ACTIVATOR ADJUVANTS: TYPES AND USE PATTERNS. John D. Nalewaja, Professor Emeritus, Department of Plant Sciences, North Dakota State University, Fargo, ND 58105-5051.

Introduction

This discussion will be limited to surfactants, oils, and blend adjuvants. Salt adjuvants used to overcome antagonism by spray carrier ions or to directly enhance efficacy will be discussed by others. An adjuvant generally is required to obtain the full potential of a postemergence herbicide or to allow their full potential under various application practices. For example, the efficacy of several sulfonylurea herbicides was increased four-fold when applied with methylated seed oil and two-fold with petroleum oil when compared to a nonionic surfactant (Roehl 1992). Not all adjuvants within a classification type are equal in efficacy. There are many types of surfactants and oils so their efficacy can vary by product. Most commercial products were selected for efficacy but may differ in effectiveness depending on the herbicide. Some factors influencing adjuvant efficacy will be discussed to indicate characteristics to be considered during formulation of commercial products and to indicate that one commercial product may not maximize efficacy of all herbicides.

Postemergent herbicide efficacy, first, requires spray retention by weeds and, second, herbicide absorption from the spray deposit by the weed. These two processes are influenced by many spray, plant, herbicide, and environmental conditions. Spray droplet retention is influenced by adjuvant type, spray water volume, spray droplet size, plant leaf wax characteristics, and leaf orientation, as is well known. The role of various adjuvants in herbicide absorption is less understood. Absorption of a herbicide from the spray deposit is complex and involves an adjuvant's ability to dissolve the herbicide and plant wax, to make contact with the leaf surface, and to leave a spray deposit with physical and chemical characteristics conducive to herbicide diffusion into the weed. Physical spray deposit characteristics include degree of contact with the leaf waxes for direct passage of the herbicide into the leaf and a deposit mass to provide adequate herbicide concentration for absorption that result in a toxic response. The chemical composition of a spray deposit required for absorption is a complex solubility interrelationship among the herbicide, adjuvant, and plant cuticle, as well as the minerals in the spray carrier water.

The role of surfactants, oils, and blend adjuvants in spray retention and herbicide efficacy will be discussed using specific examples. These examples are to present basic concepts for specific herbicides and adjuvants with their solubility characteristics and may not always be applicable to other herbicides and adjuvants.

Surfactants

Surfactants by definition are surface active agents that reduce interfacial tension and thus would reduce the surface tension of water used as a spray carrier. Water with a low surface tension will improve water's ability to wet the lipid surfaces of leaves for better spray droplet retention and better contact of the droplet deposit with the leaf surface. However, surfactants differ in their ability to enhance spray retention. Surfactants with a low dynamic surface tension were important to good spray retention (Holloway 1995). Spray droplets as they leave the sprayer nozzle are mixing vigorously and the time between droplet formation and contact with the target is too short for the droplet mixture to reach a static state. Thus, surfactants that give a low surface tension under dynamic conditions are best for spray retention. The ability of a surfactant to give a low dynamic surface tension depends on the surfactant's chemistry, molecular size, and concentration in the spray solution.

Originally surfactants were believed to function mainly to enhance spray retention, so a concentration of 0.25% v/v generally was considered adequate because that would exceed the critical micelle concentration (CMC). CMC is the concentration at which static surface tension is at a minimum for most surfactants. However, this did not consider that a low dynamic surface tension is needed for good spray retention. I (Nalewaja) once stated that surfactants generally are for spray retention so usage should be on a percentage basis and oils are mainly for absorption so their usage should be on a per area basis. The assumption was that sprays applied on a percentage surfactant basis would result in the same retention regardless of spray volume. The function of oils was considered mainly for herbicide absorption so application on an area basis would give the proper amount for herbicide absorption regardless of spray volume.

Spray retention enhancement depends upon surfactant chemistry and its hydrophilic-lipophilic balance (HLB), concentration in the spray solution, and leaf wax characteristics of the plant (Bruns and Nalewaja 1998; Manthey et al. 1998). Low HLB surfactants generally give greater spray retention than those with a high HLB but the response depends on the surfactant chemistry and plant species involved. Spray retention generally increased as surfactant concentration increased, but increasing a low-HLB secondary-alcohol surfactant concentration to 4% v/v decreased retention on easy-to-wet redroot pigweed.

Spray retention certainly is essential for foliar-applied herbicide efficacy, but surfactants giving high retention were not always the most efficacious (Manthey et al. 1998). This indicates that the surfactant's chemical characteristics that enhance herbicide absorption are more important for efficacy than small differences in spray retention.

Surfactants have been important for herbicide efficacy in many literature reports. High HLB surfactants with similar lipophiles generally are more effective than low HLB surfactants for water-soluble herbicides and lower HLB surfactants are more effective for oil-soluble herbicides (Green 2005; Nalewaja and Matysiak 2001; Stock and Holloway 1993). These results indicate that surfactants had a function as solvents to aid in herbicide absorption. The importance of herbicide solubility in a surfactant was demonstrated by herbicide crystals remaining in deposits with certain surfactants but not others (Nalewaja and Matysiak 2000; Woznica et al. 2003). Sulfonylurea herbicides were more effective in a spray with high pH than low pH (Green 2005; Nalewaja and Matysiak 2001; Woznica et al. 2000). High HLB surfactants were more effective at high pH than low pH because at high pH nicosulfuron was more soluble in the high HLB surfactants (Green and Cahill 2006). Solubility of nicosulfuron in the surfactant was important for efficacy. Crystals were observed in spray deposits with certain non-effective surfactants, which were assumed to be the herbicide (Nalewaja and Matysiak 2000; Woznica et al. 2000; Woznica et al. 2003).

Surfactants, depending upon their chemistry and other materials in the spray mixture, influence the characteristics of the spray droplet deposit (Green and Cahill 2006). A spray deposit of glyphosate, a water soluble herbicide, and high HLB linear alcohol ethoxylates left relatively thick deposits with good leaf surface contact that was efficacious (Nalewaja and Matysiak 1995). Surfactants that caused extensive droplet spread were not effective with glyphosate. These spreading surfactants are more lipophilic than the non-spreaders and would not be good solvents for highly water-soluble glyphosate, thereby reducing absorption. However, the importance of a concentrated deposit over a small area to glyphosate efficacy has been shown with concentrated droplets (Cramner and Linscott 1990) and low spray volumes (Ramsdale and Messersmith 2002; Ramsdale et al. 2003).

Conversely, efficacy of oil-soluble fluazifop was less influenced by deposit spread (Nalewaja and Matysiak 1995). The less viscous 6-10 carbon alcohol ethoxylates were generally more efficacious with fluazifop than those with 16-18 carbon. Surfactants that give an amorphous spray deposit with good leaf surface contact generally are positive for efficacy of water-soluble herbicides.

Minerals in the spray carrier water or fertilizer added to the spray mixture generally lower the optimum surfactant HLB for efficacy (Nalewaja et al. 2001). These minerals appear to cause a coarse granular deposit that may prevent good herbicide diffusion through the deposit to the leaf surface. Surfactants with a low HLB are less viscous, resulting in a deposit that is more liquid through which the herbicide may better diffuse for absorption and efficacy (Nalewaja and Matysiak 2000).

Oils

Oil adjuvants are petroleum or vegetable oil in origin. Oil adjuvants vary greatly. Petroleum oil adjuvants are selected for non-toxicity to plants and can vary in chemical composition, viscosity and emulsifier content. Petroleum oils with 17% or more of a specific emulsifier were called “crop oil concentrate” because they have equal efficacy with atrazine when used at 2.3 L/ha compared to 9.2 L/ha required for petroleum oil with 5% or less emulsifier. Vegetable oils are from several plant sources and are either refined oil or esterified oil, usually the methyl ester.

Petroleum and vegetable oil efficacy with nicosulfuron generally increased as emulsifier percentage in the adjuvant increased from 3 to 25 or 35% (Nalewaja et al. 1995). However, percentage emulsifier in the methylated oil adjuvant did not greatly influence efficacy. Thus, methylated oil was effective independent of the emulsifier and would only need enough emulsifier for good dispersion in the spray carrier water.

Spray retention generally increased as the percentage of oil adjuvants in the spray mixture increased (Bruns and Nalewaja 1998; Hall et al. 1997; Western et al. 1998). However, spray retention with an oil adjuvant was less with oil at 4% v/v than with surfactants at 0.25% v/v (Bruns and Nalewaja 1998). Spray retention for oil adjuvants, all with 15% v/v of the same emulsifier, generally was esterified vegetable > vegetable > petroleum oil, (Bruns and Nalewaja 1998). Thus, the function of oil adjuvants is more to aid absorption than spray retention. The above results were for adjuvants in water without herbicide, but addition of a sulfonylurea herbicide did not influence retention. Oils increase in effectiveness with increased concentration in the spray mixture so they usually are applied on an area basis and in amounts that give high percentages in the spray mixture, especially at low spray volumes.

Petroleum oils used with herbicides have a 70 or 110 second viscosity. These oils were used commonly as horticultural spray oils and were adapted for herbicide use because they were not toxic to plant tissue (Nalewaja 2002). Oil viscosity influenced efficacy of sethoxydim (Matysiak and Nalewaja 1999). Sethoxydim applied at 10 C was more efficacious when mixed with 70 second petroleum oil adjuvants than 110 second oil but the opposite occurred when applied at 25 C. High temperature appeared to cause the low viscosity oil to spread excessively, thereby reducing the sethoxydim deposit concentration for absorption. Conversely, at low temperature the high viscosity oil did not spread and gave poor droplet deposit contact with the leaf surface. Esterified vegetable oil was equally effective at both temperatures, providing deposits that spread with close contact to the leaf surface. The greater solvency of esterified oils than petroleum oils in cuticle may account for their efficacy, even though the deposits were thin (Manthey and Nalewaja 1992). Esterified vegetable oil was more efficacious than petroleum oils, regardless of temperature.

Solvency and viscosity characteristics of oil adjuvants do not always relate to efficacy with all herbicides (Nalewaja 1994). If cuticle solvency was primary to herbicide absorption, then esterified vegetable oil adjuvants would be most effective with all herbicides. However, for grass control, methylated sunflower oil was only equal to petroleum oil with diclofop, quizalofop, and fluazifop, but the methylated oil was more effective with sethoxydim, fenoxaprop and haloxyfop. For broadleaf control, methylated oil was more effective than petroleum oil with acifluorfen, fomesafen and imazaquin, equally effective with bentazon, and less effective with lactofen. Sunflower oil was less effective than petroleum oil with all of these grass control herbicides, but equal with sethoxydim. For broadleaf control with lactofen, a soybean oil adjuvant was only less effective than petroleum oil. These oils all had the same emulsifier (15% Atplus 300F). In general, methylated vegetable oils were equally or more effective than petroleum oil. Vegetable oils were equal to petroleum oil, except less effective with quizalofop, fluazifop, and lactofen.

Blended adjuvants

Many adjuvants are blends. All oil adjuvants are blended with an emulsifier but are not considered blend adjuvants. Basic blend adjuvant was first used to define a blend of fertilizer, surfactant, and basic pH enhancer. Basic blend also would apply to the high pH, oil, fertilizer, and surfactant adjuvants presently on the market. The term acid blend could be used for the low pH fertilizer blends used for glyphosate. Further, pH-lowering oils are marketed to protonate herbicides to overcome antagonistic salt herbicides or minerals in the spray water (Wanamarta et al. 1989). Blend adjuvant classification perhaps should be limited to those that are intended to change pH for efficacy. For example, when the blend is designed to raise pH it could be a basic blend and when to lower pH an acidic blend. Many adjuvants contain ammonium sulfate or other nitrogen compounds with or without a surfactant. These have been classified as nitrogen adjuvants.

Basic blends came into existence with nicosulfuron because the high pH helped to dissolve the herbicide for enhanced efficacy in presence of an ammonium salt and a surfactant specific to the high pH and salts in the adjuvant (Nalewaja et al. 2001). High HLB of the surfactant was positive to efficacy of nicosulfuron, which is water soluble at high pH (Green 2005). However, with ammonium salts as in a basic blend adjuvant, the optimum HLB was lower than without the salts (Nalewaja et al. 2001). Thus, the efficacy of a basic blend would depend upon the specific combinations of surfactant type, ammonium salt, and pH enhancer.

Adjuvant use patterns

The concept that oils are to be applied on an area basis and surfactants on a percentage basis may not be proper unless application on an area basis was independent of spray volume. The number of experiments that concurrently test various amounts of adjuvant and spray volumes is limited. One experiment was found where methylated vegetable oil and petroleum oil adjuvants at 0.4 and 0.8 L/ha were equally as effective with sulfonylureas when applied in 80 or 160 L/ha (Roehl 1992). Efficacy was greater at 0.8 than 0.4 L/ha for both oils.

Adjuvant percentage concentration decreases as spray volume increases when adjuvants are applied on an area basis. Thus, low spray volume would give a high percentage adjuvant in the spray without increasing the cost for adjuvant. Adjuvants applied on a percentage basis would require more adjuvant as volumes increase. Most research indicates that herbicide efficacy increased as oil adjuvant concentration in the spray increased because of a decrease in spray volume, regardless if spray volume was reduced by increased sprayer travel speed or a reduction in nozzle size (Nalewaja and Ahrens 1998; Ramsdale and Nalewaja 2001). Imazamox efficacy increased as percentage of methylated vegetable oil or nonionic surfactant increased independent of spray volume. Most reports indicate that increasing percentage of surfactant, oil, or basic blend adjuvant increases efficacy (Zollinger and Howatt 2005). In the previous research, the conclusion was that oil adjuvants should be applied on an area basis because control was greatest when applied at 1.75 L/ha. However, this also would have been the highest percentage if expressed as a percentage. Since surfactants and oil both function in spray retention and absorption, probably all adjuvants should be applied on a percentage basis. The percentages would need to be selected for the specific adjuvant. High percentages can be attained by using low spray volume without increasing the total adjuvant amount applied or cost.

Low spray volume of 47 L/ha has been equally or more effective than higher spray volumes for most herbicides (Manthey and Nalewaja 1992; Ramsdale and Messersmith 2002; Ramsdale et al. 2003). Low spray volume originally were considered important to glyphosate efficacy because it would reduce the ratio between glyphosate and antagonistic cations in the spray solution. However, low spray volumes have enhanced glyphosate efficacy, probably because of higher glyphosate concentration in the deposit (Cramner and Linscott 1990) and imazethapyr (Ramsdale and Messersmith 2002). It would seem logical that the highly concentrated droplets with low volume would be positive for translocated herbicides, but low spray volume also was positive to paraquat, a contact herbicide (unpublished NDSU data). Low spray volumes usually imply use of small nozzles that give small droplets, which are subject to off-target drift. However, nozzles have been developed that produce ‘large’ droplets at low volume. These larger droplets have been equally effective as small droplets for glyphosate in low spray volumes (Ramsdale et al. 2003).

Adjuvants are important to efficacy of postemergence herbicides. There are many types of surfactants and oils and their characteristics greatly influence efficacy. Commercial adjuvants have been selected for efficacy, but adjuvant types differ in effectiveness for different herbicides. These adjuvants need to be selected based upon their specific efficacies. For example, atrazine in mixture with nicosulfuron should be applied with a methylated vegetable oil that is effective with both herbicides. A basic blend adjuvant would be slightly more effective with nicosulfuron, but less effective with atrazine. Adjuvants, surfactants, oils, and blends generally increase herbicide efficacy with an increase in concentration. The economics for the proper concentration has not been established through research. Over time growers or adjuvant producers through experience usually establish an acceptable use rate.

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