., tallow amines) are available for use as nonionic adjuvants and formulation components (e.g., Roundup) and as cationic quaternary amine adjuvants (often called "quats"). Another type of nonionic surfactant uses one or more glucose molecules as the hydrophilic polar group (Hoyle and Holloway, 1996). These are often called alkyl polysaccharides or alkyl polyglycosides. The "saccharide" name comes from containing sugar (glucose) and the "glycoside" comes from the covalent bonding of two sugars via a glycosidic bond (a hydroxyl group on one sugar bonded with a carbon on another sugar). Although more expensive than conventional nonionic surfactants, they are more biodegradable and more compatible (mixable) with ammonium based fertilizer solutions used as surfactants. Often these surfactants are sold as mixtures with ammonium sulfate.

Surfactants are often assigned a "hydrophilic-lipophilic balance"(HLB) value. For nonionic surfactants this value is approximated by the weight percent of the total weight of the surfactant that is hydrophilic. For ionic surfactants the HLB is less straight forward and is usually determined experimentally. In one popular system (from ICI), HLB has been given a numerical range from 1 to 20. HLB values can be estimated by observing dispersibility in water (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+). Lipophilic (lipid soluble) surfactants are assigned HLB numbers of 8 and below. Surfactants with HLB numbers between 9 and 11 are intermediate, and those with HLB numbers above 11 are hydrophilic in nature (water soluble). Surfactants used as wetting agents have HLB values of 7 to 9. A Surfactant with optimal HLB for a particular herbicide can be predicted based the water solubility of the herbicide --> low HLB surfactants for water insoluble herbicides and high HLB surfactants for water soluble herbicides. For example, de Ruiter, Uffing and Meinen (1996) and Nalewaja, Devilliers and Matysiak (1996) showed that high HLB surfactants were more effective at increasing glyphosate (water soluble) efficacy than low HLB surfactants. Tan and Crabtree (1992) reported that for polyethylene-glycol based surfactants, absorption of adjuvant into plant cuticles was inversely related to HLB numbers (i.e lower HLBs absorbed better). This is not surprising because low HLB surfactants are more lipophilic thus more able to diffuse into the lipophilic cuticle than high HLB surfactants that are less lipophilic.

At very low concentrations surfactants are soluble in water; however, as the surfactant concentration is raised to those commonly used in weed control, the lipophilic groups associate with one another to form "micelles". The surfactant concentration where micelle formation occurs is called the "critical micelle concentration" (CMC). These micelles can emulsify lipophilic substances, including herbicides, oils and perhaps cuticular components. The emulsifying agents used in EC formulations are usually blends of surfactants.

An important aspect of surfactants used as adjuvants is to reduce the surface tension of a spray solution in order to allow a more intimate contact between spray droplet and plant surface. Many surfactant effects occur at concentrations well above the CMC; therefore, the mechanism of action of surfactants must be more than just reducing the surface tension of the spray solution (Tan and Crabtree, 1992). For example, Wirth, Storp, and Jacobsen (1991) have shown that rebound of spray droplets from plant surfaces was reduced only when surfactant concentrations were well above the CMC.

Any substance that will bring the herbicide into a more intimate contact with the leaf surface and keep it in a soluble form has the potential of aiding absorption. Surfactants achieve this by:

1. Causing a more uniform spreading of the spray solution and a uniform wetting of the plant.
2. Helping spray droplets stick to the plant, resulting in less runoff.
3. Assuring that droplets do not remain suspended on hairs, scales or other surface projections.
4. Partially solubilizing the lipoidal plant cuticle substances (controversial).
5. Preventing crystallization of the active ingredient on the leaf surface by being a solvent.
6. Slowing the drying of, and increasing the water retention in, spray droplets once on the leaf surface.

After passing through the cuticle, surfactants may also increase movement of herbicides (e.g. glyphosate) through the plasma membrane (Wade, et al., 1993 and de Ruiter and Meinen, 1996).

An important action of adjuvants is their penetration into the plant cuticle. The amount of a nonionic surfactant that absorbs into and across the cuticle is dependent on the EO content. For octylphenol nonionic surfactants, Coret, et al. (1993) showed movement into the cuticle was highest for those with low EO contents (more lipophilic). The mechanism of action of nonionic surfactants once inside the cuticle is not fully understood, but progress is being made. Most evidence shows surfactants used in herbicide applications do not simply "solubilize" the cuticle (Riederer and Schonheff, 1990). The mechanism may well be different for high EO (hydrophilic) and low EO (lipophilic) nonionic surfactants. Increased water permeability of the cuticle can be measured after application of many high EO surfactants (Riederer and Schbnherr, 1990). In detailed studies Coret and Chamel (1993, 1995) have shown that at a given relative humidity, surfactants with high EO contents can increase the hydration state of the cuticle. For example, for the relative humidities tested (20 to 80%) a nonylphenol surfactant with 17 EO's greatly increased the water absorption into isolated tomato fruit cuticles when compared to no surfactant. However, when the EO content of the nonylphenol was 4, there was no increased water absorption when compared to no surfactant. An increased hydration state of the cuticle induced by high EU surfactants may well increase the diffusion of water soluble herbicides across the cuticle. The questions then arises as to how surfactants increase the absorption of oil soluble herbicides. Coret and Chamel (1994, 1995) used differential scanning calorimetry to show wax melting begins at a lower temperature after absorption of some surfactants (nonylphenol; 4 EO). They suggested the increased absorption of oil soluble herbicides (chlorotoluron was their model) may be due to an increase in wax fluidity which would increase the rate of diffusion across the cuticle. Schreiber (1995) and Schreiber, Riederer and Schom (1996) proposed that surfactants induce a unspecific and reversible "plasticizing" interaction between surfactant and cuticular wax which enhances solubility of the herbicide in the wax. Because the effect was reversible, the surfactant did not alter the molecular wax structure (solubilizing the wax or changing its crystalline nature). Substances other than surfactants can influence cuticle fluidity. Schonherr (1993a) showed alcohols with 7 to 10 carbon atoms increase the movement of herbicides across the cuticle by increasing its fluidity.

Thus, the prediction would be absorption of hydrophilic herbicides are aided most by surfactants with high EO content and lipophilic herbicides are aided most by surfactants with low EO contents (see the review by Kirkwood, 1993). This has been confirmed by experimental evidence (e.g., Riechers, et al., 1995; Sharma, Kirkwood and Whateley, 1996). Surfactants with an EO content of 11 to 20 were more effective than surfactants with 6 EO in increasing glyphosate (water soluble) activity on oats (van Toor et al., 1994). Coret and Chamel (1994) found that chlorotoluron (water insoluble) movement across isolated box-tree cuticles was greater for surfactants with low EO content (3 to 6) than for surfactants with high EO content (16 to 20). These authors also found that the concentration of surfactant in the cuticle was higher for low EO surfactants when compared to high EO surfactants. Picking the best surfactant also depends on the lipophilic portion of the surfactant. For example, at a given EO content, Coret and Chamel (1993) found glyphosate transfer across an isolated cuticle was greatest when the lipophilic portion of the surfactant (termed the hydrophobe) was a primary aliphatic amine and least when an aliphatic alcohol.

Some surfactants have a detergent action. The maximum detergent action occurs when the surfactant has a hydrophobe carbon chain length of from 12 to 14 and a total EO content of greater than 60% of the weight of the surfactant. Current evidence, however, suggests the detergent action of surfactants do not play much of a role, if any, in enhancement of herbicide absorption (Stock and Holloway, 1993). Riederer and Schbnherr (1990) found no detectable amounts of aliphatic wax constituents were lost when the cuticles of orange and pear were treated with excessive amounts of nonionic and ionic surfactants and subsequently washed with water. It is also unlikely surfactants solubilize wax constituents in the cuticle. As Riederer and Schonheff (1990) point out, wax solubilization would be expected to be slow because much of the cuticular wax is in an ordered crystalline state and contain very long hydrophobic alkyl chains.

The addition of a surfactant can enhance foliar herbicide penetration in all types of plants. Therefore, a surfactant may reduce the tolerance of the herbicide to a crop if that tolerance is dependent upon selective foliar penetration (e.g., see Grayson, Webb and Pack, 1993).

Stomatal penetration (infiltration) of spray droplets from a water based solution is a complex process and does not occur in field applications of herbicides without surfactants. Stomatal infiltration is not possible unless the surface tension of the spray solution is significantly reduced by the use of surfactants in the formulation or spray tank. Most surfactants are not able to reduce the surface tension adequately to allow stomatal infiltration. However, the organosilicone surfactants (described below) reduce surface tension to the point where stomatal infiltration occurs. Even after stomatal infiltration, the herbicide must still penetrate a thin cuticle that exists on the cell surfaces of the cavity below the stomata.

The overall action of surfactants in enhancing herbicide absorption is complex and no doubt due to several factors. This fact was well stated by Stock and Holloway (1993): "Different surfactants do different things to different agrichemicals on different target species."

## Organosilicone surfactants

During the past few years there has been a significant increase in the interest of using organosilicone adjuvants for herbicide applications. Excellent overviews of organosilicone surfactants have been published by Stevens (1993) and Knoche (1994).

Organosilicone surfactants are often composed of a trisiloxane-backbone (lipophilic or hydrophobe portion) with an ethylene oxide chain (hydrophilic portion) attached to one of the silicon atoms. The hydrophilicity can be reduced by using a mix of EO and PO or modifying the EO end-cap. Silicone backbones other than trisiloxane are being investigated. The hydrophobicity of the silicone backbone is not associated with the presence of silicon, but rather with the flexibility of the siloxane chain enabling exposure of methyl groups at the interfaces between the surfactant and its environment. Methyl groups are more hydrophobic than the methylene (CH<sub>2</sub>) groups which make up the bulk of the hydrophobe in conventional surfactants. The most commonly used organosilicone surfactant is Silwet L-77, which has a relatively low polarity due to the EO content being only 8. A newer product, Silwet 806, contains both EO and randomly distributed PO and is said to be cost competitive with emulsifiable oils for application of graminicide herbicides (Policello, Stevens, and Murphy, 1996).

Organosilicone surfactants yield a reduction of surface tension of water based spray solutions greater than other surfactants. Organosilicone surfactants cause substantially greater spreading of the spray drop than would be predicted by the reduction in surface tension. This increased spreading is proposed by Ananthapadmanabhan, Goddard and Chander (1990) to be due to the compact size of the lipophilic portion of the trisiloxane moiety allowing it to transfer readily from the liquid/air interface of the advancing solution to a leaf surface. This action has often been termed "molecular zippering." Organosilicone surfactants with less compact hydrophobes exhibit reduced spreading. The ultimate limit to spreading may well be the depletion of the surfactant in the solution by adsorption at the expanding cuticle/liquid interface. Spreading is often less on leaves having increased surface area due to the presence of microcrystalline wax (e.g. grass species). The intense spreading of organosilicone surfactant solutions can lead to reduced spray retention on some plants if the application volume is high (due to run-off). However, the increased spreading characteristic allows better adherence of spray drops to those leaves that are highly water repellent. The increased spreading of a spray drop increases its evaporative surface which can lead to rapid drop drying (and reduced absorption); however, organosilicone surfactants have significant humectant properties which slow drying. Organosilicone surfactants are not only effective at increasing the overall absorption of herbicides, but are effective at decreasing the time needed for rainfastness (Roggenbuck, et al., 1993 and Sun, Foy and Witt, 1996).

One mechanism for organosilicone surfactant effectiveness is they induce direct stomatal infiltration (flooding) of the spray solution (Field and Bishop, 1988, and Buick, Robson and Field, 1992). For stomatal infiltration to occur surface tension of the spray solution needs to be less than the critical surface tension for stomatal infiltration. For example, in one study the critical surface tension of field bean (*Vicia faba* L.) for stomatal infiltration was determined to be 19.5 to 22.9 mNm<sup>-1</sup> (Buick, Buchan and Field, 1993). The surface tension of a surfactant solution containing Silwet L-77 organosilicone surfactant (2.5 to 5.0 ml/L; CMC about 0.1

nil/L) averaged  $22 \text{ mNm}^{-1}$ , which was low enough to permit stomatal infiltration. Stomatal infiltration is most closely controlled by surfactant concentration (Green, et al., 1996). However, many reports also show that organosilicone surfactants influence absorption of herbicides through the cuticle after stomatal infiltration is complete.

One problem with these surfactants is they are unstable when the pH of the spray solution is not within the range of 6 to 8 (Murphy, Policello and Ruckle, 1991). Hydrolysis of siliconoxygen bonds occur under acidic as well as basic conditions. This effect can be reduced by buffering the spray solution to a neutral pH. An organosilicone surfactant containing only one silicon atom (thus no silicon-oxygen bonds) is claimed to be as effective as trisiloxanes (Klein, Wilkowski and Selby, 1996). The best surfactants of this type have a trimethyl silane group attached to a short hydrocarbon chain (six was reported to be optimal) which is attached to an EO chain (see diagram). The surface tension of aqueous solutions containing this surfactant were low enough ( $23 \text{ mN/m}$  at 0.1%) to allow stomatal infiltration.

Another disadvantage of trisiloxane surfactants is their high degree of spreading is lost when mixed with other non-organosilicone adjuvants (Murphy, Policello and Ruckle, 1991). The incompatibility is attributed to competition between the compact hydrophobe of the organosilicone and the bulky hydrophobe of the conventional surfactants for the interface between the spreading drop and the leaf (jamming the zipper). However, surfactants have now been identified that can be effectively mixed with the organosilicones. The extreme surface activity of these surfactants can cause excess foaming. This is managed by including a commercial antifoaming agent in the spray solution. Because of the extreme surface active characteristics of these surfactants, eye and skin contact must be avoided. A final problem is, to date, the cost of these adjuvants is significantly above conventional surfactants. This cost is associated with the need to distill the trisiloxane from bulk silicone fluid.

Organosilicone surfactants are not effective for all herbicides. For example, including organosilicone surfactants with glyphosate (Roundup) sprays can cause antagonism [see Knoche (1994) for review]. The cause is not known, but may be associated with the rapid drying of spray droplets due to extensive spreading. Gaskin and Stevens (1993a) proposed another explanation for the antagonism. They reported rapid glyphosate absorption in grass species immediately after application with organosilicone surfactants (stomatal infiltration), but glyphosate absorption slowed significantly 1 hr after application when compared to glyphosate absorption without organosilicone surfactants. This result confirms organosilicone surfactants have a cuticular absorption affect in addition to their inducing stomatal infiltration. These authors did not find any interaction between the organosilicone surfactant and the tallow amine ethoxylate surfactant present in Roundup. They suggested the antagonism occurred within the cuticle due to the rapid penetration of the organosilicone surfactant somehow impeding the pathway for further glyphosate absorption. In a related study, Gaskin and Stevens (1993b) reported the antagonism of glyphosate absorption was decreased by increasing the polarity (e.g., increasing the EO content) of the organosilicone surfactant.

## Oils as Carriers and Adjuvants

Oils used in agriculture are of two primary types: refined mineral oil (petroleum based) and seed oils (sometimes called vegetable oils). Mineral oils are specific "cuts" from the distillation of petroleum. These oils require an extensive refining procedure prior to use as agricultural adjuvants. This involves solvent extraction to remove aromatics, dewaxing, and a final fractionation to recover a narrow boiling range oil. Nonphytotoxic mineral oils used as adjuvants usually have a high proportion of paraffin oils (long straight or branched chain hydrocarbons with chain lengths usually from 18 to 30 carbons). Seed oils are extracted from plants by pressing or solvent extraction. The hydrocarbon chain length of seed oils are even numbered with 16 or 18 carbons dominating. Seed oils need further purification to remove gums, mucilages, and phospholipids (e.g., precipitated with phosphoric acid then neutralized with sodium hydroxide) as well as color (e.g., heating in the presence of Fuller's earth) and short-chain aldehydes, ketones, acids and hydrocarbons (e.g., injecting steam into heated oil). Citric acid can be added to chelate metals which can cause oxidation and rancidity.

There are two main types of seed oils used in agriculture: "triglycerides" and "methylated oils." Triglyceride oils have a glycerol backbone with fatty acids esterified to each of the three carbon atoms in the glycerol. The fatty acids attached to each carbon of the glycerol are often different and overall, triglyceride oils have a higher viscosity than methylated oils. Seed oils are primarily triglycerides when isolated. Triglyceride oils need to be liquid at application temperatures, thus the attached fatty acids are often oleic (18: 1) or linoleic (18:2). While these oils can be used directly in agricultural applications they often perform better as adjuvants when in the methylated oil form (Nalewaja, 1994, Urvoy, Pollacsek and Gauvrit, 1992 and Nalewaja, Praczyk and Matysiak, 1995). In this case the fatty acids are removed from the glycerol backbone during processing and then esterified with methyl alcohol (methyl esters of fatty acids, which are termed methylated oils). This can be accomplished by hydrolyzing the triglyceride to yield free fatty acids, then esterifying them with methyl alcohol or by inducing a transesterification in which the triglyceride is reacted with methanol in the presence of sodium methoxide. Other esters have been prepared and tested (ethyl, butyl), but show little or no advantage over the methyl esters (Nalewaja, 1994). For a review of oil chemistry see Hamilton (1993). The composition of triglyceride oils varies depending on the seed source and consequently the composition of methylated oils will also vary depending on the source. The fatty acid composition does influence efficacy; however, the optimum composition varies for different herbicides and must be determined experimentally (Nalewaja, 1994).

There are two ways oils can be used in weed control: as a carrier for synthetic herbicides and as an adjuvant for spray solutions. Nonphytotoxic oils have been used as carriers for oil soluble herbicides applied postemergence; however, the application volumes originally used are no longer practical. Research on delivery systems such as the air-assist spray nozzle (McWhorter, Fulgham and Barrentine, 1988) and positive displacement pump (Hanks and McWhorter, 1991) has rekindled the interest of using oils as carriers for oil soluble herbicides at ultra low volumes (1/4 to 1 gallon per acre) (Bohannon and Jordan, 1995). There are several advantages of using oils as carriers in low volume postemergence applications of oil soluble herbicides rather than water: low surface tension results in good wetting and spreading on treated leaves (McWhorter, Ouzts and Hanks, 1993), quicker and more thorough absorption of the

herbicide yields higher activity, rapid rainfastness, the herbicide is less affected by cuticle composition, and there is less loss of the carrier during and after application.

Emulsifiable oils can be used as adjuvants (the usual volume is about 1 quart per acre). These adjuvants contain a nonphytotoxic oil (80 to 98%) and a surfactant (2 to 20%), and are often called crop oil concentrates (COC) when containing 15 to 20% surfactant and crop oils (CO) when containing 2 to 5% surfactant (note - this nomenclature is not universally accepted). The oil is usually a highly refined paraffin based oil or a methylated seed oil. There is significant interest in using seed oils as emulsifiable oils. Methylated esters obtained from seed oils usually perform better than the parent triglyceride oils and are often comparable to petroleum oils (Nalewaja, 1994). In one study, the absorption of diclofop-methyl was increased 11.8 fold when a methyl oleate oil was included in the formulation (Urvoy and Gauvrit, 1991). There was a 72% absorption of the oil itself during a 27 hour period. Emulsifiable oils usually enhance oil soluble herbicide absorption more than the corresponding surfactant alone. The purpose of the surfactant in the mixture is to emulsify the oil in the water based spray solution and lower the surface tension of the spray solution, but they can also can interact with the cuticle and assist herbicide absorption. In one study (de Ruiter, Uffing, and Meinen, 1997) the emulsifier was as effective as the oil + emulsifier (surfactant) at increasing efficacy of three out of four herbicides tested. The exact mode of action of these oils is unknown, but they enhance spreading of the droplet on the sprayed plant surface and increase the absorption of the herbicide into the plant (Gauvrit and Cabanne, 1993). Santier and Chamel (1996) proposed that after oils partition into the cuticle they increase the fluidity of cuticular components which increases the diffusion of oil soluble herbicides through the cuticle. Whether oils act as solvents of cuticular components (waxes) is controversial. For example, Manthey and Nalewaja (1992) reported methylated sunflower oil completely dissolved wax isolated from green foxtail, whereas Gauvrit and Cabanne (1993) reported methylated rapeseed oil did not dissolve wax extracted from several different plant species.

### **Salts of Fertilizers as Adjuvants**

There is an increasing interest in using fertilizers as adjuvants in water based spray solutions. Many publications (see "Fertilizer Solutions" reference section for examples) show that adding ammonium sulfate, ammonium nitrate or urea plus ammonium nitrate (28% UAN) to postemergence herbicide spray solutions increases efficacy. Other salts have also been shown to increase herbicide performance. For example, sodium bisulfate increased the activity of imazamethabenz in wild oat (Liu, et al., 1995).

Although the exact mechanism of action is unknown, there are several reports of increased herbicide absorption when these fertilizers are used as adjuvants. In one study (Fielding and Stoller, 1990) the absorption of thifensulfuron into velvetleaf was increased from 4% without adjuvant to 45% with the addition of 28% UAN (9 L/ha; about 1 gal/acre). With regard to mode of action, one report (MacIsaac, Paul and Devine, 1991) suggested ammonium sulfate reduces the precipitation (crystallization) of herbicides (glyphosate) on the plant surface. Another mechanism may be the formation of ammonium salts of weak acid herbicides on the leaf surface (Wanamarta, Kells and Penner, 1993). Generally, an ammonium salt of herbicides more freely diffuses across the cuticle than the corresponding inorganic salt (e.g. sodium or potassium salt).

Ammonium sulfate used as an adjuvant has also been successful at overcoming decreased herbicidal activity due to antagonism with another component in the spray solution. Calcium, sodium, potassium, and magnesium salts in water used as a spray carrier have been reported to antagonize the efficacy of herbicides such as 2,4-D, bentazon, dicamba, acifluorfen, imazethapyr, glyphosate, nicosulfuron and clethodim (Nalewaja and Matysiak, 1993a, 1993b, McMullan, 1994 and Nalewaja, Praczyk and Matysiak, 1995). These authors showed the application of ammonium sulfate to the spray solution, in many instances, overcame the antagonism. Citric acid was found to overcome the antagonism of calcium on glyphosate activity by formation of calcium citrate which prevented the formation of the calcium salt of glyphosate (Thelen, Jackson and Penner, 1995b). Nalewaja, Devilliers and Matysiak (1996) showed that the uptake of glyphosate salts in wheat was isopropylamine > ammonium > sodium > calcium. In a spray solutions containing calcium and sodium ions, adding ammonium sulfate will reduce the effect of these ions on glyphosate absorption during drop drying by forming calcium sulfate (lower solubility than calcium glyphosate) and ammonium glyphosate prior to the formation of sodium glyphosate. In some cases antagonism between herbicides [e.g. bentazon plus sethoxydim (Wanamarta, Kells and Penner, 1993) and primisulfuron plus atrazine, dicamba or bentazon (Hart, Kells and Penner, 1992)] can be reduced by adding ammonium sulfate to the spray solution.

## **Humectants**

The majority of herbicide is absorbed into the plant when it is in true solution on the leaf surface. Once the herbicide solution becomes dry and crystalline on the leaf surface, absorption decreases. Therefore humectants, in theory, should be ideal adjuvants. Although humectants have been evaluated as adjuvants, they are not extensively used in commercial applications of herbicides. In one study, Sundaram et al., (1996) showed glycerol addition to glyphosate spray solution containing Silwet L-77 organosilicone surfactant increased rainfastness as well as control of aspen trees.

## **Buffers**

Buffers are adjuvants that modify and then maintain the pH (acid or base nature) of spray solutions. Buffers are defined as "systems capable of resisting changes in pH." They consist of molecules having a conjugate acid-base pair which can act as a proton donor and proton acceptor. Some herbicides are not stable in aqueous solutions unless they are maintained at near a neutral pH (near 7). When the pH of the spray solution is away from neutral, the herbicides can be subject to base or acid hydrolysis.

In agricultural applications buffers are primarily added to spray solutions when the water used is either acidic or basic. These buffers bring the pH of the water back to near neutral and then maintain it near neutral. Buffers are most frequently used to reduce the pH of water from basic to neutral or slightly acidic. The most common commercial buffers to reduce the pH of a spray solution contain phosphoric acid (Buffercide®) or phosphoric acid plus surfactant (Bufferplus®). Another common agricultural buffer (Buffer X®) contained free fatty acids to

reduce the pH of the spray solution and a surfactant. If the pH of the spray solution is too low, sodium carbonate (soda ash) is the most common additive.

## Reference on Adjuvants

### *General Overviews*

In 1992 a book titled "Adjuvants for Agrichemicals" (edited by C.L. Foy) was published by CRC Press, Boca Raton, FL. This book is based on papers presented at the Second International Symposium on Adjuvants for Agrichemicals. Included in this book (pages 3-15) is a biographical survey written by P.N.P. Chow and C.A. Grant containing 1490 references divided into nine subject categories.

Twelve papers on adjuvants from The Third International Symposium on Adjuvants for Agrichemicals were published in Pesticide Science during 1993 (Volume 37 Number 2). An additional 18 papers were published in Volume 38 Number 2/3.

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