III.10 ADJUVANTS

OVERVIEW

An adjuvant is any material added to a herbicide spray solution that modifies or enhances the action of that solution. Many herbicides already contain adjuvants as part of their formulations. Some of these formulations can be used directly whereas others need to be applied in conjunction with one or more adjuvants. There are over 3,000 adjuvants available for use. These can be grouped into three general types of adjuvants, including activators, spray modifiers and utility modifiers.

Activators increase the activity of herbicides by modifying certain herbicide characteristics, including particle size of the herbicide spray, distribution of the spray on the plant, spray viscosity, evaporation rate, rate of herbicide uptake or solubility of the herbicide in the spray solution. Activators can be either nonionic (producing little or no ionization in water) or ionic (having a positive or negative charge). It is generally recommended that a cationic (positively charged) herbicide should not be used with an anionic (negatively charged) adjuvant (and vice versa) because oppositely charged compounds could react, diminishing the effects of the herbicide. Most activators have no charge and thus can be mixed readily with any herbicide. There are three categories of activators including surfactants, wetting agents and oils.

Surfactants primarily influence the ability of herbicides to penetrate the leaf's waxy cuticle. Emersed and floating aquatic plants develop waxy cuticles similar to terrestrial plants, whereas submersed plants do not. Most herbicides are prepared in a solution of water. Water is a chemically polar material and thus can be repelled by the waxy surface of leaves. Activators reduce the surface tension of water on plants, and allow the herbicide formulation to wet leaf surfaces and enter into the plant.

Wetting agents increase the ability of water to displace air or liquids from the leaf surface, allowing it to be wet by the herbicide. (Surfactants also have wetting properties but they vary in the degree of wetting they provide.) Wetting agents help spread the solution more evenly over the leaf.

Oils are usually marketed at a concentration of about 80% oil/20% surfactant and are added to water to increase the retention time of a solution on leaves, allowing for an increase in herbicide uptake.

Spray modifiers influence the delivery and placement of spray solution. They confine or alter the characteristics of the spray solution. They include thickening agents (i.e., invert emulsions and polymers), stickers, spreaders, spreader-stickers and foaming agents, which reduce herbicide drift and allow for more exact placement of the herbicide.

Thickening agents modify the viscosity of formulations to reduce or control drift, aid in dispersal and promote sinking. Inverts and polymers are two types of thickening agents commonly used in aquatic herbicide applications.

Invert emulsions are mixtures of inverting oil and water, having a mayonnaise-like appearance on the water surface and a snowflake-like appearance under the water surface. Depending on their solubility, herbicides dissolve in either the oil or water component. The adjuvant/herbicide emulsion sticks to leaves and stems of plants, thus reducing drift and increasing herbicide contact time with plants.

Polymers are long-chain carbon molecules which are up to 40,000 carbons in length, forming a thick mucus-like material which helps to break the surface tension of water and enhance sinking of herbicides. Higher molecular weight polymers are generally formulated as an emulsion and are used as sinking agents. Lower molecular weight polymers are usually formulated as solutions and are used for drift control. Polymers are not very effective in water with a flow rate of greater than 3 cm/sec. as the herbicides/adjuvant mixtures may be washed off leaves before effective contact time is achieved. However, polymers are effective in still waters.

Stickers are made of vegetable gels, resins, mineral oils, vegetable oils, waxes or latex polymers. They promote the sticking of a spray to the sprayed surface. Stickers are usually used for application of fungicides and insecticides rather than herbicides.

Spreaders are blends of primarily nonionic surfactants used for spreading and sticking a spray to plant leaves. They are not as cost-effective as most surfactants but they can increase the effectiveness of some herbicides.

Spreader-stickers are combinations of the above two materials which provide additional retention of herbicide in wet conditions. These adjuvants are more expensive than surfactants and are not used very much in herbicide applications but they are used with fungicides and insecticides.

Foaming Agents are surfactants which are used with specialized spray applicators to create foam for reducing drift and evaporation. These agents are used infrequently for drift control of herbicide applications.

Utility Modifiers are rarely used in aquatic plant control. The addition of modifiers to a herbicide formulation expands the range of conditions (e.g., pH, hardness, etc.) under which a formulation can be used. Types of modifiers include emulsifiers, dispersants and stabilizing agents (including buffering agents and anti-foam agents). Buffering agents and anti-foam agents are used for aquatic plant management. Buffering agents are used to increase the dispersion or solubility of herbicides in alkaline or acid waters used in making up an herbicide solution. Anti-foam agents are mostly silicone-based and are used to eliminate foam in the spray tank, especially useful when mixing herbicides with soft water which usually creates a foaming problem. (above information adapted from: Aquatic Plant Identification and Herbicide Use Guide, 1988; Langeland, 1991)

COMMONLY USED ADJUVANTS

Table III.10-1 contains a partial listing of adjuvants used with aquatic herbicides.

TOXICITY

The toxicity of adjuvants is not as well characterized as the toxicity of herbicides. Very commonly, a study of the toxicity of a herbicide focuses on the active ingredient in the herbicide and neglects to consider the toxicity of adjuvants used during application of that herbicide.

Part of the reason for the limited toxicity information of adjuvants is that the regulation of adjuvants is not very rigorous. Adjuvants which are used in the application of herbicides on food crops come under the jurisdiction of the Food and Drug Administration (FDA). If an adjuvant is included in a pesticide's formulation, unless it has herbicidal properties, it is listed together with all other additives under "inert ingredients". If a herbicide formulation specifies on its EPA label that a particular adjuvant should be used during application, then the adjuvant also falls under the jurisdiction of the EPA. It is obvious that many adjuvants are not regulated at all. As a result, there are very few toxicity testing requirements and unless the manufacturer has conducted their own testing, there is little or no data available o the toxicity of these compounds (Edwards, personal communication, 1995).

Table III.10-1. Commonly Used Adjuvants

Name	Type	Action
Big Wet (E,F)	activator	nonionic/anion spreader, wetting agent, penetrant
Cide-Kick (E,F,S)	activator	nonionic wetting agent, activator, penetrant
Cide-Kick II (E,F,S)	activator	nonionic wetting agent, activator, penetrant
Ortho X-77 Spreader (E,F)	activator	nonionic spreader, activator
Asgrow "403" Invert Emulsifier (E,F,S)	spray modifier-invert	invert emulsion, drift control, reduce evaporation, increase droplet spreading and penetration, resist washoff
Bivert (E,F,S)	spray modifier-invert	invert emulsion, chemical encapsulating, suspending agent, deposition and retention agent, reduce drift and washoff
I'vod Inverting Oil (E,F,S)	Spray modifier-invert	invert emulsion, drift control, reduce evaporation, increase droplet spreading and penetration, resist washoff. (Dilution with #2 diesel oil or water required.)
Spra-Mate Invert Emulsion (E,F,S)	Spray modifier-invert emulsion	invert emulsion, drift control, reduce evaporation, increase droplet spreading and penetration, resist washoff (Dilution with #2 diesel oil or xylene required.)
Visko-Rhap (E,F,S)	Spray modifier-inverting oil	invert emulsion, reduce drift. (Can be diluted with #2 fuel oil or kerosene, if necessary)
Nalquatic (S)	Spray modifier-polymer	improve sinking, herbicide confinement and contact properties
Nalco-Trol (E)	Spray modifier-polymer	drift control, developed for Rodeo (glyphosate), diquat and 2,4-D; sinking agent for Hydrothal 191 (endothall)
Nalco-Trol II (E,S)	Spray modifier-polymer	sinking agent developed for Hydrothol 191 (endothall) and drift control for RODEO (glyphosate)
Poly Control	Spray modifier-polymer	drift control, sticking agent, nonionic
Poly Control 2 (S)	Spray modifier-polymer	drift control, sticking agent, nonionic
Submerge (S)	Spray modifier-polymer	sinking agent, contact confinement of herbicides (manufactured in both anionic and nonionic forms)

E - emersed plants
S - submersed plants
F - floating plants

(Aquatic Plant Identification and Herbicide Use Guide, 1988)

A survey of several adjuvant manufacturers indicated that while limited information on acute ecological toxicity (i.e., fish and aquatic invertebrates) was available, there was practically no information available on longer-term ecological toxicity. In addition, there was very little information available on the toxicity of adjuvants to mammals. An occasional acute toxicity test result was available, which was based on a single active ingredient in the adjuvant mixture. Such studies are of very limited usefulness in terms of characterizing the toxicity of an adjuvant since the toxicity of individual active ingredients in an adjuvant formulation can vary depending on the nature of the other compounds in the mixture.

In addition, even the available ecological acute toxicity tests are of limited usefulness. Often, in these tests, the adjuvant is tested as a full-strength material whereas during actual field application, an adjuvant is used in dilute form. Acute toxicity tests are useful in that they allow for a comparison of the acute toxicities between various materials. However, they offer no information on toxicity upon longer-term exposures to these materials at actual concentrations used.

Table III.10-2 summarizes the available ecological toxicity information for a number of adjuvants. Although use of adjuvants in Massachusetts is not as common as it is in areas with milder climates, such as Florida where herbicide applications are much more prevalent, selected adjuvants are still occasionally used by applicators in the state (Smith, personal communication, 1995).

For each adjuvant, the type of adjuvant is specified as well as the 96-hour LC50 value for rainbow trout and/or bluegill sunfish as well as the 48-hour LC50 for *Daphnia*, an aquatic invertebrate. The LC50 is defined as the concentration in water (in mg/l) which will kill fifty percent of the organisms in a specific test situation. The table also includes a qualitative toxicity designation (Christenson, 1976) for each adjuvant for fish and for invertebrates as defined below:

LC50	Classification
<1 mg/l	HT (Highly Toxic)
1-10 mg/l	MT (Moderately Toxic)
10-100 mg/l	ST (Slightly Toxic)
100, 1,000 mg/l	PN (Practically Nontoxic)
>1,000 mg/l	IH (Insignificant Hazard)

Table III.10-2. TOXICITY STUDIES IN AQUATIC ORGANISMS FOR SELECTED ADJUVANTS

Adjuvant	Adjuvant Type	96-hr LC50 (mg/l) rainbow trout	96-hr LC50 (mg/l) bluegill sunfish	REF	TOX	48-hr LC50 (mg/l) Daphnia	REF	TOX
#4 Fuel Oil	surfactant	---	91.0	1	ST	---		
"403"	invert emulsifier	---	37.0	1	ST	---		
Activator 90	surfactant	1.4	2.0	2	MT	2.0	2	MT
Agri-Dex	surfactant	>1,000	>1,000	2	PN	>1,000	2	IH
Arbor Chem (same as X-77)[7]	nonionic spreader; activator	4.2	4.3	3	MT	2.0	2	MT
Big Wet	nonionic/anionic spreader; wetting agent; penetrant	---	112.0	3	PN	---		
Big Sur 90	wetter/spreader	---	112.0	1	PN	---		
Cide-Kick	nonionic wetting agent; activator; penetrant	---	5.2	1,3	MT	3.9	4	MT
Entry II	surfactant	4.2	1.3	2	MT	2.0	2	MT
Frigate	surfactant	3.6	2.4	2	MT	11.0	2	ST
Herbex	surfactant	---	8100.0	1,3	IH	---		
I'VOD	spray modifer/invert	---	37.0	1	ST	---		
Induce	surfactant	5.6	7.5	2	MT	18.0	2	ST
Latex Paint	surfactant	---	560.0	1	PN	---		
LI-700	surfactant	130.0	210	2	PN	170.0	2	PN
Liqua-Wet	surfactant	13.0	11.0	2	T	7.2	2	MT
Nalco-trol	spray modifier polymer	>1,000	---	5	IH	280	5	PN
Nalcotrol II	spray modifier/polymer	>1,000	---	5	IH	270	5	PN

Table III.10-2. TOXICITY STUDIES IN AQUATIC ORGANISMS FOR SELECTED ADJUVANTS

Adjuvant	Adjuvant Type	96-hr LC50 (mg/l) rainbow trout	96-hr LC50 (mg/l) bluegill sunfish	REF	TOX	48-hr LC50 (mg/l) Daphnia	REF	TOX
Nalcotrolb	spray modifier/polymer	---	>1,000	5		---		
Nalquatic	spray modifier polymer	---	200.0	1	PN	---		
No Foam A	surfactant	3.3	6.0	2	MT	7.3	2	MT
Passage	surfactant	52.0	75.0	2	ST	17	2	ST
Polysar Latex	surfactant	---	3600.0	1	IH	---		
R-11	surfactant	3.8	4.2	2	MT	19	2	ST
Spra-Mate	spray modifer/invert	---	0.96	1	HT	---		
Spreader-Sticker	surfactant	36.0	35.0	2	ST	48.0	2	ST
Super Spreader 200	surfactant	4.2	9.3	2	MT	24.0	2	ST
Widespread	surfactant	6.6	7.0	2	MT	16.0	2	ST
X-77	nonionic spreader; activator	4.2	4.3	3	MT	2.0	2	MT

Explanatory Notes for Table III.10-2

TOXICITY CLASSIFICATION [6]

LC50	Classification
<1 mg/l	HT (Highly Toxic)
1 - 10 mg/l	MT (Moderately Toxic)
10-100 mg/l	ST (Slightly Toxic)
100-1,000 mg/l	PN (Practically Nontoxic)
>1,000 mg/l	IH (Insignificant Hazard)

References for Table III.10-2

1. Watkins *et al*., 1983.
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3. JLB International Chemical, Inc., 1983.
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7. Lentz, 1996.

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