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SPRAY ADJUVANTS ARE MANAGEMENT TOOLS[1]

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Abstract. The various classes of spray adjuvants are defined and explained; what they are, how they work, and what they do. Primary benefits as well as major problems and limitations are covered. I conclude with major considerations for adjuvant selection and a use guide.

Confusion swirls around spray adjuvants because so few people understand them. From the manufacturers and the people writing labels, to the agricultural authorities we depend on for spray recommendations, from consultants and suppliers, to the users and their hired sprayman, the confusion continues. *We don't use a common terminology to discuss the subject.* Too often, all spray adjuvants are simply considered as 'spreader-stickers.'

Let's educate both the educator and the educatee. We'll start with product labeling, define the classes of adjuvants, discuss how they work, and some of their characteristics, uses, and limitations. Finally, we'll discuss selecting spray adjuvants.

ADJUVANT is defined as 'an additive to help or improve.' Then, *spray adjuvants are additives to sprays to help or improve some phase of spraying between initial spray mixing and final activity of the spray after application.*

The most expensive spray is the one that fails to accomplish the purpose for which it is applied. Regardless of whether it was the wrong pesticide, inadequate coverage, washed off, or whatever. Could an adjuvant have made it work? Manufacturers cannot formulate for all plants and all conditions. You may need a spreader for spraying waxy plants and a sticker if rain loss is a hazard.

Labeling

The labeling of spray adjuvants is basically unregulated, except in California, and there is little consistency from one label format to another. To be legal they must have a tolerance established by the EPA or be classified 'tolerance exempt.'

Many spray adjuvant products are misnamed or mislabeled, either purposely or out of ignorance. Labels may or may not show their chemistry and level of activity and are often stated in misleading ways or misleading terms. There is no easy way to determine exactly what's in a product when the supplier wants to write a deceptive label. You need a dependable supplier.

Definitions

These definitions are not dictionary precise but are geared to the subject of spraying and are accurate for that purpose. I hope they will begin to clarify the present state of confusion swirling around the whole subject of spray adjuvants.

Spreader, Wetting Agent, and Surfactant (these are synonymous terms referring to a broad group of surface active agents) *Chemicals that reduce the surface tension of spray solutions so spray droplets spread out, covering a greater surface area.* (NOTE. **Ad**sorb = onto the surface of the spray target. **Ab**sorb = into or taken in through the surface, inside the plant or spray target. The word "surfactant" is coined from the phrase SURface ACTive AgeNT).

Spreading action is especially important for achieving good spray coverage on waxy or pubescent (hairy) plant parts, for getting spray into cracks and other small openings such as leaf

1. Presented at the annual conference of the International Society of Arboriculture in Milwaukee in August 1985.

sheaths and under bark scales, and to help move systemic chemicals or contact herbicides through waxy cuticles into the plant tissue. *(NOTE. This greater coverage and increased penetration also increases the danger of phytotoxicity when plant tolerance is close.)*

Surfactants are divided according to their chemical reactivity (1) and may or may not be labeled as nonionic, anionic or cationic, or combinations like nonionic/anionic blends: *Nonionic* surfactants do not ionize in water, they are essentially non-reactive. *Anionic* surfactants ionize into negatively charged ions in water, they are negatively reactive. *Cationic* surfactants ionize into positively charged ions in water, they are positively reactive. They are also phytotoxic and almost never used in spraying.

Nonionic spreaders are the surfactant group most commonly recommended. This is presupposing that the anionic surfactants might react chemically with some pesticides, but this author is not aware of any data confirming this as a significant problem. *Nonionic re-wetting is far more serious than anionic reactivity. But you never hear about it.*

Rewetting, a problem with nonionics. Pesticide spray residues are washed away easier and faster by rain, dew, and irrigation when applied with a nonionic spreader than they are if applied without any adjuvant. Nonionic surfactants are stable, non-volatile compounds that remain as active residue on plant surfaces after a spray dries. They are then re-activated by free moisture from rain, irrigation, or dew and function as detergents (detergent cleaning compounds are made from these same surfactants), hastening and increasing pesticide wash-off. This has caused many pesticide failures for which there was no apparent explanation.

A special note. Detergent cleaning compounds such as kitchen or laundry detergents, engine cleaners, etc., should NOT be used as spray adjuvants because (1) the 'builders' they contain increase pesticide wash-off, (2) most are illegal in sprays, lacking EPA clearance, and (3) many contain alkaline materials which degrade some pesticides (see acidifiers below).

How Spreaders Work. A spreader (surfactant) molecule is somewhat like a tadpole: the 'head' is soluble in aliphatic substances (oils, petrosolvents, etc.) and is water repellent (hydrophobic). The 'tail' is insoluble in aliphatic substances and is water attracted (hydrophilic). In water, the water repellent 'head' moves the molecule to and through the water surface, while the 'tail' remains in the water. Wherever a molecule penetrates the surface, surface tension is broken and reduced. The greater the number of breaks, the more surface tension is reduced (Fig. 1). The result of surface tension reduction is easily seen when drops of water are dropped onto waxed paper (Fig. 2). The same thing happens on waxy leaves and other plant surfaces.

Pubescent (hairy) plants and plant parts have a special spraying problem; the surface tension of water sprays holds spray droplets up on the hairs of pubescent plants and prevents wetting of the actual plant surfaces. The addition of a spreader

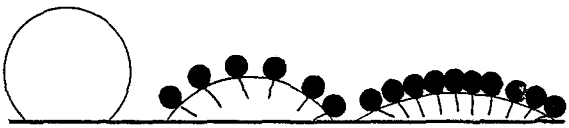


Figure 1. Surfactant molecules break the surface tension of water when the water repellent 'head' protrudes through the water surface. The greater the number of molecules the more surface tension is reduced.

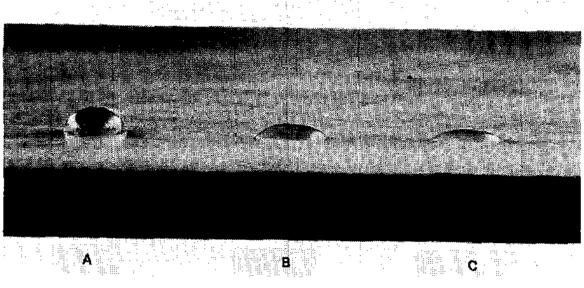


Figure 2. Drops of water on waxed paper: (a) no surfactant, (b) with 1 pint Ortho X-77® (non-ionic spreader) and (c) with 2 pints Ortho X-77 per 100 gallons.

will permit the droplets to move down the hairs, onto the leaf or plant surfaces.

High rates of spreader are as bad as low rates. Excessive spreader causes water sprays to runoff or flow into depression areas of the sprayed surface, mainly off, onto the ground. Poor coverage and insufficient redistribution of the pesticides with reduced effectiveness can be the result (see Figure 3).

Emulsifier. *Surfactants are called "emulsifiers" when they are used in aliphatic substances so they will mix with water.* Emulsifiable concentrate pesticides are formulated by first dissolving the technical pesticide(s) in a solvent, then adding emulsifiers so the solution will mix into water. When emulsifiable pesticides are put into water, the reverse of the action described above for surfactants in water occurs; the 'tail' moves the molecule to the surface of the aliphatic and protrudes through the surface into the water while the 'head' remains in the aliphatic. Surface tension of the aliphatic is weakened, allowing water to intermingle with it, forming an emulsion.

Emulsifiable oils are very special oils containing specially blended emulsifiers (about 1 to 2%) so they will mix with ("emulsify" in) water. When an oil spray strikes the spray target, the oil separates out onto the sprayed surface while the water carrier and emulsifier run-off onto the ground or evaporate away. The oil is then without emulsifier, is no longer water miscible, and is not readily washed off of the spray target.

Figure 3. On waxy leaves: (a) spray without spreader does not deposit satisfactorily; (b) high spreader rates 'slide' deposits to the ground or into depressions; (c) proper spreader-sticker gives good spray coverage.

Crop oil concentrates (COC's): Mixtures of petroleum or vegetable oils with 15 to 20% surfactant as emulsifiers. They function mainly as spreaders but have some holding action by oil deposited onto the sprayed surface. The oil is somewhat of a sticker but serves mainly as a penetrant to help the movement of herbicides through plant cuticles.

Sticker. *A sticking agent gives an adhesive effect to protect spray residues against loss due to rain, dew, or irrigation and wind erosion, leaf abrasion, etc.* They also increase spray chemical deposition, i.e. as a deposition aide.

A problem: Stickers, if used at high rates, can hold pesticide residues so tightly they are literally entombed and useless. This can also occur when full rates of stickers are combined with pesticides already containing an effective sticker.

Spreader-sticker. *An adjuvant with both spreading and adhesive qualities,* that is, having surfactant activity to give initial spray coverage plus adhesive protection for the spray residue after the spray has dried.

Note. The greatest area of misrepresentation, confusion, and misunderstanding in the whole subject of spray adjuvants is the promiscuous use of the term 'spreader-sticker!' Many products labeled 'spreader-sticker' are nothing more than a nonionic spreader, having no adhesive quality whatsoever.

Extender. *A spreader-sticker with additional qualities to prolong or e-x-t-e-n-d the active life of pesticides after application,* more than just sticking them in place. NU-FILM-17®, for example, is an ultra-violet radiation screener that protects spray residues from solar heat and photodecomposition which degrade many pesticides. This is exactly the same as people protecting themselves against sunburn by using a sun screening suntan lotion (Fig. 4).

Activator. (See spreader, wetting agent, and surfactant above.) All spreaders activate and all commercial 'activators' are spreaders; 'activator' therefore is not truly a separate class of spray adjuvants.

Compatibility agent. *An adjuvant to improve* *the mixing of chemicals that do not otherwise mix in a spray solution without objectionable changes.* Any spray mixture that takes on a 'grainy' appearance or appears to curdle or flocculate has a compatibility problem and will not be as effective, if it can even be sprayed. A compatibility agent will often prevent such separation, if anticipated, and will occasionally enable the re-mixing of an already separated spray solution (Fig. 5).

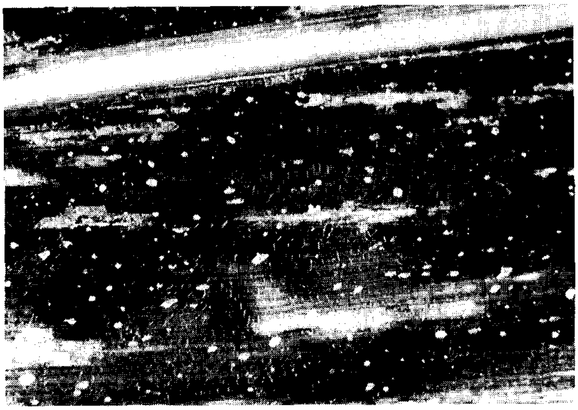


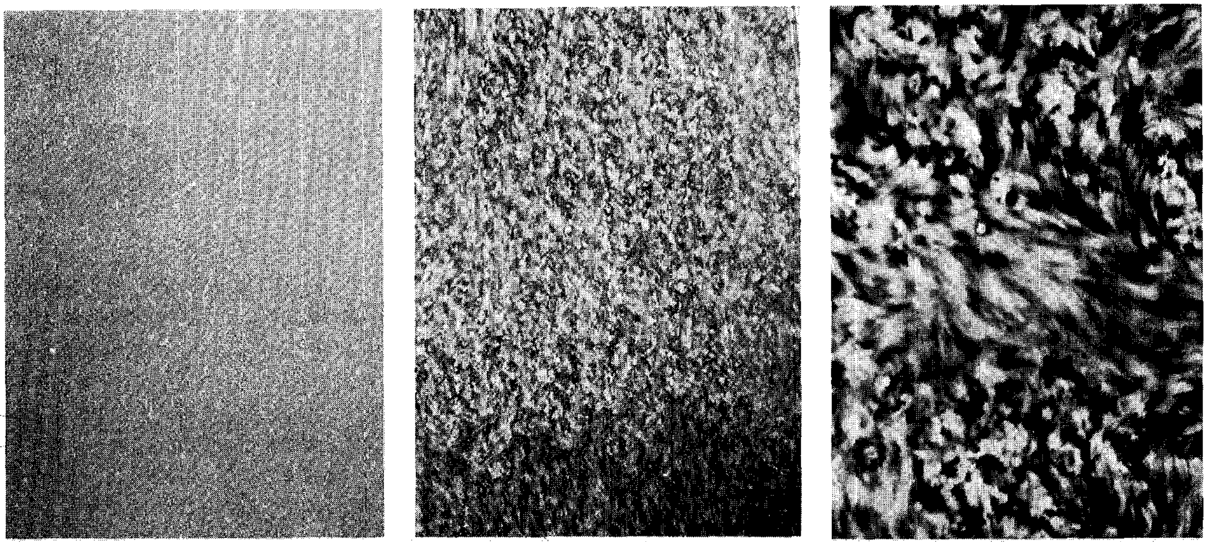
Figure 4. Manzate® 200 spray residue held by Nu-Film-17® on seed corn leaf a full month after application. Blight control was excellent, despite the few lesions showing in this September photograph.

Acidifying agent, acidifier, or buffer. *Acid adjuvants to lower the pH of alkaline spray solutions.* An acidifier with buffering action not only lowers the pH but also helps maintain a desired pH range. Spray solution pH should be around pH 6.0 for best results with most pesticide chemicals.

Alkaline water, even mildly alkaline, causes alkaline hydrolysis (degradation) of many pesticide chemicals, some in less time than it takes to put out a tank of spray. This problem is much more serious than generally recognized (Table 1).

Very few sprayer operators know the pH of the water they are using. Check the pH of water sources and determine corrective procedures if needed. Periodic rechecks through the spraying season are also important, especially for surface water and shallow well sources (Appendix 2).

Some spray ingredients and pesticides have an acid or an alkaline effect in sprays that should not be overlooked. Many soluble and liquid fertilizers are excellent acidifiers. Alkaline products such as lime sulfur, Bordeaux mix, calcium chloride, etc., should generally not be combined with other



A B C

Figure 5. Physical compatibility: In a good smooth spray mixture (a) the individual particles of pesticide are not distinguishable while an incompatible or flocculated mixture (b & c) usually shows a visible separation though it may be more subtle than shown here.

pesticides. Checking compatibility charts should be a routine part of spray planning by spray operators and managers!

Defoamer or anti-foam agents. *Adjuvants to break foam or prevent its formation in spray tanks.* Every sprayer should have some defoamer with it at all times, just in case a foam problem develops. Defoamers are much cheaper than down time!

Drift control agents. *Adjuvants to reduce the breakup of sprays into fine droplets that can drift out of the spray zone.* Spray drift is double jeopardy: first, it reduces the effectiveness of the spray application, second, it creates contamination hazards for adjacent properties, crops, and people; with a potential for serious legal implications. However, the effective reach of a hydraulic hand gun and a low concentrate air blast sprayer is increased by drift control agents. Larger average size drops have greater momentum and 10% to 20% range increases are normal (Fig. 6).

A problem: all commercially available drift control agents seriously increase the pH of spray solutions to which they are added. See the discussion of alkaline hydrolysis above.

Deposition aide. *Adjuvants that increase the amount of pesticide actually deposited on spray*

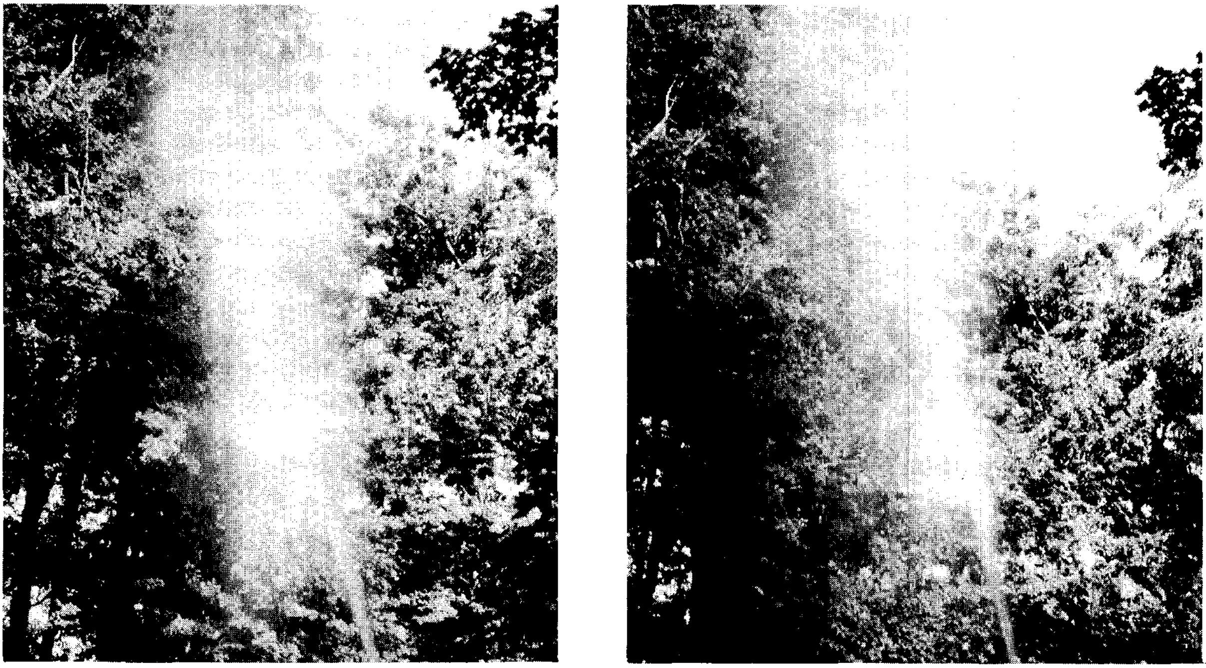
Table 1. Alkaline Hydrolysis. Effect of high pH spray solutions on some commonly used pesticides.

Chemical	*Common name*	*Comments*
Dyrene®	Anilazine	Subject to hydrolysis
Difolitan®	Captafol	Decomposes rapidly above 9.0.
Furadan®	Carbofuran	Unstable under alkaline conditions.
Dylox® Proxol® Dipterex	Trichlorfon " "	Degrades rapidly (approx. 99% of applied degraded in 2 hrs) in alkaline pond water (pH 8.5) at room temperature.
Counter®	Terbufos	Subject to hydrolysis under alkaline conditions.
Systox®	Demeton	Subject to hydrolysis under alkaline conditions.
Cygon®	Dimethoate	pH 6.0 ½ life = 12 hours. Unstable in alkaline water.
Diazinon®	Diazinon	pH 6.0 ½ life = 37 hours. Hydrolysis rapid in strong acid or alkaline water.
Imidan®	Phosmet	pH 8.0 ½ life = 4 hours pH 7.0 ½ life = 12 hours pH 4.5 ½ life = 13 days
Captan®	Captan	pH 10.0 ½ life = greater than 2 minutes pH 4.0 ½ life = 4 hours
Malathion®	Malathion	Stable at pH 5.0-7.0 but rapid hydrolysis in more acidic or alkaline solutions
Polyram®	Polyram	Unstable under strongly acidic or alkaline conditions

The truth about a couple of fungicides commonly maligned about alkaline hydrolysis.

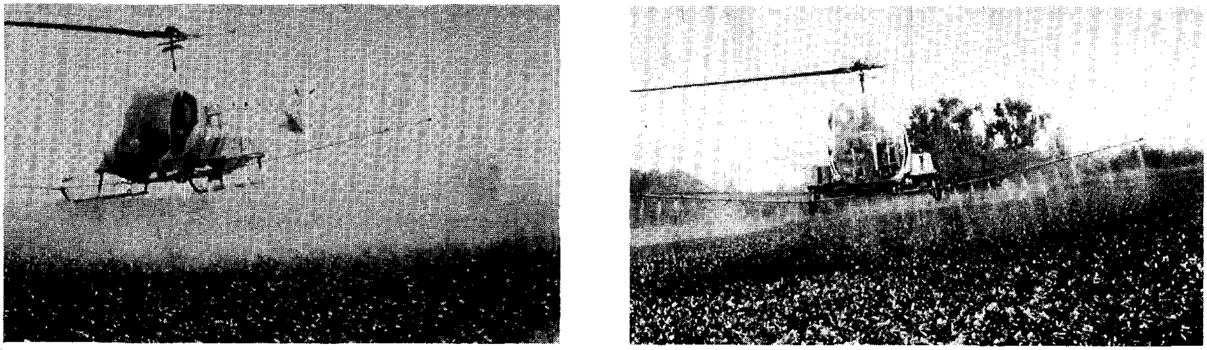
BENLATE® or TERSAN® 1991. Benomyl is systematically fungicidal and quite stable in mildly acid to slightly alkaline water solutions. The first breakdown of benomyl is MBC (Methyl 2-benzimidazole carbamate) which is essentially as effective fungicidally. fungicidally.

BRAVO® . pH 7.0 or lower: no hydrolysis in aqueous solutions. pH 9.0: Rate of decline 1.8% per day (half life = 38.1 days).



Hydraulic handgun

Air blast sprayer



Helicopter spraying

Figure 6. Drift control agents reduce the breakup of sprays into fine droplets that can drift on the wind and increase the range of air blast sprayers and hydraulic hand gun sprayers.

targets. Drift control agents are also effective deposition aides because (1) more of the spray remains in the spray zone to be deposited on the spray target and (2) the spray drops resist running off of plant surfaces. Pesticide deposit increases of 25% to 35% are common for sprays which include a drift control agent.

Suspending agents. *Thickeners and dispersants to maintain more uniform dispersions of chemicals in spray solutions.* They prevent or slow the separation of solid and non-miscible spray components such as wettable powders and fertilizers.

Others. There are other spray adjuvants such as chelating agents, foaming agents, coloring agents, fluorescent materials, etc. Usually their names indicate their primary uses. If you have a special need, contact a good chemical supplier. The product may exist.

'SERPENTOLIA': Snake-oil products and selling methods. A whole array of cleaning compounds, some real shyster products and some good products are being sold by housewives, farm hands, students, and others. Don't be a sucker! Buy your spray adjuvants from reliable spray chemical suppliers.

Conclusion

A functional knowledge of adjuvants is important in order for spray managers to obtain maximum benefits and returns from every dollar spent for spray chemicals. By giving some careful thought to the spray needs to be met, the spraying conditions expected, and the weather for the next 7 to 10 days, the adjuvant(s) needed will become more apparent. Use the following selection guide.

Things to remember and do.

1. Select adjuvants as carefully as pesticides. Read the pesticide labels and select adjuvants that not only meets label requirements but also the conditions under which the spray will be applied and expected to perform (Appendix 1).
2. Buy spray adjuvants, as well as spray chemicals, from a reliable, professional chemical supplier who will be there when you need him: one who knows spray adjuvants as well as pesticide chemicals and keeps up with the constant changes.
3. Bottle test spray mixtures for compatibility. If anything in a spray mix is new or different (the water source, the pesticide mix, the brands of chemicals), test before mixing a full batch of spray. It could save you a bundle of money and headaches (Appendix 3).
4. Check the spread of some drops of the spray mixture on the plants to be sprayed. Somewhat mounded spray drops that stay in place are what is wanted. High standing, round drops that fall off or shake off easily indicate the need for more spreader. Flat drops that tend to slide easily off of the plant surfaces, leaving a wet line, indicate too much spreader. For pubescent (hairy) plants, the drops should flow down among the hairs but not readily flow off of a vertical leaf surface.
5. If a rain or heavy dew is likely before the next regular spray, use a sticker. If the outside of the sprayer is easily or even readily washed off after a day's spraying, the sprays will wash off the plants just as easily; more or a better sticker is indicated.
6. If it is windy, the humidity is low, or there is a temperature inversion near the ground, use a drift control agent.
7. When using alkaline spray water, lower the pH to below pH 7.0 with an acidifying agent. Lower the pH to about 6.0 if the spray must stand in the tank overnight or longer than a normal application time.
8. When spraying a solar heat or ultra-violet radiation sensitive pesticide (a surprising number are), use an extender.

Acknowledgments. Rohm and Haas Company, Philadelphia, PA, for my very valuable training, sales and use experience with surfactants; their uses in agricultural chemicals, formulations and spraying as well as household and industrial products applications.

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APPENDIX 1

SPRAY ADJUVANT SELECTION GUIDE

Spray water
- pH test
  - For desired acidity and rate of acidifier, if needed (see pH Testing Spray Water, Appendix 2)

Spray target
- Plant(s) to be sprayed
  - Normal - little or no spreader needed
  - Waxy - spreading action needed
  - Very waxy - good spreading needed
  - Pubescent - good spreading needed
- Pesticide(s)
  - Spreader-activator needed? (See product label)

Weather
- Today
- Next 10 days
  - Windy during spraying - drift retardant needed
  - Rain, irrigation, windy or heavy dew likely on spray day or within 7 to 10 days - sticker needed
  - Ultra-violet sensitive chemicals - extender needed.

Pre-Spray Mixing
- Bottle Test
  - For compatibility and acidifier rate, if needed. (see bottle test for spray mixtures, Appendix 3)

Spray Mixing
- Mix tank of spray for work
  - Re-check pH in tank after adding acidifier and before adding other ingredients
  - Check for any compatability problems
  - Add pesticides
    - Add de-foamer if needed
  - Check spray on target plants for coverage
    - Add more spreader if needed

During Spraying
- Be ready to make changes as work progresses and situations or conditions indicate

APPENDIX 2

pH TESTING SPRAY WATER

This test procedure, if properly completed, will give a good indication of spray solution pH AND an approximate use rate for acidifier additions when tank mixing:

pH 6.0 to pH 6.5 is best for most spray chemicals but below pH 7.0 is generally satisfactory unless the spray solution is to stand overnight or for several hours. Then the pH should be dropped to about pH 6.0

NOTE: 3 drops of acidifier per 1 pint of solution = approximately 2 fluid ounces per 100 gallons of spray solution. (6 drops = ¼ pint or 4 fl. oz.; 9 drops = 6 fl. oz.; etc.)

Equipment required
- pH meter, pH test kit, pHYDRION® Papers or other means to determine pH.
- clean, 1 quart, container.
- standard eye dropper.
- clean stirring implement.
- sample of the intended spray water or spray solution.
- sample of SPRAY-AIDE© or other acidifying agent intended for use in the spraying operation.

Procedure
(May be accomplished as part of the 'bottle test')
1. Place one (1) measured pint of the intended spray water or solution in the clean container.
2. Check the pH of the sample.
3. Adjust the pH of the sample, if necessary, by:
   a. add 3 drops of acidifier to the solution -stir- check pH
   b. if needed, continue pH adjustment by adding 3 drops of acidifier, stirring and checking, until desired pH is achieved.
   c. the number of acidifier additions (3 drop groups) will give an approximate use rate of acidifier per 100 gallons of spray water or spray solution (see NOTE above).

Finally
When the spray tank has been filled and the acidifier added, CHECK THE pH AGAIN and make a final adjustment if needed. The above test gives an approximate acidifier rate.

APPENDIX 3

BOTTLE TEST FOR SPRAY MIXTURES

(Check your compatibility before getting tanked-up)

This test is approximately 8X concentration and is intended as a stress test to accentuate compatibility problems for normal spraying operations. (See note below for higher concentrations)

Equipment needed

- **clean, 1 qt., clear glass bottles = 1 per test or re-test.**
- **measuring spoons, standard kitchen = 1 teaspoon, 1 tablespoon.**
- **suitable stirring rods or spoons.**
- **standard eye dropper.**
- **all intended spray ingredients.**

Procedure

1. *Measure 1 pint of intended spray water or spray solution into a bottle.*
2. Check the pH of the liquid (see appendix 2, pH testing) and adjust if necessary.
3. Add other intended spray ingredients: (In order) (use level filled measures)
   a. surfactants (spreaders), acidifiers, compatibility agents, or activators: add 1 teaspoon for each pint/100 gals. of each of these adjuvants intended.
   b. dry ingredients: add 1 tablespoon for each lb./100 gals.
   c. flowable ingredients: add 1 teaspoon for each pint/100 gals.
   d. liquid ingredients: add 1 teaspoon for each pint/100 gals.
   e. soluble ingredients: add 1 tablespoon for each lb./100 gals.
   f. spreader-stickers or spreader-sticker-extenders.

NOTE: If any incompatibility shows up at any point, stop.

1. Add compatibility agent to the mix in increments of 6 drops per addition with stirring or agitation. Some incompatibilities can be corrected after separation has occurred but most cannot.
2. If this does not smooth the mix, start the test over again in a clean bottle. BEGIN THE RE-TEST by first adding 6 drops *of compatibility agent to the water (equivalent to 4 oz/100* gals) then proceed as above. Additional tests can be run by increasing the drops of compatibility agent in 6 drop increments (12, 18, etc.)
3. Check the need for a *De-foamer,* add if necessary.
4. Let the bottle stand for one hour after a smooth mix has been achieved. Then re-agitate by stirring or shaking: Does the spray solution reform into a smooth mix?
   a. If yes, go to work.
   b. If no,
      1. add some compatibility agent as described above; if the mix smooths out, go to work.
      2. try different brands or change forms of the pesticides, wettable to emulsifiable, etc.
      3. change chemicals and try again. Some chemicals are *totally incompatible and a satisfactory spray cannot be* made combining them.
5. *Keep watching* any spray mix that has shown any incompatibility in bottle test. It should be carefully checked when mixed in the spray tank and watched regularly during spraying operations. Changes that may bring a problem back include:

   changing brands of chemicals or batches within a brand,

   changes of temperature, water, or air,

   changing water sources (individual water sources vary during the spraying season, check them periodically.)

   changes in order of mixing,

   and others, keep watching these potentials.

REMEMBER, 'Whenever things seem to be going real good, you've probably overlooked something.'

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