Surfactant Chemistry

Research Report 129 **September 2006**

Jerre Creighton, Virginia Department of Forestry Research Program Manager

Abstract

Surfactants are used to alter spray solution properties so that herbicides can be more effectively applied to and absorbed by target plant foliage. By altering the surface tension of droplets, they shift the properties of liquid herbicide formulations to a more water- or oil-like state. This in turn optimizes the polarity, penetration, spreading, elasticity, drying, shearing and cost of the spray solution. In particular, glyphosate (Accord) is a very water-like herbicide whose performance can be enhanced for site preparation by the addition of a surfactant that imparts more oil-like characteristics. However, for pine release treatments there is increased likelihood of pine foliage and leader damage. Therefore, to widen the differential between conifer and broadleaf uptake, a more water-like surfactant is required. Historically, only Entry II (a cationic tallow amine surfactant) has been recommended for release treatments. Entry II is no longer marketed, so replacements of similar or identical chemistry are being tested. In a replicated study of several surfactants in 1991, all treatments caused pine leader mortality (up to 42%), but all damaged pines had recovered and were growing as well as or better than the untreated checks within four years after release.

Introduction

For landowners seeking to maximize the growth of conifer plantations, control of non-crop woody competition is a very important consideration. For example, in a long-term study in Alabama, plots containing 20 percent of their basal area in hardwood species experienced a 50 percent loss in loblolly pine volume by age 24 (Glover and Dickens 1985, Burkhart and Sprinz 1984).

Most competition control is accomplished using herbicides applied either before (site prep) or after (release) planting of the pine crop. Because spray solution properties can significantly affect the uptake of the herbicide by the target plants and the crop species, surfactants and emulsifiers are often used to adjust them. The choice of surfactant can be critical in determining the outcome of an herbicide application. With that in mind, it is worthwhile to review some important facts regarding solution chemistry and surfactants. Much of the material that follows is paraphrased from Burkhalter's excellent summary (Burkhalter 1994).

Solution Chemistry

Surfactants are emulsion chemicals – oil-water hybrids. Part of the chemical acts like water and part acts like oil. By definition, a surfactant is a long-chain organic molecule that has a polar (water-like) and a non-polar (oil-like) end. Emulsifiers also have water- and oil-like ends, but are used to aid in the temporary mixing of oil and water to form an emulsion. By contrast, a solution is a stable mixture of two materials (like salt in water) that will not separate if left undisturbed. And a suspension is a temporary mixing of solid material in water or oil that will re-separate if left unagitated because the fine solids never really go into solution. The "ideal" droplet for most spray operations is neither totally like water nor totally like oil. By changing surfactants we can modify spray solutions, suspensions, or emulsions to be more oil- or water-like, resulting in marked differences in results. Some important spray solution properties that surfactants affect include:

1. **Polarity**: Water molecules are polar; they have a small negative charge imparted by the oxygen and a small positive charge due to the hydrogen. This makes water molecules act a lot like tiny magnets, and their attraction for each other is what causes water to form droplets with tension on the surface layer (much like small basketballs). Surfactants reduce that surface tension because the polar end of the surfactant attracts to the water molecule and the non-polar end orients toward the surface. Surfactants make water behave more like a non-polar molecule (oil).

2. **Penetration**: Because water molecules are polar and highly attracted to each other, water doesn't separate easily into smaller droplets. It is therefore a poor penetrant of fine spaces and micropores such as those on plant leaf surfaces. Surfactants enhance penetration by reducing surface tension and allowing the spray solution to break up into smaller droplets. Oils are excellent penetrants.

3. **Spreading**: Surface tension also causes water to be a poor spreader. Even when applied as small droplets, water can pull back together to form larger droplets on a leaf surface, and if the leaf is not oriented horizontally they will run off. This reduces coverage of the leaf surface area and diminishes herbicide efficacy. By reducing surface tension, surfactants minimize this effect, increase spreading, and increase herbicide efficacy. Oils are excellent spreaders.

4. **Elasticity**: Surface tension on water droplets can allow them to bounce off of target foliage completely. Again, surfactants break up the surface tension and cause the spray solution to stay on the leaf. Oil droplets are inelastic; they hit a surface and spread without bouncing.

5. **Shearing**: One very good side effect of the high surface tension of water droplets is that they are less likely to form fines when sprayed under pressure through application equipment, which in turn reduces the risk of spray drift. Spray solutions containing surfactants (or oils) are therefore more prone to shattering of water droplets, formation of fines, and off-site drift. Note however that spray drift potential can be (and is) mitigated by the proper selection of application equipment and conditions.

6. **Drying**: Another beneficial effect of surface tension in water is increased drying time. Large droplets dry more slowly than the thin sheets of solution formed by surfactants. Especially for herbicides formulated as solids, accelerated drying means that the herbicide returns quickly to the solid state on the leaf or soil surface, and solids are poor penetrants indeed (unless, of course, they are fired as a projectile, but that is another story). Oils spread quickly into fine sheets and may dry very quickly (depending on the type of oil).

7. **Cost**: Water is the least expensive component of any spray solution, so if the herbicide is water-like or can be made more water-like by use of a surfactant (often the second least expensive component) then it can be dissolved in water, making it more easily usable. Herbicides that are oils are usually formulated with an emulsifier so they can be blended with water a carrier in a high-volume emulsion.

States of Herbicides

Like everything else, herbicides exist in three states – solid, liquid and gas. The state in which the herbicide is formulated is important in determining its mixing requirements and characteristics, plant uptake patterns and surfactant requirements.

1. **Solids**: Some herbicides are not very soluble, and may be formulated as wettable powders or liquid suspensions. Solids – even in suspension – do not move very easily into leaves, so they tend to be absorbed into plants more through the root system (i.e. soil active). Surfactants usually have relatively little effect on solid herbicides.

2. **Liquids**: Many common forestry herbicides are formulated as liquids; either the herbicide is a liquid in its pure state or it is a solid dissolved in water or oil to make a solution before being used. Surfactants are most important for liquid state herbicides – for the reasons described above.

3. **Gases**: Gases can penetrate better than any other pesticide, but no forestry herbicides are formulated as gases. However, it is important to remember that the three states of matter are in equilibrium; therefore even solid or liquid herbicides volatilize to some extent. We generally tend to underestimate the role of this gas fraction in plant uptake. For example, triclopyr (Garlon) volatility at high temperatures is well documented. Gas phase uptake of herbicides compensates for more application errors (and contributes to more off-target movement) than many of us realize. However, surfactants have little effect on the gas phase.

Types of Surfactants

Surfactants are often characterized as ionic or non-ionic, depending on whether they physically dissociate into positive and negative particles in water. Most fall into the latter classification.

1. **Ionic**: Ionic surfactants dissociate in water. If the oil-like part of the surfactant carries the positive charge, it is referred to as a cationic surfactant. If the oil-like part retains the negative charge, it is an anionic surfactant. Because ionic surfactants bond well with water they tend to impart more water-like properties. Also, because many forestry

herbicides are also ionic, they may react with the ionic surfactant resulting in very bad outcomes. It is therefore important to have either specific label instructions or previous positive experience before using ionic surfactants in spray solutions.

2. **Nonionic**: The most common surfactants are non-ionic; they do not separate into negative and positive ions in water. Their charges are weaker and built into the molecules, so they are not likely to react directly with the herbicide molecules. This also tends to make them more oil-like than ionic surfactants. This is the class of surfactants to use for most applications, and certainly is preferred whenever there is any doubt as to possible herbicide interactions.

Hydrophile:Lipophile Balance (HLB)

Hydrophile:lipophile balance is just a chemist's way of saying water:oil balance. Oils are closer to 1, and water is closer to 20. But there is a simple way to approximately test for HLB. Mix the recommended ratio of surfactant in water in a small volume and observe. The clearer the resulting solution the more water-like it is. If there are clear layers (no mixing), the HLB is between 1 and 4 (oil). If droplets form in the mix, HLB is between 3 and 6. If a milky solution forms, HLB is between 6 and 10. Translucent to nearly clear indicates HLB between 10 and 13. And a clear solution is between 13 and 20 (water).

Surfactant Effects Specific to Glyphosate

(Accord Concentrate, Razor Pro, Glypro, etc.)

Glyphosate is a broad-spectrum, nonselective systemic herbicide used for control of annual and perennial plants including grasses, sedges, broad-leaved weeds, and woody plants. It is a very water-like herbicide and therefore is often used with a surfactant to bring more oil-like properties to the spray mix. There are also instances where very specific surfactants, very little surfactant, or no surfactant at all are recommended in order to expand the margin of safety for certain crop plants. Without a surfactant, the glyphosate rate must be increased in order to achieve equivalent results on the pest plant. As a rule, any surfactant is usually better than none for insuring weed control.

The surfactant prescription for glyphosate progresses from more water-like to more oil-like as the target changes from more annual, to herbaceous, to woody, to evergreen plants. This is because in general the ability of the plant to translocate a water-like herbicide across its leaf cuticle decreases along the spectrum from annual to waxy-type evergreen plants. Other leaf factors like orientation and texture can also impact spray uptake (Knoche and Bukovac 1993). If leaves or needles grow upright or hang vertically, water-like droplets may drop to the ground with near-zero uptake. On leaves with hairy or pubescent surfaces, water droplets can suspend above the leaf surface and never penetrate unless surface tension is reduced. In both cases, surfactants can be beneficial in accelerating plant uptake and improving rainfastness (Reddy and Singh 1992).

Site prep recommendations usually include an oil-type surfactant to increase injury to and control of volunteer pines and other evergreen species. Note that "oil-like" surfactant is not the same as “oil-based”; an “oil-like” surfactant brings non-polar attributes to the spray mix but does not contain oil as a filler. Because glyphosate is insoluble in oil, its performance will diminish quickly as the oil content of the spray mix increases.

For conifer release, on the other hand, the only surfactant recommended is a polyethoxylated tallow amine (aka polyoxyethyleneamine) formerly marketed under the trade name Entry II (Burkhalter 1994, Creighton 1996). Entry II was a cationic tallow amine which is very water-like (HLB of 16-20), and research has shown that these properties are optimal for glyphosate uptake in many annual and broad-leaved weeds (Riechers et al.1995). Unfortunately, Entry II is no longer marketed, but several similar or identical surfactants are being tested as replacements. Since pines are evergreen waxy-leaved plants whose foliage is difficult to penetrate or wet effectively, this choice of surfactant widens the differential between the broadleaf deciduous target species and the crop pines. It is also important that the pine buds be dormant (“set”) before applying the herbicide, which further protects the tree from herbicide uptake.

The current label for Accord Concentrate states the following in regards to conifer release:

> “Broadcast application must be made after formation of final conifer resting buds in the fall or prior to initial bud swelling in the spring.”
>
> “Injury may occur to conifers treated for release, especially where spray patterns overlap or higher rates are applied. Damage can be accentuated if applications are made when conifers are actively growing or are under stress from drought, flood water, improper planting, insects, animal damage or diseases.”
>
> “Accord Concentrate may require use with a surfactant. Use a nonionic surfactant recommended for over-the-top foliar spray at the recommended labeled rate.”

The 1999 label for Accord Herbicide contained the following instructions specific to broadcast forestry conifer and hardwood release:

> “This product may require use with a surfactant. Unless otherwise recommended in this section of this label, use Entry II surfactant at 10 to 30 fluid ounces per acre.”

A Case Study

A replicated study initiated 1991 by Westvaco (now MeadWestvaco) in West Virginia tested label rates of – among others – CideKick II (0.25%), TimberSurf 90 (0.5%) and Entry II (10 oz./acre) with Arsenal / Accord tank mixes for release of pitch x loblolly pines at the end of the second growing season after planting. Table 1 summarizes the hardwood control, pine damage and growth results. Within two months of application, all treatments caused at least some pine leader damage, but Entry II caused significantly less than the other surfactants. For example, with 8 oz. of Arsenal and 1 qt. of Accord, percent leader kill with Entry II, TimberSurf 90 and CideKick II averaged 9, 42, and 37 percent, respectively. Five years after application, all of the release treatments had controlled hardwoods and improved the free-to-grow rating of the stand compared to the untreated check, and hardwood control improved when Arsenal rate was increased from 4 to 8 oz. per acre in a tank mix with 1 qt. of Accord. Entry II provided the lowest residual hardwood densities, and the best pine diameter and height growth of all the treatments. In spite of the early foliar burn and leader kill, there were no survival effects of treatment (all plots exceeded 93% survival after treatment) and by age seven all plots were growing as well as or better than the untreated checks (MeadWestvaco 2005).

Table 1. Hardwood control and pine growth data from a 1991 study of surfactant effects on the efficacy and pine tolerance of operational release treatments (8 oz. Arsenal + 1 qt. Accord + either TimberSurf 90 (TS 90), Cide-Kick II (CK) or Entry II per acre).

Treatment	Hardwood Age 7			60-Day	Pine Age 7					
	Density (trees/ acre)	Average Height (ft.)	Sum of Heights (ft./acre)	Leader Kill (%)	FTG Rating (1-4)	Height (ft.)	DBH (in.)	Survival (%)	Pine Volume ($ft.^3$/ acre)	Volume Gain (%)
Untreated	5058	6.6	34190	1	1.73	17.9	3.1	96	585	---
8 + TS 90	1794	4.3	8318	42	1.26	17.5	3.5	98	744	27
8 + CK	1991	4.5	8581	37	1.15	18.5	3.5	96	771	32
8 + Entry	1507	4.1	6480	9	1.16	19.6	3.7	99	941	61
4 + TS 90	3291	6.0	20012	30	1.38	18.0	3.2	93	607	4
4 + CK	2457	5.0	14350	42	1.20	18.0	3.3	98	681	16
4 + Entry	2483	4.0	10464	20	1.20	19.0	3.5	97	800	37

Conclusions

Surfactant chemistry is complicated because many surfactants are mixtures of related materials, and many formulations are proprietary. But surfactants are important because they can affect the outcome of forestry herbicide applications. For pine release with glyphosate in particular, only a cationic polyethoxylated tallow amine similar to Entry II can provide maximum hardwood control with minimum risk of pine damage. Other surfactants can be used but will be much more prone to pine terminal damage, especially if application occurs before bud set. Evidence from a study conducted in 1991 indicate that even stands with 40 percent + of pine terminals killed can outgrow untreated plots in volume within a few years after treatment. Results of that study also indicated that surfactant damage alone (i.e. in the absence of other damage or stress due to insects, disease, herbivory, drought, etc.) did not cause pine mortality.

References

Burkhalter, A.P. 1994. Surfactants – emulsion chemistry. Auburn University Silvicultural Herbicide Cooperative Information Note 94-1, Auburn University, AL. 12 pp.

Burkhart, H. E. and P.T. Sprinz. 1984. A model for assessing hardwood competition effects on yields of loblolly pine plantations. Department of Forestry, College of Natural Resources, VPI & SU, Blacksburg, VA, FWS-3-84. 55 pp.

MeadWestvaco unpublished data. 2005. Surfactant effects on the efficacy and pine tolerance of operational pine release tank mixes in West Virginia. Westvaco Appalachian Forest Research Center.

Glover, G. R. and D.E. Dickens. 1985. Impact of competing vegetation on yield of the southern pines. Georgia Forestry Commission Research Paper 59. 14 pp.

Knoche, M. and M.J. Bukovac. 1993. Interaction of surfactant and leaf surface in glyphosate absorption. Weed Science 41: 87-93.

Reddy, K.N. and M Singh. 1992. Organosilicone adjuvant effects on glyphosate efficacy and rainfastness. Weed Technology 6: 361-365.

Riechers, D. E., L. M. Wax, R. A. Liebl, and D. G. Bullock. 1995. Surfactant effects on glyphosate efficacy. Weed Technology 9: 281-285.