

**CHARACTERIZATION OF ORGANOSILICONE SURFACTANTS AND
THEIR EFFECTS ON SULFONYLUREA HERBICIDE ACTIVITY**

by
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(ABSTRACT)

This research focused on the characterization of organosilicone surfactants and their effects on sulfonylurea herbicide activity. The project included efficacy tests, rainfastness studies in the greenhouse, radiotracer studies on herbicide uptake, fluorescent dye studies on surface deposition, and various measurements of physico-chemical properties.

In measuring physico-chemical properties, a logistic dose response relationship was found between adjuvant concentration and contact angle on parafilm. An AsymSigR relationship existed between adjuvant concentration and surface tension for all the adjuvants. The organosilicones, Silwet L-77, Silwet 408, and Sylgard 309, and Kinetic (a blend of an organosilicone with a nonionic surfactant) gave equilibrium surface tension values around 20 dyne/cm and showed great spreading ability on the foliage of velvetleaf. With the conventional adjuvants, Agri-Dex, methylated soybean oil, Rigo oil concentration, and X-77, and Dyne-Amic (a blend of an organosilicone with a crop oil concentrate), surface tension was rarely below 28 dyne/cm and spreading ability was limited on velvetleaf. In addition, the organosilicone surfactants and Kinetic also lowered dynamic surface tension, which may improve droplet retention on leaf surfaces. The differences in physico-chemical properties between Kinetic and Dyne-Amic confirmed that carefully selecting a co-adjuvant for an organosilicone blend is critical to avoid antagonism with trisiloxane molecules and retain the unique physico-chemical properties of organosilicone in the blends.

Studies involving structurally-related organosilicones showed that the end structure in the trisiloxane hydrophilic group has little or no effect on surface tension, contact angle, spread pattern, herbicide uptake and translocation, and efficacy of primisulfuron on velvetleaf. It may be suggested that there is not a strict requirement to purify the end structure during the synthesis process, which is time consuming and expensive.

When ^{14}C - primisulfuron was combined with organosilicones or the blends, the uptake of ^{14}C at 1 or 2 h after herbicide application was significantly higher than when combined with conventional adjuvants in velvetleaf. In the greenhouse, organosilicone surfactants greatly increased the rainfastness of primisulfuron in velvetleaf. The effect was immediate and dramatic, even when simulated rainfall was applied 0.25 h after treatment. In addition, herbicide efficacy on marginally susceptible weed species, velvetleaf and barnyardgrass, was significantly increased.

A very complicated relationship exists between herbicides and adjuvants. The enhancement effects of adjuvants are often herbicide specific, weed species specific, and even environment specific. No one type of adjuvant functions well in all circumstances. Therefore, there is a need to understand the properties and functions of each class of adjuvants and locate the 'right' niche for each individual adjuvant.

This dissertation is dedicated to my parents, for their unfailing love, and many years of sacrifice.

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CHAPTER 1. LITERATURE REVIEW

INTRODUCTION

The contribution of agricultural chemicals to the world's agricultural economy is tremendous and increasing by providing protection against damages caused by various insects, diseases, and weeds. The world pesticide market in 1989 was estimated to be \$20 billion. The U.S. represents the single largest market, making up 25% (\$5 billion) of the world's total (Underwood, 1992). Among various pesticides, Foy (1993) reported that product labels of 19 agrichemical companies, involving approximately 485 formulations of crop protection chemicals for use in 1992, recommend the use of adjuvants with 49% of such formulations and 71% of the herbicide formulations. Underwood (1992) reported that sales of emulsifiers and spray adjuvants in the U.S. in 1989 were estimated to be \$300 million which represents a total 6% of the U.S. pesticide market; and spray tank adjuvants also comprise an estimated \$150-million market. According to Rogiers (1995) the world adjuvant market is worth around US \$500 million in 1995 - approximately 2.5% of the total pesticide market. The total world consumption of surfactants as adjuvants in agriculture was estimated at 60,000 tons in 1993. In any case, the importance of pesticides, and the adjuvants that are used with them is clearly evident. On the other hand, during the past 20 years, the economics of petroleum-based materials from which most herbicides are derived have changed and their components are no longer cheap. In many cases, it has become impractical in both economy and environment to continue to use great amounts of herbicides to obtain the desired high level of weed control. Because of these changes, university and industry researchers have worked to develop more effective and less expensive adjuvants and herbicides. Their efforts have been fruitful and many research papers have been published. Most of their results have proved that adding adjuvants with agrichemicals, especially with herbicides, can greatly increase their efficacy compared with those products used alone. There are many adjuvant

companies and dealers in Europe and North America now, and the overall sale of adjuvants and the development of specialty 'value-added' products have increased in recent years (Foy, 1993).

From many research results, those additives can produce various effects on herbicide activity. They may improve the emulsifying, dispersing, spreading, wetting, solubilizing, and/or surface modifying properties of herbicide formulations to bring about enhancement of foliar penetration and herbicidal action. Surfactants normally reduce surface tension of aqueous systems and improve wetting. All of those may favor both stomatal and cuticular penetration. But herbicide-surfactant-plant surface interactions subtler and more specific than mere surface tension lowering and increased wetting are suggested. The nature of total surfactant action is complex and not fully understood.

ORGANOSILICONES

History.

Organosilicone compounds, as a new generation of agrichemical adjuvants, have been actively used with different agrichemicals, especially with herbicides, in recent years. By March, 1995 (Gaskin and Stevens, 1995), 261 papers had been published on Silwet organosilicone surfactants as agricultural adjuvants. Organosilicone compounds used as herbicide adjuvants were first reported by Jansen (1973). He tested several structurally related organosilicones and tried to provide the information for the comparative effectiveness of organosilicones as enhancing adjuvants on several weed species for several herbicides; the relative influence of structural and property variations in the organosilicones on efficacy; and the potential applications of organosilicones in agriculture. Ten herbicides, three crops, and five weed species, were included in his experiments. Jansen's research showed that the efficacy of the organosilicones was associated with weed species, particularly some grasses, which were relatively resistant to herbicides applied without adjuvants. Also, organosilicones

had a greater ability to enhance herbicide activity with very low water solubility. In conclusion, the author pointed out the potential to use organosilicone compounds as a new class of adjuvants for herbicides in the future (Jansen, 1973). However, this pioneer paper did not generate much interest in using organosilicone compounds as agrichemical adjuvants at that time. Some published researches used organosilicone compounds as adjuvants for growth regulators, and foliar nutrients including iron, potassium, and nitrogen rather than herbicides (Coker *et al.*, 1987; Greenberg and Goldschmidt, 1988a, 1988b, 1990; Greenberg, *et al.*, 1984, 1986, 1987, 1990, 1991; Hartley and Hodson, 1990; Leece and Dirou, 1979; Weinbaum and Neumann, 1977). More attention was given to the development of new herbicides. During that period, several new herbicidal families, e.g. sulfonyleureas and imidazolinones were marketed. These herbicides have distinguishing characteristics compared with conventional herbicide families, such as extremely high activity, very specific selectivity, and very low toxicity to mammals. However, this trend changed after the mid-eighties. Recent data show that moving a new compound from the research stage to market requires about a decade and costs around \$100 million and, usually, one successful herbicide is selected from more than 20,000 tested compounds (OSi Specialties, 1995). At the same time, public concerns over the environment, and strict EPA requirements have also placed pressure on new herbicide development. In the past, the agricultural industry had the tendency to think that all problems caused by pests could be solved by using the appropriate pesticide at the optimal lethal concentration. Adjuvants were not widely used because pesticides were simple, inexpensive products. Today, pesticides have become more complex and they now account for an important part of the farmer's budget. As a result, there is now a huge incentive for formulators and basic pesticide producers to pay greater attention to the development of synergistic, activating, penetrating adjuvants. During this process, organosilicone compounds as a new class of agriculture adjuvants have begun to attract attention. Among 261 organosilicone references, 242 of them have been published since 1985.

General structure, physico-chemical properties, and spreading mechanism.

There are two basic groups of compounds used to synthesize organosilicones; these are silane and hydroxysilane (Figure 1) (Jansen, 1973). Polymerization among these groups can produce long chain organosilicone substances. The final product can be controlled by altering the number of silicon atoms and changing the R groups.

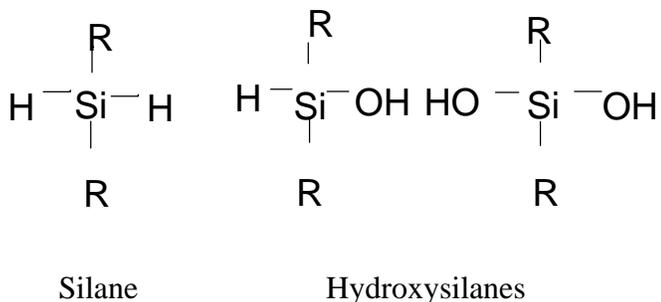


Figure 1. Silicone compounds used in organosilicones synthesis. Source: Jansen, 1973.

Murphy *et al.* (1991), in studies on the influence of organosilicones on spreading ability, showed that only the solutions containing organosilicones can dramatically increase the relative spread area. The spreading area of the solution containing Silwet L-77 on paraffin film was 179 times larger than that of water used alone (Murphy *et al.* 1991). According to Gaskin and Zabkiewicz (1989), when a biological surface was used, the spread area of the solution with Silwet L-77 was approximately 100 times greater than that of the glyphosate solution alone; the other surfactant solutions also substantially enhanced droplet spread but to a lesser extent on common velvetgrass (*Holcus lanatus* L.) upper and lower leaf surfaces. Most research results have shown that only the tri-organosilicone with a methylated group has super spreading ability (Murphy *et al.*, 1993). To date, all commercialized agricultural surfactants are trisiloxanes. The general trisiloxane structure is shown in Figure 2.

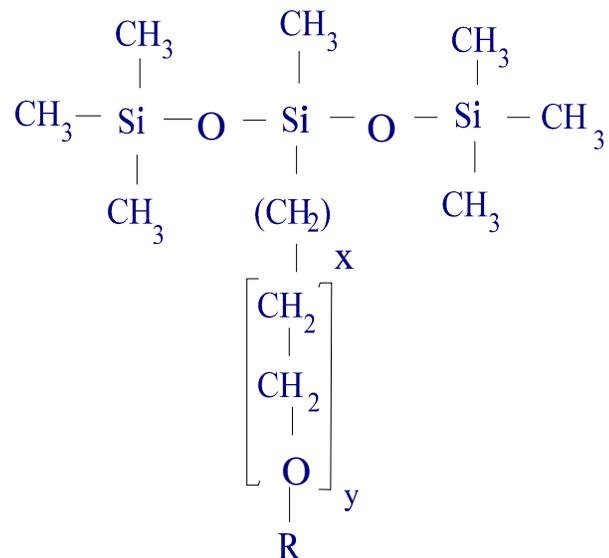


Figure 2. General trisiloxane structure (Knoche, 1994)

The structure of the organosilicone surfactant plays a vital role in the spreading of aqueous solutions on the target surface. The high density of methyl groups characteristic of siloxane backbones of organosilicone surfactants accounts for the non-polar character (Knoche, 1994). The spreading mechanism, proposed by Ananthpadmanabhan *et al.* (1990) suggests that the compact size of the hydrophobic portion of the trisiloxane allows it to transfer readily from the liquid/air interface of the advancing solution to a low energy surface, such as a waxy leaf cuticle. This phenomenon is illustrated in Figure 3 and has been linked to a “molecular zipping” of the liquid/solid interface.

Due to the extremely low static surface tension and the “molecular zipping” effect, aqueous solutions of the silicone surfactants spread completely on most hydrophobic surfaces. However, according to Murphy *et al.* (1991), surface tension lowering does not always enhance spreading. They used fluorocarbon as an adjuvant

which confers to water the lowest surface tension (around 16 dyne/cm), but the relative spread area was not increased much compared with water alone.

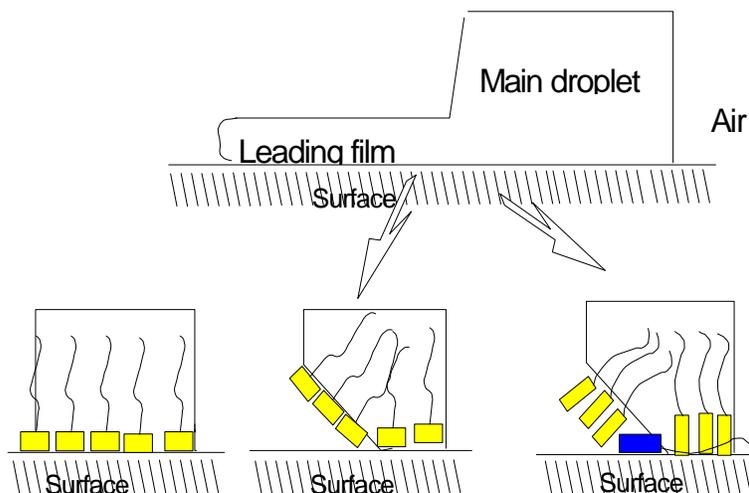


Figure 3. Molecular zippering hypothesis (Source: Ananthapadmanabhan *et al.*, 1990)

Murphy *et al.* (1991) also found that when an organosilicone combined with a conventional adjuvant form a blend, the molecular “zipper model” suggested that the conventional surfactant may compete with the organosilicone molecules in the liquid/solid interface. Therefore, a large hydrophobic group in the convention adjuvant (co-surfactant) might impede the spreading of the conventional surfactants.

Contact angle and surface tension are two important concepts related to adjuvants. Surface tension is determined by the physico-chemical properties of adjuvants. Contact angle is the result of interaction between droplet and target surface. Zabkiewicz *et al.* (1985) reported that formulations with contact angle from 50 degrees or less are considered as having good wetting capability, while complete wetting is possible if the value is 20 degrees or less. Even this criterion seems to be somewhat arbitrary.

Extensive work related to organosilicone surfactant physico-chemical properties has been done by Murphy *et al.* (1991, 1993), Policello *et al.* (1991, 1993), Stevens and Zabkiewicz (1990), Stevens *et al.* (1988, 1990, 1992a, 1992b), and Zabkiewicz *et al.* (1988). From various reports, trisiloxanes have some unique properties including extremely low surface tension, superior spreading ability, and relatively low phytotoxicity.

Stability.

The silicon-oxygen bonds in the backbone of organosilicones are susceptible to hydrolytic cleavage (Knoche, 1994). Hydrolysis of organosilicone surfactants has been investigated in detail (Knoche *et al.*, 1991a, 1991b). The organosilicone surfactant Silwet L-77 degrades in acidic (pH 2 to 5) and alkaline (pH 9 to 10) spray solutions (Knoche *et al.* 1991a) and these pH levels are not unusual for some commonly used agrichemicals (Knoche *et al.* 1991b). During degradation, changes in turbidity and increases in surface tension of the spray solutions may be used as indicators of surfactant breakdown (Knoche *et al.*, 1991b). An organosilicone review paper published in 1993 showed an example of the molecular re-arrangements that can occur due to degradation and rearrangement of the silicone-oxygen bonds (Figure 4) (Stevens, 1993). During the hydrolysis process, two trisiloxane co-polymers may form a tetrasiloxane co-polymer and hexamethyldisiloxane. The latter is a water-insoluble silicone oil, while the former has reduced surface activity, being more water-soluble than its parent trisiloxane because it has a siloxane : polyether (PE) ratio of 4:2, in contrast to the original 3:1. While such a tetrasiloxane is likely to retain good surface activity, clearly this illustration is one of the first steps in an iterative process that will give rise to much larger polysiloxane co-polymers, with greatly reduced surface activity.

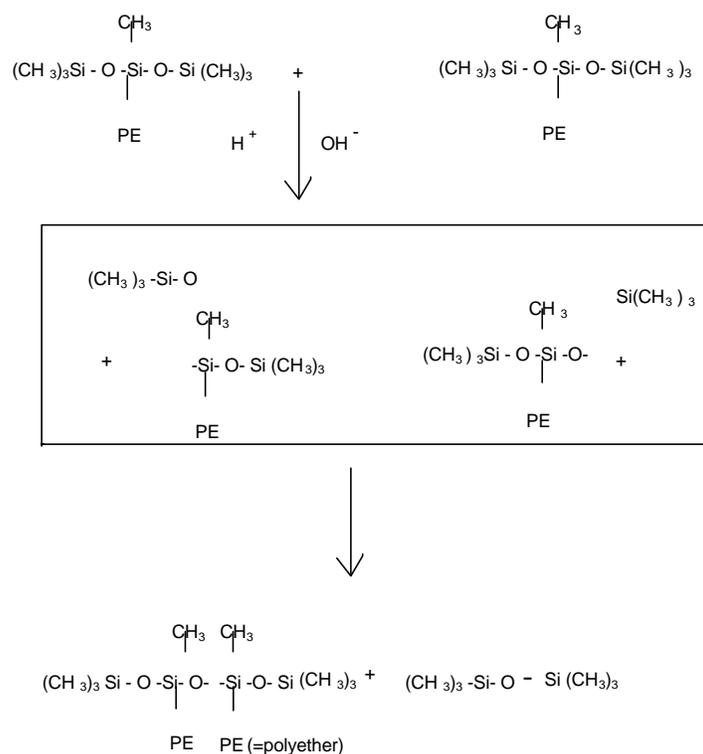


Figure 4. Example of hydrolytic degradation of a trisiloxane. (Source: Stevens, 1993)

Effect on herbicide efficacy.

To date, more than 26 herbicides of various herbicide families have been tested with organosilicones on different weed species in the field and greenhouse. Most of the work concentrated on glyphosate [*N*-(phosphonomethyl)glycine], acifluorfen {5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid}, and chlorimuron {ethyl 2-[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate} (Balneaves, 1985, 1987, 1988, 1992a, 1992b; Balneaves and Fredric, 1983, 1988; Balneaves *et al.*, 1993; Bishop and Field, 1983; Bourdot *et al.*, 1989; Bovey *et al.*, 1993; Gaskin and Kirkwood, 1987; Gaskin and Murray, 1988; Gaskin *et al.*, 1986a; Karjalainen and Boomsma, 1989; Monsanto, 1986, 1989; Popay *et al.*, 1985; Singh and Mack, 1993). From that research, the following conclusions can be derived:

The effects of organosilicone surfactants on herbicide performance are herbicide and weed species specific. Generally, the efficacy of herbicides is increased by organosilicones. The results are equal to or better (rarely poorer) than those with conventional adjuvants. However, antagonism occurred when glyphosate was combined with organosilicones on several grass species (Field and Bishop, 1988a, 1988b; Field and Tisdall, 1990; Field *et al.* 1992).

Numerous studies have shown that organosilicone surfactants improved the rainfastness of herbicides by inducing stomatal infiltration (Field and Bishop, 1987; Kudsk, 1992; Roggenbuck *et al.*, 1990, 1993). Simulated rainfall applied 2 h after spray application of glyphosate had no effect on the response of perennial ryegrass (*Lolium perenne* L.) in the presence of Silwet L-77, but in the absence of organosilicone surfactant, rain reduced herbicide effectiveness for up to 10 h after herbicide application (Field and Bishop, 1988a). Similar data were reported for glyphosate plus Silwet L-77 applied to quackgrass [*Elytrigia repens* (L.) Nevski.] (Thonke *et al.*, 1989) and for acifluorfen plus the organosilicone surfactant Q2-5309 applied to velvetleaf (*Abutilon theophrasti* Medikus) (Roggenbuck *et al.*, 1990).

Effect on herbicide foliar uptake and translocation.

The effects of organosilicone surfactants on the foliar uptake of agrochemicals have been extensively investigated. Until now, the effects of organosilicone surfactants on herbicide uptake and translocation have been studied with at least 11 radiolabelled herbicides and more than 22 weed species. The extensive work on uptake and translocation was done by Gaskin and Kirkwood (1986a, 1986b); Gaskin and Stevens (1993a, 1993b); Gaskin and Zabkiewicz (1988, 1989, 1990, 1991, 1992); Gaskin *et al.*, (1986b); Stevens and Zabkiewicz (1988); Stevens *et al.* (1991, 1992a); Zabkiewicz and Gaskin (1989, 1991); and Zabkiewicz *et al.*(1985, 1988, 1993). The general trends from these research results show that herbicide uptake was significantly or slightly increased by organosilicone surfactants. However, uptake antagonism on several grass species occurred only when glyphosate was combined with

organosilicones. These weed species included colonial bentgrass (*Agrostis tenuis* Sibth.), orchardgrass (*Dactylis glomerata* L.), quackgrass, perennial ryegrass (*Lolium perenne* L.), dallisgrass (*Paspalum dilatatum* Poir.) (Field *et al.* 1988b, 1992). These results are consistent with reports on efficacy.

Zabkiewicz *et al.* (1993) reported that, when Silwet L-77 and ^{14}C -glyphosate were applied alone and in combination with each other to the upper surfaces of leaves of broad bean (*Vicia faba* L.), over 80% of the glyphosate was taken up within 10 min in the presence of 5 g liter^{-1} Silwet L-77, with no further uptake over the remaining period. A similar pattern of uptake was observed with 2 g liter^{-1} Silwet L-77, but only 30% was taken up initially. In the presence of 1 g liter^{-1} Silwet L-77 initial glyphosate uptake was only 15%, but uptake continued, subsequently reaching 25% after 6 h. This behavior was essentially the same as that of glyphosate applied without surfactant. The authors concluded that when using bean plants and deoxyglucose as a model system, increased deoxyglucose uptake was dependent upon the surfactant concentration. Above a threshold of 2 g liter^{-1} considerable stomatal infiltration occurred, but at or below this concentration cuticular penetration was the predominant pathway (Zabkiewicz *et al.* 1993).

Gaskin and Murray (1988) reported that addition of organosilicone compound could enhance uptake of glyphosate into pampasgrass [*Cortaderia selloana* (Schult.) Asch. & Graebn.] foliage, but subsequent translocation out of the treatment zone was dependent on the amount of damage to the subcuticular membrane.

When a herbicide solution is applied to a leaf surface, there are two pathways for herbicide active ingredient to enter the plants. One is to penetrate the cuticular layer; in most situations this is the main pathway. Another way is to enter the stomatal cavity directly. According to Schönherr and Bukovac (1972) and Greene and Bukovac (1974), for stomatal infiltration to occur, the surface tension of the formulation must be equal to or less than the critical surface tension of the target surface (Schönherr and Bukovac, 1972). The critical surface tension of most leaf surfaces ranges from 20

dyne/cm with sugarbeet (*Beta vulgaris* L.) to about 30 dyne/cm with broccoli (*Brassica oleracea* var botrytis L.), or *Zebrina purposii* (Knoche and Bukovac, 1993; Schönherr and Bukovac, 1972). Since the surface tension of organosilicone solutions is always below this range, the promotion of herbicide uptake via stomatal pores by organosilicones was proposed by Field and Bishop (1988a, 1988b) and Stevens *et al.* (1991, 1992a). The solution that enters into the substomatal cavity by stomatal infiltration provides easier diffusion of the active ingredient into the adjacent cells, since the cuticle lining the substomatal cavity is thinner.

Study results showed that triclopyr {[3,5,6-trichloro-2-pyridinyl)oxy]acetic acid}, glyphosate, and deoxyglucose did enter through stomatal pores when Silwet L-77 was present by using fluorescent dye and electron microscopic techniques (Buick and Field, 1990; Buick *et al.*, 1992, 1993; Field and Bishop, 1988a, 1988b; Stevens *et al.*, 1991, 1992a).

The advantages of induced stomatal infiltration, very well summarized by Stevens *et al.* (1992a), are listed below:

1. The active ingredient (a.i.) taken up in this manner is immediately rendered rainfast.
2. Other factors that also may erode deposits of a.i. on the exterior of foliage, e.g. volatilization and photodegradation, are attenuated.
3. Penetration of a.i. into the tissues is facilitated by the relatively thin cuticle lining and large surface area of the convoluted intercellular air spaces.
4. Deposition of a.i. within the leaf in close proximity to the vascular tissues may assist translocation and thus enhance systemic activity.

Stevens *et al.* (1991) determined the relative contributions of the stomatal and cuticular pathways to the uptake of a model polar active ingredient in combination with two organosilicone surfactants and concluded that ability to access stomatal pathways was exclusive of an ability to enhance cuticular penetration. Dependent on their structure, organosilicone surfactants have been shown to reduce the cuticular penetration of the polar herbicide glyphosate into grasses (Gaskin and Stevens, 1993a,

1993b). Recently, Gaskin (1995) in studying the effect of four organosilicone surfactants (0.2% w/v) on the foliar uptake of three herbicides, glyphosate, metsulfuron {methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate} and haloxyfop {(±)-2-[4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid}, by broad bean and wheat (*Triticum aestivum* L.) showed that surfactant-induced uptake of all three herbicides into broad bean was mainly via stomatal infiltration; nevertheless, stomatal infiltration was rarely observed on wheat in which depending on active ingredient, organosilicone surfactants could substantially enhance, reduce, or have no effect on the cuticular penetration of herbicides in this species. However, Roggenbuck *et al.* (1994) have stated that rapid, organosilicone-induced uptake of acifluorfen and bentazon [3-(1-methylethyl)-(1*H*)-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide] into velvetleaf does not depend on stomatal infiltration, but is due solely to cuticular penetration. Therefore, after extensively studying the mechanism of stomatal infiltration promoted by organosilicones, there is still a need to better understand their action within plant cuticles.

Environmental fate and registration.

Since organosilicones have become widely used with different agrichemicals, their fate in the environment also is of concern. Until now, however, the literature on this aspect is very limited. Stevens (1995) indicated that Silwet L-77 is quickly inactivated in soil and water, initially being rapidly adsorbed onto soil particles and subsequently degraded by hydrolysis. The adsorptive capacity of soil for this organosilicone adjuvant is massive; therefore, the material is unlikely to contaminate groundwater.

Since there are both hydrophilic and hydrophobic groups in organosilicones that are similar to conventional adjuvants, when organosilicones are used as agrichemical adjuvants, their registration is also the same as for conventional adjuvants, which are under the US Environmental Protection Agency regulation 40CFR 180.1001(c):

“Chemicals that can be used in formulations for applying a pesticide to growing crops or raw agricultural commodities after harvest.”

This means that methylated silicones are exempt from the requirement of a residue tolerance when used in accordance with good agricultural practices as inert ingredients on crops or raw agricultural commodities after harvest (Stevens, 1993).

Future development.

Structure variation of organosilicones.

More than 90% of published papers on organosilicones are on Silwet L-77. Though the tri-silicone and methyl-group seem to be required for maximum activity, the structure of the hydrophilic parts of organosilicones can still be changed. These structure changes could improve the activity of organosilicones or reduce the cost during syntheses.

Since trisiloxanes contain an alkyl linkage via a silicon-carbon bond, these trisiloxane surfactants have little stability in aqueous solutions because of susceptibility to hydrolytic degradation. The cleavage of the trisiloxane moiety produces oligomers exhibiting very poor surfactant properties. Recently, Klein *et al.* (1995) reported that hydrolytically stable silanes with outstanding surfactant properties can be synthesized via new magnesium hydride technology. Unlike trisiloxane-based technology, trimethyl silane surfactants have outstanding resistance to hydrolysis in conditions of extreme pH. In addition, Policello *et al.* (1995) found that alkylsilicones showed promise as additives for spray oil applications and oil based pesticide formulations.

Blends of organosilicones and conventional adjuvants.

Certain components in conventional adjuvants have special functions, e.g. oil in oil concentrate can increase the solubility of some herbicides and increase cuticular penetration. It is worthwhile to combine advantages of both organosilicones and conventional adjuvants. The activity of adjuvants may be increased and the cost may

decreased by this process. However, it is critical to select the proper co-adjuvant to avoid jamming 'the zippering' spread process of trisiloxanes.

Low volume sprays.

Because of the superior spreading ability of organosilicones, a run-off problem could occur when organosilicones are used in high volume sprays. It is reasonable to reduce spray volume or use low volume spray technology when using organosilicones as adjuvants.

Use of organosilicones with other agrichemicals.

Organosilicones were used as herbicide adjuvants in at least 64% of published papers. Combining other agrichemicals such as insecticides, fungicides, growth regulators, etc. with organosilicones could also be beneficial. When combined with the protectant chemical, the superior spreading ability of organosilicones can give complete coverage on the target surface, resulting in better efficacy.

Environmental fate.

When organosilicones are used more widely with agrichemicals, their metabolism and environmental fate must be studied. Obviously this part of the work will become important in the near future.

SULFONYLUREA HERBICIDES

Chemistry and physical characteristics.

The discovery of sulfonylureas began a new era in the herbicide research field. This group of herbicides had heretofore unexpected activity and virtually an unlimited number of possible structural variations (Beyer *et al.*, 1988). The most significant characteristics of sulfonylureas are their very low use rates, excellent crop selectivity, and low mammalian toxicity (Beyer *et al.*, 1988).

The general structure of sulfonylurea herbicides is shown in Figure 5:

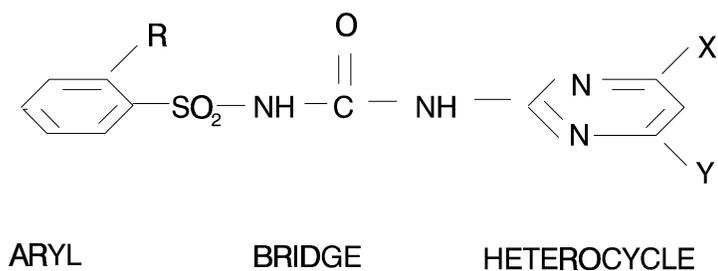


Figure 5. The general structure of sulfonamide herbicides (Source: Beyer *et al.*, 1988)

The molecule consists of three parts: an aryl group, the sulfonamide bridge, and a nitrogen-including heterocycle. When the heterocyclic portion of this structure is a symmetrical-pyrimidine or symmetrical-triazine containing lower alkyl or lower alkoxy substitutes, the substance has a high activity.

Nicosulfuron {2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-*N,N*-dimethyl-3-pyridinecarboxamide} is a selective herbicide for the control of annual and perennial grass weeds and selected broadleaf weeds when applied postemergence to field corn or popcorn. Nicosulfuron provides weed control mainly through foliar absorption, so it should be applied after weeds have emerged (Ahrens, 1994).

Primisulfuron {methyl 2-[[[[[4,6-bis(difluoromethoxy)-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl]benzoate} is also a selective herbicide applied postemergence for the control of grasses, especially some difficult-to-control perennial grasses, and certain other broadleaf weeds in field corn (*Zea mays* L.) for silage or grain and in popcorn (Ahrens, 1994).

Most sulfonamides have an acidic pKa, which is attributed to sulfonamide nitrogen, which is acidic (Beyer *et al.*, 1988). The pKa of sulfonamides is an important factor which influences their adsorption, leaching, and persistence in soil.

Phytotoxicity.

Both the roots and foliage of plants can absorb sulfonamides easily and plants can translocate sulfonamides in both the xylem and phloem (Beyer *et al.*, 1988). The

effect of the sulfonylurea herbicides is dramatic. Traditional herbicides have use rates of 0.5 to 2.0 kg/ha, sometimes higher. Sulfonylureas, on the other hand, have use rates as low as 2 g/ha (Devine and Vanden Born, 1985). Plant growth is strongly inhibited by sulfonylureas and the inhibition is usually very rapid. One to two days after treatment, some symptoms become visible in the rapidly growing parts of plants. At the same time, secondary plant responses, including enhanced anthocyanin formation, loss of leaf nyctinasty, abscission, vein discoloration, terminal bud death, chlorosis, and necrosis can occur. However, total plant death sometimes does not occur until a week or more after treatment (Beyer *et al.*, 1988). Inhibition of plant growth is one of the most noticeable plant responses caused by sulfonylureas.

Selectivity in different plants.

The main difference between tolerant and susceptible plants is their ability to detoxify sulfonylureas. Many published papers revealed only very slight differences in retention, penetration, and translocation, but a great difference in metabolism between tolerant and susceptible species. Therefore rapid inactivation or detoxification of sulfonylureas by crops has been found to be the basis of crop tolerance. Wheat, oat (*Avena sativa* L.), and barley (*Hordeum vulgare* L.) are tolerant to chlorsulfuron, because they can metabolize the herbicide to a nonpolar, biologically inactive substance inside these plants. In contrast, sensitive broadleaf crops, such as sugarbeet, soybean [*Glycine max* (L.) Merr.], mustard (*Brassica* spp.), and cotton (*Gossypium hirsutum* L.) are totally unable to metabolize chlorsulfuron. Hageman and Behrens (1984) reported that susceptible velvetleaf was 20,000 times more sensitive to chlorsulfuron than was eastern black nightshade (*Solanum ptycanthum* Dun.). Velvetleaf could not metabolize chlorsulfuron, whereas tolerant eastern black nightshade metabolized chlorsulfuron quickly.

Mode of action.

Most research work on mode of sulfonylurea action has been concentrated on chlorsulfuron {2-chloro-*N*-[[4-methoxy-6-methyl-1,3,5-triazin-2-

yl)amino]carbonyl]benzenesulfonamide}. Ray (1982) on the mode of action of chlorsulfuron indicated that it acted by inhibiting plant cell division. This effect can be observed in corn root tips within 2 h of treatment and at concentrations as low as 0.01 ppm (2.8×10^{-3} M) (Devilliers *et al.*, 1980). At this concentration and time, photosynthesis, and RNA, protein, and lipid synthesis are not affected (Devilliers *et al.*, 1980; Ray, 1982). Ray's further studies proved that no inhibitory effects were observed on DNA synthesis in isolated plant nuclei, nor inhibitory effects upon the enzymes DNA synthesis in isolated plant nuclei, specifically the enzymes involved in DNA polymerase and thymidine kinase. These results indicate that chlorsulfuron does not inhibit plant cell division by a direct inhibition of DNA synthesis. Finally, it has been discovered that the mechanism by sulfonylurea herbicide families is to inhibit acetolactate synthase (ALS, EC 4.1.3.18, also known as acetohydroxy acid synthase) activity (Falco *et al.*, 1987; Matsunaka *et al.*, 1985; Ray, 1984; Ray, 1985; Rost and Reynolds, 1985; Scheel and Casida, 1985). ALS is the first and the key enzyme in the biosynthesis of valine, leucine, and isoleucine, which are the essential branched-chain amino acids for normal plant and bacterial growth. Also, ALS is feedback inhibited cooperatively by valine and leucine in higher plants. Thus, it is a key controlling point for the levels of the branched chain amino acids. This reaction is located in the chloroplast. Genetic and biochemical studies on the mode of action of chlorsulfuron have demonstrated that it acts in plants to block production of the essential amino acids, valine and isoleucine, by inhibiting the enzyme ALS (Ray, 1984). This enzyme is extremely sensitive to inhibition by chlorsulfuron having I_{50} values ranging from 18 to 36 nM.

If sulfonylureas inhibit synthesis of valine, leucine, and isoleucine in plants, there should be a rapid decrease in the pool sizes of these amino acids, which could cause a decrease in protein synthesis. A lower rate of protein synthesis, in turn, could cause a slowdown in the rate of cell division and, eventually, death of the cell. The inhibition of amino acid synthesis is a relatively new mechanism of action of herbicides. Among

traditional herbicides, only very few herbicides, glyphosate and glufosinate [2-amino-4-(hydroxymethylphosphiny)butanoic acid], are known to interfere with amino acid (glutamine and aromatic amino acids) biosynthesis (Shaner *et al.*, 1984). The high effectiveness of these types of herbicides indicates that amino acid biosynthesis is a new target for future herbicides.

Environmental performance

According to Beyer *et al.*(1988), little is known about how environmental factors influence the phytotoxicity of sulfonylureas. Usually, environmental conditions favoring growth after treatment enhanced the herbicide activity of chlorsulfuron. These environmental conditions include soil nitrogen level, temperature, and relative humidity. For example, when chlorsulfuron was used to control green foxtail [*Setaria viridis* (L.) Beauv.] and kochia [*Kochia scoparia* (L.) Schrad.], chlorsulfuron phytotoxicity was greater at high (95 to 100%) than low (40% to 50%) relative humidity (Nalewaja and Woznica, 1985). Temperature was less important than relative humidity in this experiment. Soil moisture conditions favoring growth also enhanced chlorsulfuron phytotoxicity. If plants were water-stressed after chlorsulfuron treatment, they were less damaged than if they had not been water stressed or had been water stressed only before treatment. The biochemical and physiological mechanisms underlying these environmental effects still are not known. Chlorsulfuron degrades under field conditions at rates similar to, and often faster than, conventional herbicides (Beyer *et al.*, 1988). Chemical hydrolysis and microbial breakdown are the main modes of dissipation. Breakdown is generally the fastest in warm, moist, light-textured, low pH soils and slowest in cold, dry, heavy, high pH soils (Beyer *et al.*, 1988).

WEED SPECIES

During the dynamic processes of spraying and wetting, the factors which determine whether droplets impacting leaves are retained or bounce off are complex and not fully

understood. In addition to the droplet size, impact velocity, and the dynamic surface tension properties of the spray solution, it is clear that the leaf surface morphology plays an important role (Anderson and van Haaren, 1989). The epidermal layer of the leaves is the first barrier for foliarly applied systemic herbicides. In addition to the ordinary epidermal cells, which form the bulk of the epidermis, the epidermis may contain stomata, many types of appendages, or trichomes, and other kinds of cells specialized for specific functions. Stomata may occur on both sides of the leaf, but commonly are more numerous on the lower surface. Epidermal hairs, or trichomes, may occur on either or both surfaces of a leaf. Thick coats of epidermal hairs may retard water loss from leaves.

According to the basic description by Fahn (1982), the ordinary epidermal cells of the leaf, like those of the stem, are compactly arranged and covered with a cuticle that reduces water loss. In order to minimize water loss, the walls of the aerial parts contain cutin and are covered with a cuticle. The cuticle may also be covered with wax, either in smooth sheets or as rods or filaments extending upward from the surface.

Deposits of wax are often found on the surface of the cuticle. The wax gives the 'bloom' of many leaves and is important in reducing the wettability of surfaces. The forms of wax are different for different plants, e.g. granules, rods, or as continuous layers which are often found on the surface of the cuticle. Some wax mixtures fail to crystallize and may form an oily layer of irregular flat plates above the cuticle. As seen under the scanning microscope, waxes in crystalline state may form very elaborate structures. The structure and amount of the surface wax has an extremely important effect on the degree to which a surface can be wetted. This phenomenon represents one of the factors that govern the selective effect of herbicides on some crop plants.

Epidermal hairs, or trichomes, may occur on either surface or both surfaces of a leaf and vary in shape and functions. Thick coats of epidermal hairs may retard water loss from leaves.

The epidermis of leaves of different plants varies in the number of layers, its shape, structure, arrangement of stomata, appearance and arrangement of trichomes, and occurrence of specialized cells (Raven and Ray, 1978).

Two broadleaf weeds, velvetleaf and redroot pigweed (*Amaranthus retroflexus* L.), listed on the primisulfuron label, and two grasses, green foxtail and barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.], listed on the nicosulfuron label, were used in this research. Except for barnyardgrass, these species are considered among the 10 most troublesome weeds in the U.S. in 1993 (Anonymous, 1993).

RESEARCH OBJECTIVES

The current project was focused on the enhancement mechanisms of organosilicone compounds on sulfonylurea herbicide activity as compared to conventional adjuvants. Several research objectives were established for this study. Two sulfonylurea herbicides, primisulfuron and nicosulfuron, and four weed species, barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.], green foxtail [*Setaria viridis* (L.) Beauv.], redroot pigweed (*Amaranthus retroflexus* L.), and velvetleaf (*Abutilon theophrasti* Medikus), were included in the study. The tested adjuvants included three pure organosilicones, Silwet L-77, Silwet 408, and Sylgard 309; two blends of organosilicones with conventional adjuvants, Kinetic and Dyne-Amic; four conventional adjuvants, Agri-Dex, Rigo oil concentrate, methylated soybean oil, and X-77.

1. Examine and compare physical-chemical properties between organosilicones and conventional adjuvants (referred to as non-silicone adjuvants in this study). These physical-chemical properties included: static surface tension, dynamic surface tension, contact angle on both leaf surface and parafilm, wettability, and spreading pattern on leaf surface.
2. Investigate the similarity and differences of several structurally related organosilicones.
3. Analyze the effect of organosilicones on herbicide uptake and translocation with radiolabelled herbicide.
4. Study the effect of organosilicones on herbicide rainfastness.
5. Explore the effect of organosilicones on herbicide efficacy.

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**CHAPTER 2. STRUCTURALLY RELATED ORGANOSILICONE
SURFACTANTS, THEIR PHYSICO-CHEMICAL PROPERTIES, AND
EFFECTS ON UPTAKE AND EFFICACY OF PRIMISULFURON IN
VELVETLEAF (*Abutilon theophrasti* MEDIKUS).¹**

ABSTRACT

The physico-chemical properties and spread pattern on leaves of velvetleaf were similar for four structurally related organosilicones. Laboratory results indicated that the four organosilicones greatly increased the uptake of primisulfuron in velvetleaf. When primisulfuron was combined with any one of the four organosilicones, weed control was significantly increased and much more rapid than when the herbicide was used alone. There were no significant differences among the four structurally related organosilicones used as adjuvants with primisulfuron in velvetleaf.

INTRODUCTION

Organosilicones are a class of surfactants in which an array of methyl groups bonded to silicon atoms constitute the hydrophobic part of the molecule (1). These surfactants have been used with different agrochemicals to improve wetting and spreading, and increase the absorption and uptake of active ingredients. The methyl-trisiloxane with a compact hydrophobic group and extended hydrophilic polyether chain is thought to spread on the leaf surface by a 'zippering' process (1). Although the compact hydrophobic backbone of trisiloxane ethoxylate is required for the extremely low surface tension and superior spreading ability, the length of the hydrophilic polyether chain and the 'cap' at the end of this chain can be varied to form a series of structurally related organosilicone surfactants. The objectives of this study were to evaluate the influence of the chemical structure of the end cap on physico-chemical

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properties, and effects on uptake, translocation, and efficacy of primisulfuron in velvetleaf.

MATERIALS AND METHODS

Chemicals.

The four nonionic silicone surfactants evaluated were Silwet L-77, Silwet 408, Y-12719, and Y-12720 (all obtained from OSi Specialties Inc.). According to information supplied by the company, these surfactants were based on a trisiloxane containing a polyether with approximately 7.5 EO (ethylene oxide) (Figure 1). All of these materials were prepared from the same batch of polyether and trisiloxane intermediates (2).

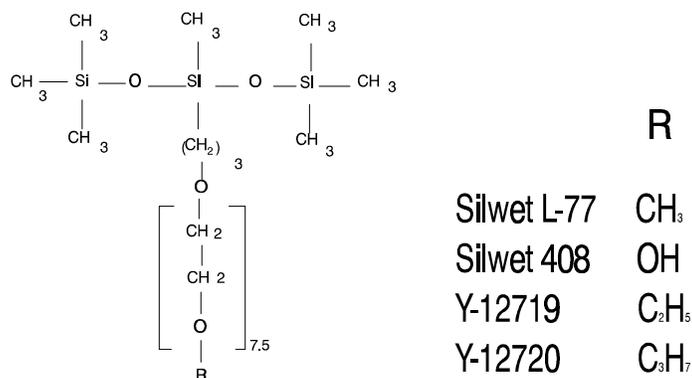


FIGURE 1. Trisiloxane surfactant structure (2)

Commercially formulated primisulfuron, 75% water dispersible granules, was used in the efficacy study in the greenhouse. ¹⁴C Phenyl ring labelled-primisulfuron, specific activity 52.4 μCi/mg, supplied by Ciba-Geigy Corporation (Greensboro, NC) was used in the uptake study.

Physico-chemical properties.

Surface tension.

The Cahn Dynamic Contact Angle Analyzer with DCA software was used to measure the surface tensions of a series of concentrations of organosilicone solutions, which were prepared in distilled water (w/w). This equipment uses the Wilhelmy plate technique. After obtaining very stable results for measuring the series of concentrations of Silwet L-77 solution with 3 replications, other solutions were measured without replication.

Contact angle and leaf (ad/ab)sorption.

The instrument above was also used to measure the contact angles of different adjuvant solutions at 0.25% (w/w) on leaves of velvetleaf. Fresh leaves were divided longitudinally and the abaxial sides taped together leaving the adaxial surfaces exposed. Rectangular sections (10 by 15 mm approximately) were excised for immersion in the test solutions. Because of the structure difference among individual leaves, each solution was measured with three replications.

During the contact angle measurements, it was found that after the sample was pulled from the solution, the weight of the sample was increased. (Note: By comparison, the weight increase was inconsequential when measuring surface tensions of different solutions with the Wilhelmy plate.) Upon careful checking of the sample, the effect was attributed to (ad/ab)sorption by the leaf sample. This phenomenon provided another way to measure liquid (ad/ab)sorption by the leaf. Sorption per unit of leaf sample was calculated by dividing total weight change of the leaf sample by the area inserted into the solution.

Spread pattern.

To facilitate determination of the droplet spreading patterns of different adjuvant solutions on velvetleaf, 0.01% fluorescent dye (Tinopal CBS-X²) was added to the different solutions. One fresh leaf of velvetleaf was mounted on the camera platform and a 2- μ l drop was deposited on the leaf. The progress of drop spread was recorded by videotaping and captured by computer imaging under UV light.

²Tinopal CBS-X: Product of Ciba-Geigy, Greensboro, NC 27419.

Uptake and translocation.

A stock solution was prepared by dissolving ^{14}C -primisulfuron and technical primisulfuron in water (pH 8.5) to form a solution containing ^{14}C -primisulfuron at 0.048 $\mu\text{Ci/ml}$, 0.42 a.i. mg/ml. Solutions containing 0.25% (v/v) organosilicone were prepared from the stock solution. The influence of organosilicones on ^{14}C uptake into velvetleaf was determined by comparing ^{14}C -primisulfuron applied alone or with different surfactants. Ten 1- μl drops of primisulfuron solution containing a total of 10,630 dpm were applied uniformly to the upper surface of the mature leaf nearest to the growing point. The plants were harvested 5 min, and 1 and 24 h after application and were sectioned into the treated leaf, shoot above treated leaf, shoot below treated leaf, and roots. Unabsorbed ^{14}C -primisulfuron was removed by washing the treated leaf in 3 ml of pH 10 buffer (K_2CO_3 - KBO_2 - KOH) in a scintillation vial (3). The ^{14}C in the wash solution was assayed by adding 15 ml of scintillation fluid and quantifying by liquid scintillation counting. All the harvested plant parts were oxidized to determine uptake and translocation. ^{14}C uptake into the plant was expressed as percent of applied ^{14}C and ^{14}C translocation from the treated leaf into the other parts of the plant was expressed as percent of ^{14}C taken up. Each treatment was replicated four times.

Efficacy.

Experiments were conducted in the greenhouse with natural sunlight as the only light source. Velvetleaf was seeded in 15-cm pots containing a commercial potting mix. Plants were fertilized as required with a 20-20-20 (N-P-K) fertilizer. Plants were uniformly 10 to 13 cm tall with six leaves at the time of treatment. Primisulfuron was applied at 40 g ai/ha with and without the organosilicone surfactants at 0.25% (v/v), in 94 L/ha of water using a CO_2 -charged, continuous moving belt laboratory sprayer. The experimental design was a randomized block with five replications. Control ratings from 0 to 100% were made at 5-day intervals until most of the plants were killed. Three separate experiments were conducted.

Statistics.

Efficacy, uptake, retention.

Results of these tests were analyzed by Duncan's multiple comparison procedures with SAS Software (6.03 Edition).

Surface tension.

Logistic models of the log concentration versus surface tension were fitted to the data by the equation $f(x) = a/(1 + \exp(b*(x-c))) + d$; where a = the range of the mean surface tension; b = the slope coefficient, i.e. the unit change of surface tension caused by unit change of the surfactant concentration; c = the concentration at the inflection point; d = the minimum mean surface tension; x = log of surfactant concentration; and $f(x)$ = mean surface tension.

RESULTS AND DISCUSSION

Physico-chemical properties.

Surface tension.

Theoretically, the relation of surfactant concentration and surface tension is a logistic distribution; therefore, a logistic model was fitted for different organosilicones. The estimated parameters in logistic models for different surfactants and the critical micelle concentration (CMC) which was calculated by the models are shown in Table 1. The four silicone surfactants all give superior performance in lowering surface tension (CMC around 21 mN/m). Of the tested surfactants, Silwet 408 reduced surface tension more slowly than the other three, which may be caused by its having only hydrogen in the cap. Except for Silwet 408, when the number of carbons in the cap increased, the minimum surface tension was slightly increased. The CMC also varied according to chemical structures. Even though the differences among the caps did not significantly affect the minimum surface tension and CMC, these did confirm that the properties of organosilicones were mainly determined by the number of silicon atoms and the methyl groups around the silicones (4).

TABLE 1. Estimated Parameters in logistic models and CMC for different surfactants

Surfactant	a	b	c	d	CMC (w/w)
				(dyne/cm)	
Silwet L-77	51.9	2.4	-6.03	20.7	4.0×10^{-4}
Silwet 408	52.9	1.5	-5.7	20.0	1.0×10^{-3}
Y-12719	51.6	2.5	-5.8	21.3	2.0×10^{-4}
Y-12720	51.8	2.3	-5.8	22.1	9.1×10^{-4}

Contact angle and leaf (ad/ab)sorption.

As all other trisiloxane organosilicone surfactant solutions can result in efficient wetting of even the most hydrophobic leaf surface, the sample leaf surface of velvetleaf also was completely wetted by any of the four surfactant solutions at 0.25%(w/w); as a result, the contact angle was zero. By contrast, the contact angles for water or primisulfuron solution used alone were 81 and 103⁰, respectively.

The surfactants tested greatly increased the (ad/ab)sorption of solutions by the sample leaf after it was removed from the tested solution and the extra liquid had run off. (Table 2).

TABLE 2. Absorption of different solutions on leaf surface of velvetleaf

Treatment	Rate	(Ad/ab)sorption (mg/mm ²)
Water alone	–	0.02e
Primisulfuron	40 g ai/ha	0.02e
Silwet L-77	0.25% (w/w)	0.09d
Silwet 408	0.25% (w/w)	0.40b
Y-12719	0.25% (w/w)	0.52a
Y-12720	0.25% (w/w)	0.29c

Note: Within columns, treatments with letters in common are not significantly different at $P = 0.05$.

When the surfactant solution completely wets the sample, the liquid closely contacts the whole leaf surface. Having both hydrophobic and hydrophilic properties, the surfactant can be sorbed at the leaf surface and hold the water at the same time. The amount of sorption is determined by the arrangement of surfactant molecules on the leaf surface and the amount of surfactant retained by the leaf surface. There were some significant differences in sorption at the leaf surface among the four tested surfactants. It may be suggested that the different cap structures caused different arrangements of the surfactants on the leaf surface. However, whether or not, and how, the cap structure may actually alter the surfactant arrangement needs further investigation.

Spread pattern.

Complete wetting of the leaf surface by all four surfactants solutions at 0.25% was demonstrated under UV light. There were no obvious differences in spread pattern among the four surfactants. During the progress of drop spread, it was clearly shown that the solution moved first along the vein, indicating that the vein was easier to wet than other areas. After that, the solution was distributed to areas of the leaf around the vein. As seen under the scanning microscope, the cells composing the vein were narrow and arranged longitudinally. When either primisulfuron solution alone or water was deposited on the leaf surface, the drop spread only slightly and did not move along the vein. Even when the drop was deposited directly over the juncture of several veins, the solution still did not completely wet the leaf surface.

Uptake and translocation.

The organosilicones significantly increased the uptake of ^{14}C -primisulfuron within 24 h after treatment (Table 3). Within 1 h after application, the total uptake of all the treatments of ^{14}C -primisulfuron with different organosilicones was significantly higher than with primisulfuron used alone. When the active ingredient enters the plant tissue,

stomatal infiltration is preferred to cuticular penetration (5). Previous research has shown that surface tension of applied solutions below about 30 dyne/cm can cause stomatal infiltration (6). Therefore, all four organosilicones would be expected to facilitate stomatal infiltration. However, there is extremely high variability in the number and degree of closure of stomata in different leaves and different plants. When mass flow occurred, the variation in the leaf structure rather than the surfactant structure played a more important role in determining the differences in the speed and amount of uptake shortly after application (5). However, after 1 h treatment, the combination of ¹⁴C-primisulfuron with any of the surfactants had reached more than 50% of the uptake, which was significantly higher than primisulfuron used alone.

TABLE 3. Effect of different surfactants (0.25%) on uptake of ¹⁴C-primisulfuron into velvetleaf (% of application)

Treatment	Time after application		
	0.083 h	1 h	24 h
Primisulfuron	6.7b	13.5c	7.2c
Silwet L-77	20.5a	67.3a	58.3ab
Silwet 408	11.2b	59.4ab	40.3b
Y-12719	7.9b	59.0ab	38.4b
Y-12720	8.9b	54.2b	66.7a

Note: Within columns, treatments with letters in common are not significantly different at P = 0.05.

When primisulfuron uptake was increased by the organosilicones, the relative amount of translocation for the total uptake of the herbicide from treated leaf to other parts of the plant was not increased at the same time compared with herbicide used alone (data not shown). These results differ from those of Stevens et. al. (5) who

studied the translocation of non-phytotoxic ^{14}C -DOG (2-deoxy-d-[U- ^{14}C]glucose). In the current study, injury was visible on the petioles of treated leaves 24 h after treatment with solutions which contained organosilicones. The color of the petiole surface was dark brown. This may have been caused by high concentration of toxic chemical which accumulated in the treated leaf within a short time. When primisulfuron translocated through the petiole, it may have damaged the living cells. As a result, total translocation from the treated leaf was not significantly increased.

Efficacy.

Primisulfuron plus any of the four organosilicones tested provided 100% control of velvetleaf 15 days after treatment. However, primisulfuron alone provided less than 40% control. There were no differences in level of control among the four surfactants. Primisulfuron alone provided marginal control of velvetleaf because the thick pubescence on the leaf surface hindered wetting by the aqueous solution.

CONCLUSIONS

On the basis of the present studies, it appears that the end 'cap' on the trisiloxane surfactants has little or no effect on surfactant physico-chemical properties, contact angle, and spread pattern, nor on the (ad/ab)sorption, uptake and translocation, and efficacy of primisulfuron. Small observed differences did not change the behavior of the organosilicones when they were used as adjuvants with primisulfuron on velvetleaf. It may be suggested that there was not a strict requirement to purify the 'cap' during the synthesis process.

ACKNOWLEDGMENTS

Thanks are expressed to Ciba-Geigy Corporation (Greensboro, NC) for supplying ^{14}C -primisulfuron for the uptake study and for permitting us to use special laboratory equipment for the physico-chemical properties study. Also we thank OSi Specialties

Inc. for synthesizing and providing the structurally related organosilicones for this specific research.

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CHAPTER 3. DIFFERENCES BETWEEN SILWET L-77 AND ITS BLENDS IN PHYSICO-CHEMICAL PROPERTIES AND HERBICIDAL ENHANCEMENT OF TWO SULFONYLUREAS IN FOUR WEED SPECIES¹

ABSTRACT

Effects of Silwet L-77 and its two blends with conventional adjuvants, Kinetic and Dyne-Amic, on the activity of nicosulfuron and primisulfuron in four weed species were investigated in the greenhouse. A conventional crop oil concentrate, Agri-Dex was included for comparison. The physico-chemical properties, spreading pattern, wetting ability, and influence of these adjuvants on ¹⁴C-primisulfuron absorption and translocation of these adjuvants were measured. Silwet L-77, Kinetic, and Dyne-Amic greatly increased the uptake of primisulfuron in *Abutilon theophrasti* within 1 h after herbicide application. Laboratory results indicated some differences in properties between Silwet L-77 and its two blends; however, there were no significant differences among Silwet L-77, Kinetic, and Dyne-Amic in enhancing herbicidal efficacy of nicosulfuron and primisulfuron in four weed species. When primisulfuron was combined with Silwet L-77 or its blends, weed control was significantly increased and was much more rapid than when the herbicide was used alone.

INTRODUCTION

Organosilicone surfactants, as a new generation of agrochemical adjuvants, have shown positive results in agricultural applications for more than 10 years. Their low dynamic surface tension may promote good adhesion of spray droplets. The molecular zipper action at the interface may provide unsurpassed spreading (Goddard and Padmanabhan, 1992; Knoche, 1994; Stevens, 1993) and the low equilibrium surface tension may allow stomatal infiltration and rainfastening. To reduce the cost as agrochemical adjuvants and combine advantages from both organosilicone surfactants

¹ This chapter, formatted as required, was submitted to the Second International Weed Control Congress (in press).

and conventional adjuvants, organosilicone surfactants have been blended with some conventional adjuvants. However, there have been very few published research papers on the properties and efficacy of these blends. The purpose of this research was to investigate the physico-chemical properties, and droplet spreading of Silwet L-77 and its two blends, Kinetic and Dyne-Amic; also their effects on foliar uptake and translocation of primisulfuron, and efficacy of nicosulfuron and primisulfuron in four weed species.

MATERIALS AND METHODS

Chemicals.

The four adjuvants evaluated were Silwet L-77², Kinetic³, Dyne-Amic³ and Agri-Dex³. Commercially formulated primisulfuron (Ciba-Geigy- Beacon^{® 4}), and nicosulfuron (DuPont - Accent^{® 5}), both 75% water dispersible granules, were used in the efficacy study. ¹⁴C-primisulfuron, specific activity 52.4 µCi/mg, supplied by Ciba-Geigy Corporation (Greensboro, NC) was used in the uptake study.

Surface tension and contact angle on *A. theophrasti* leaves.

A Cahn Dynamic Contact Angle Analyzer with DCA software⁶, based on the Wilhelmy plate technique, was used to measure surface tensions of the adjuvants over a range of concentrations. The solutions were prepared in distilled water (w/w). After obtaining very stable results with the series of concentrations of Silwet L-77 replicated three times, other solutions were measured without replication.

The instrument above was also used to determine the influence of the adjuvants on contact angles on *A. theophrasti* leaves. Fresh leaf samples were divided longitudinally and the abaxial sides taped together, leaving the adaxial surfaces

² OSi Company, Tarrytown, NY 10591.

³ Helena Chemical Company, Memphis, TN 38173.

⁴ Beacon[®]: Reg. Trademark of Ciba-Geigy. Greensboro, NC 27419.

⁵ Accent[®]: Reg. Trademark of DuPont. Wilmington, DE 19880.

⁶ Cahn Instruments, Inc. 16207 S. Carmenita Road, Cerritos, CA 90701-2275

exposed. Rectangular sections (10 by 15 mm approximately) were excised for immersion in the test fluids.

Spreading pattern.

To facilitate determination of the droplet spreading patterns of different adjuvant solutions on *A. theophrasti* leaves, 0.01% fluorescent dye⁷ was added to the different solutions. One *A. theophrasti* fresh leaf was mounted on the camera platform and a 2- μ l drop was deposited on the leaf. The progress of drop spread was recorded by videotaping and computer imaging under UV light.

Wettability measurement.

Droplets of different volumes (2, 4, 6, 8, and 10 μ l) of solutions containing Agri-Dex at 1% (w/w), or Silwet L-77, Kinetic, or Dyne-Amic at 0.25% (w/w) with nicosulfuron at 35 g ai/ha, were applied by syringe to mature *A. theophrasti* leaves. After the droplets reached an equilibrium state of spreading (ca. 30 s), the diameter of the spread area was measured. The spread area was calculated by the formula $S = 3.14 \times r^2$. Each treatment was replicated five times.

Uptake and translocation.

A stock solution was prepared by dissolving ¹⁴C-primisulfuron and technical primisulfuron in water (pH 8.5) to form a solution containing ¹⁴C-primisulfuron at 0.048 μ Ci/ml, 0.42 a.i. mg/ml. The influence of adjuvants on uptake in *A. theophrasti* was determined by applying ¹⁴C-primisulfuron alone or in solutions containing 0.25% Silwet L-77, Kinetic, Dyne-Amic or 1.0% Agri-Dex. Ten 1- μ l drops of primisulfuron solution total containing 10,630 DPM were applied uniformly to the upper surface of the mature leaf nearest to the growing point. Plants were harvested 0.083, 0.25, 0.5, and 1 h after application and sectioned into the treated leaf, shoot above treated leaf, shoot below treated leaf, and roots. Unabsorbed ¹⁴C-primisulfuron was removed by washing the treated leaf with 3 ml of pH 10 buffer⁸. The ¹⁴C wash solution, collected

⁷ Tinopal CBS-X, Ciba-Geigy Corporation, Greensboro, NC 27419.

⁸ K₂CO₃-KBO₂-KOH, Fisher Scientific, Fair Lawn, NJ 58206.

in a scintillation vial, was quantified by adding 15 ml of scintillation fluid⁹ and counted using liquid scintillation spectrometry¹⁰. All harvested plant parts were oxidized to determine uptake and translocation. ¹⁴C uptake into the plant was expressed as percent of applied total amount ¹⁴C. The ¹⁴C translocation from the treated leaf into the other parts of the plant was expressed as percent of ¹⁴C uptake. Each treatment was replicated four times.

Efficacy.

Experiments were conducted in the greenhouse with natural sunlight as the only light source. *Echinochloa crus-galli* (L.) Beauv., *Setaria viridis* (L.) Beauv., *Amaranthus retroflexus* L., and *Abutilon theophrasti* Medikus were grown in 15-cm pots containing a commercial potting mix, fertilized as required with a 20-20-20 (N-P-K) fertilizer, and were uniformly 10 to 13 cm tall at the time of treatment.

Primisulfuron at 20 and 40 g ai/ha with and without the adjuvants was applied to *A. retroflexus* L. and *A. theophrasti*. Nicosulfuron at 17 and 35 g ai/ha with and without the adjuvants was applied to *E. crus-galli* and *S. viridis*. Treatments were applied in 94 L/ha of water using a CO₂-charged, continuous moving belt laboratory sprayer equipped with a single 8001E nozzle¹¹. The experimental design was a randomized block with five replications and experiments were repeated. Control ratings from 0 to 100% were made at 5 -day intervals until most of the plants were killed.

Statistics.

Contact angle, wettability, uptake, and efficacy.

Results of these tests were analyzed by Duncan's multiple comparison procedures with SAS Software (SAS, 1989).

Surface tension.

⁹ Ecolume™ ICN Biomedicals, Inc., Radiochemicals Division, Irvine, CA 92713.

¹⁰ Model: LS 5000TA. Beckman Instruments, Inc., 2500 Harbor Boulevard, Fullerton, CA 92634-3100.

¹¹ Teejet 8001E tip, Spraying Systems Co., North Ave., Wheaton, IL 60188.

AsymSigR models for the log concentration versus surface tension were fitted to the data.

$$[\text{AsymSigR}] y = a + b (1 - (1 + \exp((x + \ln(2^{1/e} - 1)c)/d))^{-e})$$

where

x = log of adjuvant concentration, a = maximum mean surface tension, b = the difference between maximum surface tension and minimum surface tension, c, d, e, = the factors to control the surface tension reducing speed as concentration increased, y = mean surface tension.

RESULTS

Surface tension and contact angle.

AsymSigR relationship was found between the surfactant concentration and surface tension for different adjuvants. All the regression coefficients in different models were above 0.99. The parameters in the models and the CMC (critical micelle concentration) for different adjuvant are shown in Table 1. The relationships of surface tension *vs.* concentrations for different adjuvant are shown in Figure 1.

Table 1. Estimated parameter and CMC for different adjuvants

Adjuvant	a	b	c	d	e	ST(min)	CMC(w/w)
Silwet L-77	70.20	-49.06	-5.99	0.67	1.53e + 14	21.14	1.5 x 10 ⁻³
Kinetic	71.15	-51.75	-5.12	1.39	3.30e + 11	19.4	5.0 x 10 ⁻³
Dyne-Amic	70.85	-45.85	-5.24	1.22	28.07	25.0	1.0 x 10 ⁻²
Agri-Dex	70.21	-34.73	-3.80	0.013	0.02	35.5	4.0 x 10 ⁻²

* For explanation of parameters see material and methods: Surface tension.

The relationship between concentration and surface tension of Kinetic was similar to Dyne-Amic; however, the minimum surface tension of Kinetic was much lower than that of Dyne-Amic. On the other hand, both Kinetic and Silwet L-77 had a very low minimum surface tension, but when the concentration was lower than 0.01%, Silwet L-77 reduced the solution's surface tension more rapidly than did Kinetic. The minimum surface tension for Silwet L-77 and Kinetic was around 20 dyne/cm, but the CMC for Kinetic was about 3.3 times higher than that for Silwet L-77. The minimum surface tension and CMC of Dyne-Amic were similar to those of Agri-Dex which were highest among the four adjuvants.

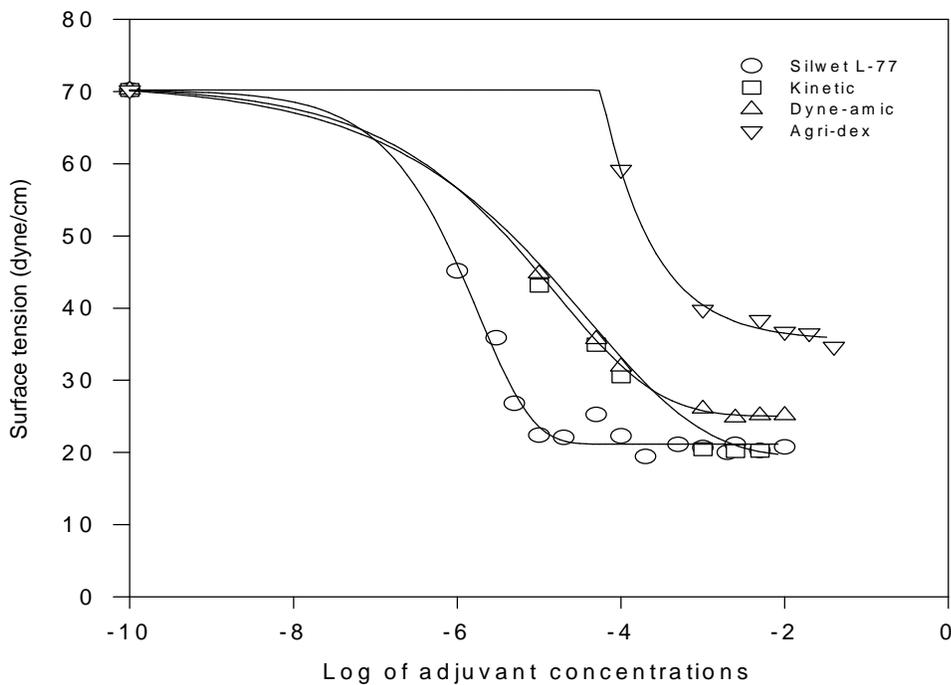


Figure 1. The relationship between surface tension and concentration for different adjuvants. Adjuvant concentrations originally prepared w/w (g/g) were transformed by log.

Solutions of Silwet L-77 and Kinetic wetted the foliage of *A. theophrasti* completely. As a result, contact angles of droplets for both solutions equaled zero. Dyne-Amic significantly reduced contact angle from 80.8° to 56.2° compared with water alone. The contact angle for Agri-Dex solution (86.5°) was not significantly different from water alone. However, when primisulfuron was added into water, the contact angle on *A. theophrasti* leaf was significantly increased to 103.1°.

Spread pattern and wettability.

Under UV light, complete wetting of the leaf surface by 0.25% Silwet L-77 or Kinetic solutions was demonstrated (Figures not shown). There were no significant differences in spreading patterns among the solutions of Dyne-Amic, Agri-Dex, nicosulfuron, and water. The size of these drops enlarged only slightly.

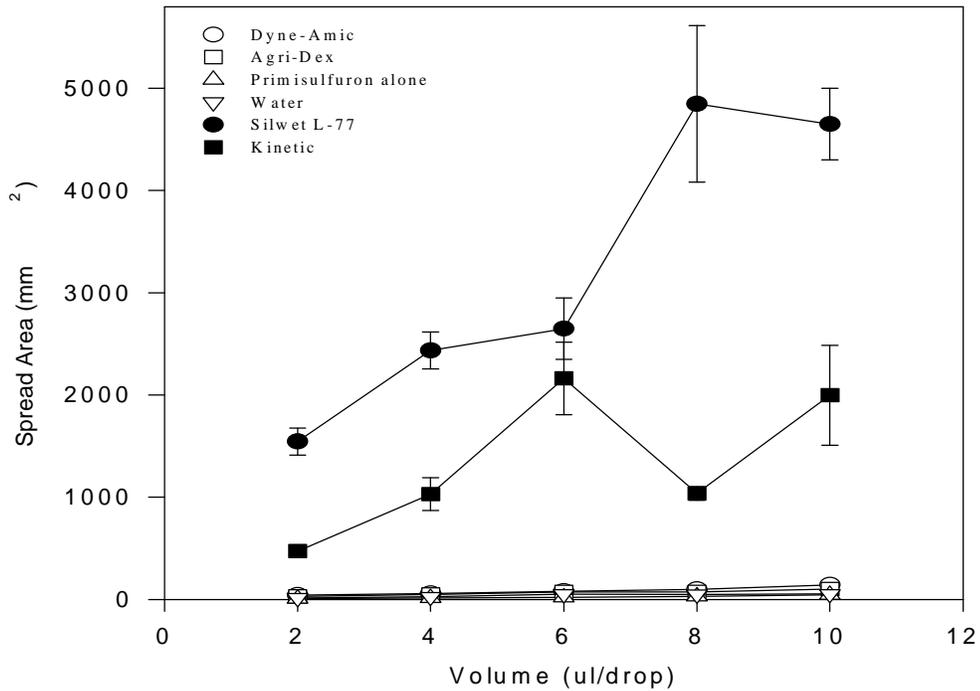


Figure 2. The spreading ability of different adjuvant solutions on *A. theophrasti* leaves. The vertical bars indicate the standard error of means

When the spreading area on *A. theophrasti* leaves was measured, there were no significant differences in spreading abilities of Dyne-Amic, Agri-Dex, nicosulfuron, and water. However, drop spreading on the leaves was dramatically increased by both Silwet L-77 and Kinetic. Silwet L-77 solutions at 2 µl/ drop increased the spreading area about 50 to 100 times compared with the Agri-Dex solution. Though both Kinetic and Silwet L-77 solutions completely wet the leaf surface, spreading ability by Kinetic was significantly lower than that by Silwet L-77. Detailed results are shown in Figure 2.

Generally, as the drop volume increased, the spreading area on the leaf increased. However, the adjuvant properties had a stronger effect on the percentage of increase than did volume alone.

Uptake and translocation of foliarly applied ¹⁴C-primisulfuron.

Within 1 h after herbicide application, Silwet L-77, Kinetic, Dyne-Amic, and Agri-Dex significantly increased uptake of ¹⁴C-primisulfuron in *A. theophrasti* compared to primisulfuron alone (Table 2.). However, no significant differences in translocation of ¹⁴C-primisulfuron among the treatments were found (data not shown).

Table 2. Effect of different adjuvant on uptake of ¹⁴C-primisulfuron into *A. theophrasti* (% of applied dose) *

Treatment	Time after herbicide application			
	0.083 h	0.25 h	0.5 h	1 h
Primisulfuron	6.1 c	5.5 c	12.6 b	15.3 c
Agri-Dex	8.0 bc	21.1 ab	18.0 b	29.5 b
Dyne-Amic	9.2 bc	17.0 b	38.5 a	66.1 a
Kinetic	16.4 ab	8.8 c	23.7 ab	72.5 a
Silwet L-77	20.7 a	25.0 a	-	70.9 a

* Means within a column followed by the same letters are not significantly different at the 5% level according to Duncan's multiple range test.

Silwet L-77 and Kinetic significantly increased primisulfuron uptake 0.083 h after treatment. Within 0.25 h after treatment, there was a significant difference between Silwet L-77 and Dyne-Amic. However, as time increased, the difference disappeared.

Efficacy.

Results indicated that all adjuvants significantly increased the activity of primisulfuron on *A. theophrasti* and *A. retroflexus*, and nicosulfuron on *E. crus-galli* and *S. viridis* (data not shown). With both recommended and one-half recommended herbicide rates, control by herbicides with different adjuvants was always significantly higher than when herbicides were used alone. Except with the low rate of primisulfuron with Kinetic on *A. theophrasti* and the low rate of nicosulfuron with Silwet L-77 on *E. crus-galli*, all the adjuvants significantly increased control to more than 75% at 20 DAT (days after treatment). However, when the two herbicides were used alone, control was not acceptable.

DISCUSSION

Silwet L-77 and Kinetic reduced the surface tension of aqueous solutions far below that which is possible with conventional adjuvants. Solutions with such low surface tension could result in efficient wetting of even the most hydrophobic leaf surfaces (Murphy *et al.*, 1991, 1993). Also, when surface tension of a spray solution is lower than the critical surface tension of the leaf surface (ranges from 20 to 30 dyne/cm), stomatal infiltration may be induced and can occur immediately after treatment (Buick, *et al.*, 1992; Greene & Bukovac, 1974, Knoche & Bukovac, 1993; Schönherr & Bukovac, 1972). The uptake results in this study confirmed this conclusion. The active ingredient taken up by stomatal infiltration can lead to increased rainfastness of the applied formulations (Field & Bishop, 1988; Greene & Bukovac, 1974; Roggenbuck *et al.*, 1993; Schönherr & Bukovac, 1972; Sun *et al.*, 1996; Zabkiewicz *et al.* 1988).

Physico-chemical property measurements showed some differences between Kinetic and Dyne-Amic. The curves from AsymSigR models for the two blends showed similar shapes and trends; Kinetic had a much lower minimum surface tension and CMC than did Dyne-Amic. Kinetic is a blend of nonionic surfactant with organosilicone and its properties (low surface tension, zero contact angle, and

complete wetting pattern on *A. theophrasti* leaves) are more like the pure trisiloxane organosilicone compound, Silwet L-77. Dyne-Amic is a blend of oil concentrate with organosilicone and its properties (25 dyne/cm surface tension, 56.2° contact angle, and drop formation on *A. theophrasti* leaf) are similar to the conventional adjuvant, Agri-Dex. These results confirmed that carefully selecting the co-adjuvant for organosilicone is critical to avoid antagonism to trisiloxane and retain its unique properties in its blends (Murphy, *et al.*, 1991). Many co-adjuvants interfere with the unique spreading ability of trisiloxanes, probably because of the large, bulky hydrophobes, typically found in conventional organic surfactants. The mechanism for this interference has been linked to ‘jamming the zipper’ (Murphy, *et al.*, 1991).

The fact that the contact angle of primisulfuron solution was larger than that of water alone on *A. theophrasti* leaf may be caused by some ingredient in the primisulfuron formulation, which changed the physico-chemical properties of water. However, further experimentation demonstrated that when both adjuvant and primisulfuron were added into water, the adjuvant was a determining factor for physico-chemical properties of the solution.

The solutions of both Silwet L-77 and Kinetic wetted *A. theophrasti* leaf surfaces completely; however, the spreading with Silwet L-77 was much larger than with Kinetic. This may be attributed to the co-surfactant in Kinetic interfering with the arrangement of Silwet L-77 molecules on the leaf surface. The wetting ability results indicated that complete wetting could increase spreading, but that spreading ability was not totally dependent on adjuvant wetting ability. In addition to the physico-chemical properties of the solution, the chemical nature of adjuvants and arrangement of their molecules on the leaf surface apparently play an important role in droplet spreading.

Results of the wettability study indicate that there were complicated interactions between surface tension, contact angle, and the physico-chemical nature of the target surface on the spreading capability of the different solutions. These results are in

agreement with other researchers who also found that the chemical nature of adjuvants plays an important role in droplet contact angle, wettability, and equilibrium spread areas (Sundaram, 1990; Zabkiewicz *et al.*, 1985, 1988).

Silwet L-77 and Kinetic significantly increased primisulfuron uptake in a short time, even 0.083 h after treatment. The instant increase in uptake of ^{14}C -primisulfuron was attributed to stomatal infiltration. Within 0.25 h after treatment, there was a significant difference between Silwet L-77 and Dyne-Amic. However, as the time increased, the difference disappeared. According to the low surface tension in the spray solution required for stomatal infiltration (Buick, *et al.*, 1992; Greene & Bukovac, 1974, Knoche & Bukovac, 1993; Schönherr & Bukovac, 1972), Agri-Dex might increase cuticular penetration rather than stomatal infiltration, which resulted in slower uptake than with Silwet L-77 and its blends. Since the chemical-physical properties of Dyne-Amic solution were more similar to those of Agri-Dex, only slight stomatal infiltration would be expected to be induced. Generally, the effect of Kinetic and Dyne-Amic on herbicide uptake was very similar, even though their physico-chemical properties and distribution patterns were significantly different. Based on the behavior of Dyne-Amic, it may be concluded that when a suitable co-adjuvant is blended with organosilicone, cuticular penetration may be increased, even without significantly increased stomatal infiltration.

Proper adjuvants can significantly increase herbicidal efficacy. Although the adjuvant effect was herbicide and weed species specific, at the normal application rate, there were no significant differences among the adjuvants for primisulfuron and nicosulfuron activities in the weed species tested.

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Thanks are expressed to Ciba-Geigy Corporation (Greensboro, NC, USA) for supplying ^{14}C -primisulfuron for the uptake study and for permitting us to use special laboratory equipment for the physico-chemical properties study.

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**CHAPTER 4. EFFECT OF ORGANOSILICONE SURFACTANTS ON THE
RAINFASTNESS OF PRIMISULFURON IN VELVETLEAF (*Abutilon
theophrasti*)¹**

ABSTRACT

Greenhouse experiments were conducted to evaluate the influence of three organosilicone surfactants (Silwet L-77, Silwet 408, and Sylgard 309) and two blends of organosilicone surfactants with conventional adjuvants (Dyne-Amic and Kinetic) on the rainfastness of primisulfuron in velvetleaf. Four conventional adjuvants, Rigo Oil Concentrate, Agri-Dex, methylated soybean oil, and X-77 were selected for comparison. Primisulfuron at 40 g ai/ha was applied alone or with the organosilicones, blends, or X-77 at 0.25% (v/v); the other adjuvants were tested at 1% (v/v). Simulated rainfall (1.25 cm/0.5 h) was applied at 0.25, 0.5, 1, or 2 h after treatment. Control ratings were made at 5-d intervals and shoot fresh weights were recorded 20 DAT. The organosilicone surfactants significantly increased the rainfastness of primisulfuron, even when simulated rainfall was applied at 0.25 or 0.5 h after treatment. Rigo Oil Concentrate and Kinetic also increased rainfastness when rainfall was applied 1 h after treatment. Differences among adjuvants were not as apparent when rainfall was applied 2 h after treatment. Regardless of the timing of simulated rainfall after treatment, there were significant differences between treatments and nontreated check; however, control was not acceptable in several instances.

Nomenclature: Primisulfuron, 2-[[[[[4,6-bis(difluoromethoxy)-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl]benzoic acid; velvetleaf, *Abutilon theophrasti* Medikus # ²**ABUTH**.

Additional index words: Conventional adjuvants, simulated rainfall, ABUTH.

¹ This chapter, formatted as required, was submitted to Weed Technology and is currently in press in Vol. 10, No. 2, 1996.

² Letters following the symbol are a WSSA computer code from Composite Lists of Weeds, Revised 1989. Available from WSSA, 108 West University Ave., Champaign, IL 61821-3133.

INTRODUCTION

To control weeds effectively, foliarly applied systemic herbicides must be taken up and translocated into the plants. The speed of uptake and translocation is determined by a number of factors. In any case, a certain rain-free period is always critical for the efficacy of most herbicides applied postemergence. Adjuvants are often included in the spray solution to reduce the impact of environmental interference. The use of adjuvants may increase spreading and/or penetration and subsequent retention on the leaf surface or translocation by preventing dilution and the physical forces of rainfall removing the herbicide (17). As a result, herbicide susceptibility to post-spraying rainfall may be reduced by the addition of an adjuvant to the spray solution.

In addition to the enhancement mechanisms of rainfastness mentioned above, it was reported in 1974 that infiltration of stomata would contribute to rainfastness of the active ingredient (5). Other reports indicated that organosilicone surfactants solutions can facilitate stomatal infiltration and increase rainfastness for some agrichemical (6, 13).

Primisulfuron is a sulfonylurea herbicide, used mainly to control johnsongrass (*Sorghum halepense* L.) and some broadleaf weeds in corn (*Zea mays* L.). A 4-h rain-free period is required for maximum herbicidal effectiveness (4).

Most published papers which relate to increasing rainfastness of herbicides by organosilicone surfactants concentrated on very few herbicides, e.g. glyphosate [*N* - (phosphonomethyl)glycine], bentazon [3-(1-methylethyl-(1*H*)-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide], metsulfuron {2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoic acid}, acifluorfen {5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid}. To our knowledge no papers addressing the rainfastness of primisulfuron have been published.

The objectives of this study were to determine the effect of three pure organosilicone surfactants, two blends of organosilicone with conventional adjuvants, and selected conventional reference adjuvants on primisulfuron activity against

velvetleaf following short-term, post-spraying simulated rainfall; also, whether or not there are significant differences between conventional adjuvants and organosilicones in enhancing rainfastness.

MATERIALS AND METHODS

Velvetleaf seeds were placed in 15-cm pots containing a commercial potting mix³, in the greenhouse with natural sunlight as the only light source. After emergence, the plants were thinned to one plant per pot. All plants were fertilized as needed with 20-20-20 water soluble N-P-K fertilizer. Herbicide treatments were made when the velvetleaf plants were at the six-leaf stage and 10 to 13 cm tall.

Primisulfuron was applied at 40 g ai/ha alone and in combination with the adjuvants listed in Table 1. The organosilicone surfactants (Silwet L-77, Silwet 408, and Sylgard 309), blends (Dyne-Amic and Kinetic), and X-77 were applied at 0.25% (v/v); the other adjuvants at 1% (v/v).

Treatments were applied in 94 L/ha of water using a CO₂-charged, continuous moving belt laboratory sprayer equipped with a single 8001E nozzle. The spray volume was 94 L/ha and the application pressure was 138 kPa. The plants received 1.25 cm simulated rainfall in a 30-min period at 0.25, 0.5, 1, or 2 h after the herbicide application. Simulated rainfall was formed using a laboratory rainfall simulator developed on the principle of droplet formation from needle tips (3).

Visual estimates of percent velvetleaf control were made at 5-d intervals and shoot fresh weights were recorded 20 DAT. Experimental design was a randomized complete block and each treatment was replicated five times. All experiments were repeated. Since the same trends were shown in two separate experiments, only the data from the first experiment are presented. The data were analyzed with an ANOVA procedure by SAS software (11).

³Promix BX, a product of Premier Brands, Inc. Redhill, PA 18076.

Table 1. Descriptions and sources of adjuvants used in the current study.

Adjuvant	Description	Source
Silwet L-77	silicone polyalkyleneoxide copolymer	OSi Company, Tarrytown, NY 10591
Silwet 408	silicone polyalkyleneoxide copolymer	OSi Company, Tarrytown, NY 10591
Sylgard 309	silicone adjuvant mixture of 2-(3-hydroxypropyl)-heptamethyltrisiloxane, ethyloxylated, acetate EO glycol, -allyl, acetate	Dow Corning Corporation, Midland, MI 48684
Kinetic	blend of polyalkyleneoxide modified polydimethylsiloxane and nonionic surfactant	Helena Chemical Company, Memphis, TN 38137
Dyne-Amic	blend of polyalkyleneoxide modified polydimethylsiloxane, nonionic surfactant and methylated vegetable oil	Helena Chemical Company, Memphis, TN 38137
X-77	a mixture of alkylaryl polyoxyethylene glycols, free fatty acids, and isopropanol	Loveland Industries, Greeley, CO 80632
MSO	methylated soybean oil concentrate	Terra Riverside, Sioux City, IA 51101
Rigo Oil Concentrate (ROC)	83% paraffin base petroleum oil and 17% nonionic surfactant/emulsifier	Wilbur-Ellis Company, San Francisco, CA 94104
Agri-Dex	83% paraffinic mineral oil and 17% polyoxyethylene sorbitan fatty acid esters	Helena Chemical Company, Memphis, TN 38137

RESULTS AND DISCUSSION

Trends in efficacy, at 5-d intervals of the adjuvants tested on primisulfuron activity in velvetleaf are shown in Figures 1 through 5. For easier readability, statistical details are omitted from the figures. However, significant differences in the results are indicated in the text.

When no simulated rainfall was applied, all adjuvants enhanced primisulfuron activity. Control of velvetleaf was significantly higher than when the herbicide was used alone. However, there were no statistically significant differences among adjuvants (Figure 1).

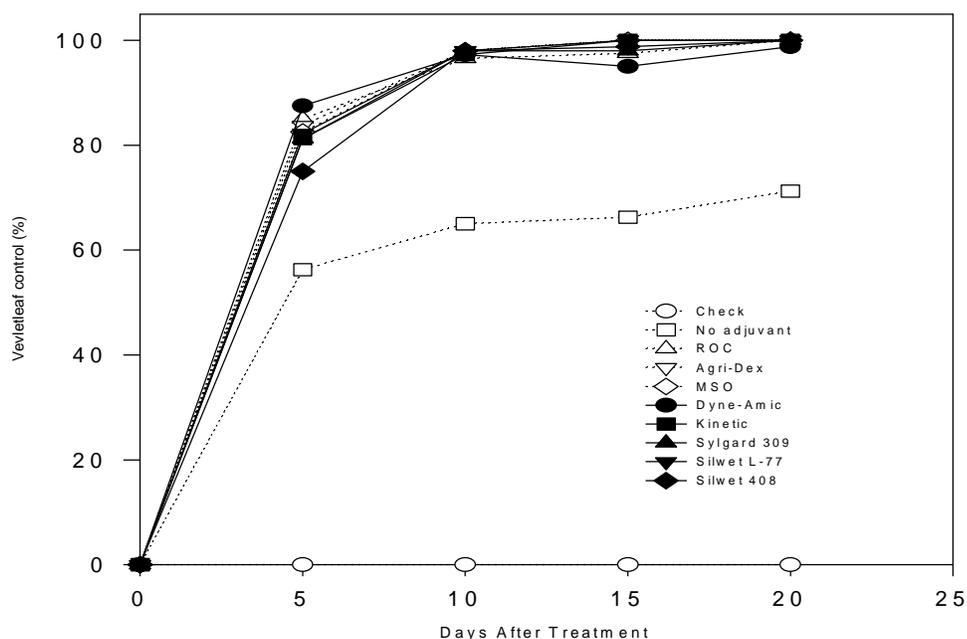


Figure 1. Efficacy of different adjuvants on primisulfuron in velvetleaf (without rainfall)

The organosilicone surfactants were significantly more effective than other adjuvants when simulated rainfall was applied at 0.25 (Figure 2) or 0.5 h (Figure 3) after treatment.

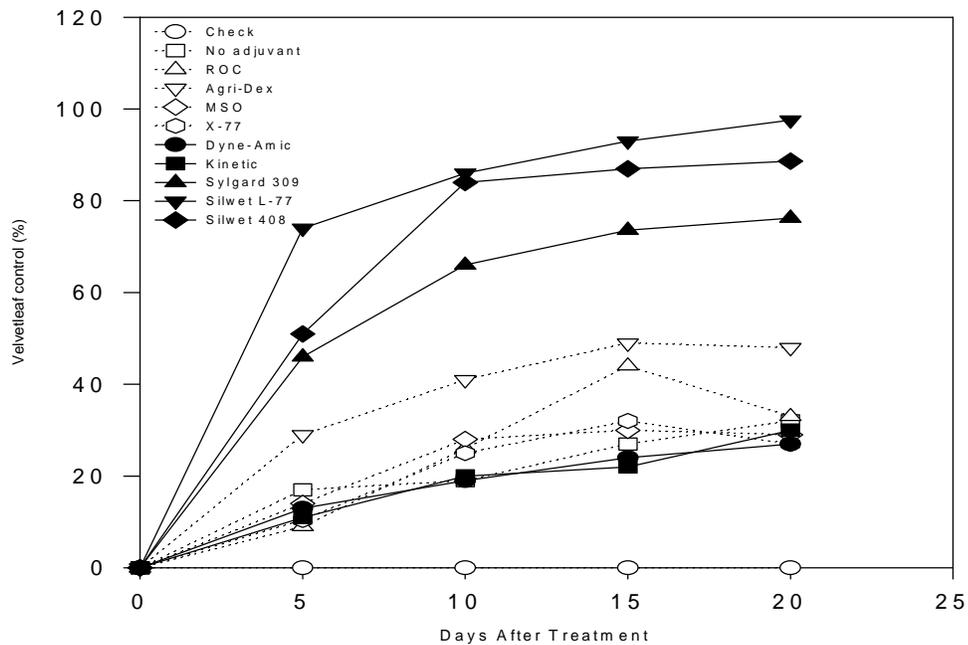


Figure 2. Efficacy of different adjuvants on primisulfuron in velvetleaf (simulated rainfall applied 0.25 h after treatment)

The results show that differences among adjuvants were reduced when simulated rainfall was applied at 1 (Figure 4) or 2 h (Figure 5.) after treatment. However, Silwet L-77, Silwet 408, and Sylgard 309 were still among the most effective adjuvants for primisulfuron on velvetleaf.

More detailed data are presented for efficacy at 20 DAT, the final evaluation date (Table 2).

In the absence of rainfall after herbicide treatment, all the adjuvants tested significantly enhanced primisulfuron efficacy on velvetleaf compared with primisulfuron alone (X-77 was not included in this test). Primisulfuron alone provided 71% control of velvetleaf; adjuvants enhanced primisulfuron activity to 100% or nearly so. There were no significant differences among the adjuvants under no rainfall conditions.

When the critical rain-free period was reduced to either 0.25 or 0.5 h after treatment, only the three pure organosilicones, Sylgard 309, Silwet L-77, and Silwet 408 were effective in increasing primisulfuron activity on velvetleaf (Table 2). Control of velvetleaf by primisulfuron plus ROC, MSO, Agri-Dex, X-77, Kinetic, or Dyne-Amic was similar to or less than that with primisulfuron alone.

When simulated rainfall was applied 1 h after treatment, ROC, MSO, Kinetic, Sylgard 309, Silwet L-77, and Silwet 408 enhanced the efficacy of primisulfuron on velvetleaf. Agri-Dex, X-77, and Dyne-Amic failed to improve primisulfuron activity (Table 2).

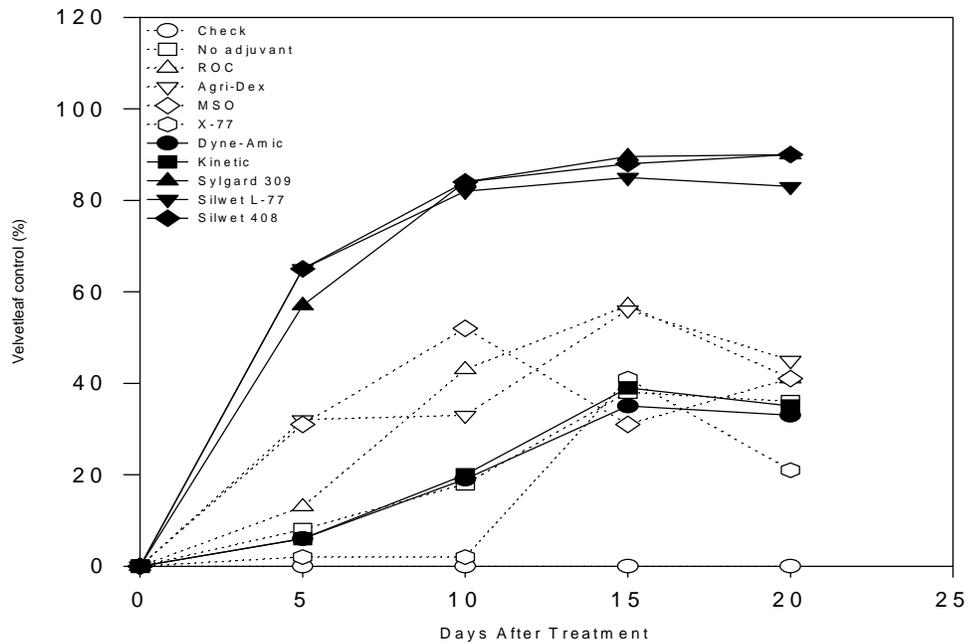


Figure 3. Efficacy of different adjuvants on primisulfuron in velvetleaf (simulated rainfall applied 0.5 h after treatment)

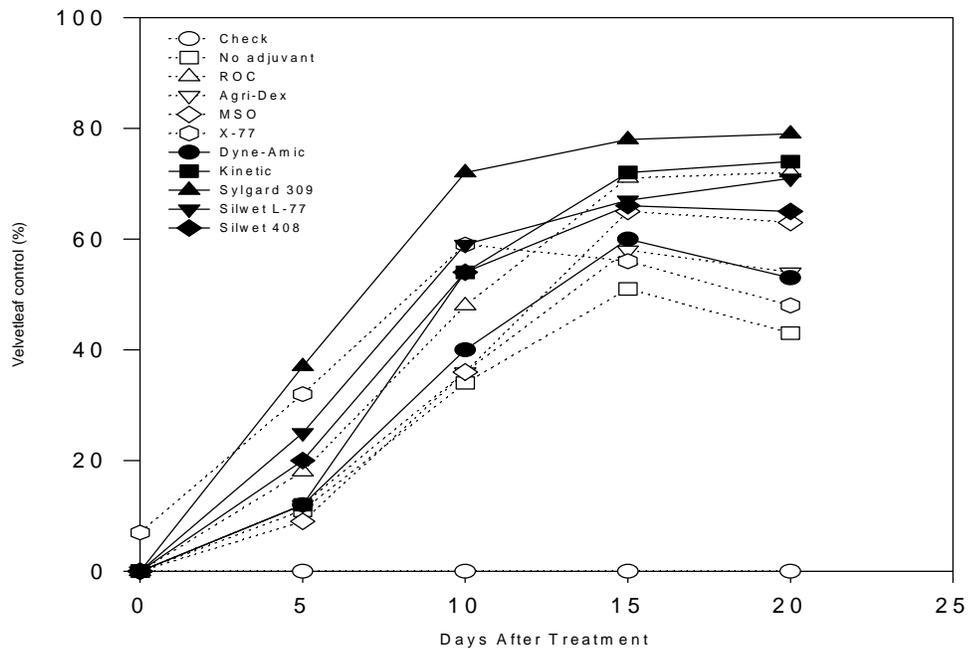


Figure 4. Efficacy of different on primisulfuron in velvetlea (simulated rainfall applied 1 h after treatment)

Generally, across all treatments, rainfall within 2 h after herbicide application tended to reduce primisulfuron efficacy on velvetleaf. However, the effect was different for the different adjuvants. When simulated rainfall was applied to velvetleaf 2 h after herbicide application, only Kinetic, Sylgard 309, and ROC improved rainfastness compared with primisulfuron alone. It has been widely reported that organosilicone surfactants can induce stomatal infiltration (2, 5, 7, 12, 14,). Fifty, 35 and 20% of deoxyglucose applied with Silwet L-77 had penetrated the stomatous leaf surfaces of field bean (*Vicia faba* L.), oat (*Avena sativa* L.), and wheat (*Triticum aestivum* L.) respectively, at 10 min after application (15). A large portion of active ingredient entering into the plant by stomatal infiltration could contribute to rainfastness. However, the stomatal infiltration induced by conventional adjuvants was very small and most of the applied herbicide remained on the leaf surface to be washed off by simulated rainfall applied a short time after herbicide treatment (15).

The longer the critical rain-free period, the more active ingredient was taken into the plant by cuticular penetration. Consequently, the interference of rainfall was reduced. This could explain why efficacy of the conventional adjuvants tested increased as the interval between treatment and simulated rainfall increased from 0.25 or 0.5 h to 1 or 2 h.

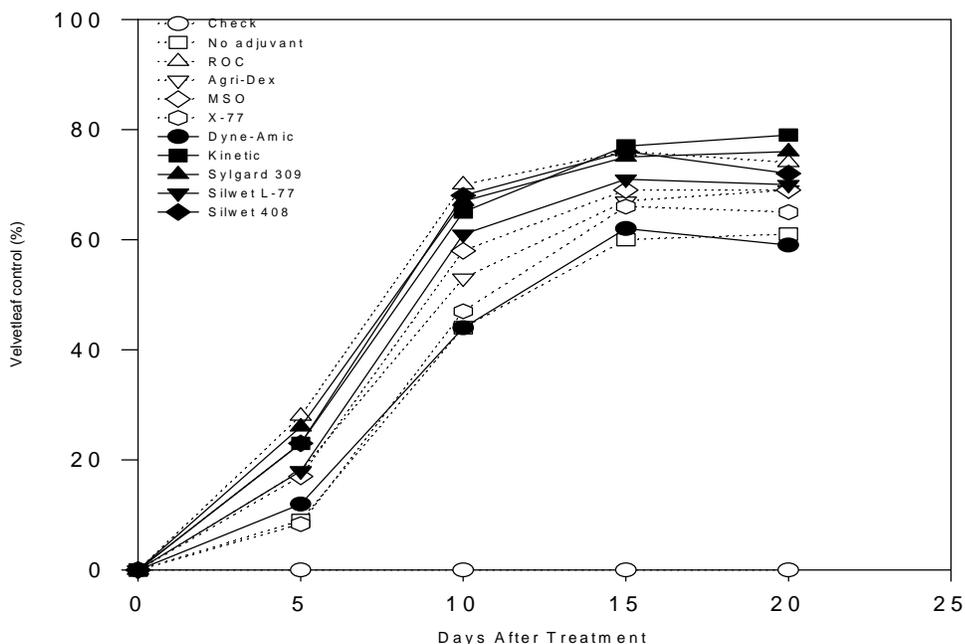


Figure 5. Efficacy of different adjuvants on primisulfuron in velvetleaf (simulated rainfall applied 2 h after treatment)

Carefully selected the co-adjuvant for organosilicones was very important to avoid competition between the organosilicone and co-surfactant molecules for the interface (1, 8, 9). The physico-chemical properties of two blends of organosilicones with conventional adjuvants are significantly different (16). Kinetic is a blend of nonionic surfactant with organosilicone, and its physico-chemical properties are more like the pure organosilicone. Dyne-Amic is a blend of oil concentrate with organosilicone, and

its physico-chemical properties are more similar to the conventional adjuvants; only a small portion of stomatal infiltration would be induced for rainfastness by Dyne-Amic.

Table 2. Velvetleaf control 20 DAT with primisulfuron at 40 g ai/ha alone or with adjuvants.

Adjuvant	Concentration % (v/v)	Control ^a				
		Time of simulated rainfall after treatment				
		No rainfall	0.25 h	0.5 h	1 hr	2 hr
				%		
Control	-	0 c	0 c	0 d	0 f	0 e
No adjuvant	-	71 b	32 b	36 bc	43 e	61 cd
ROC	1.0	100 a	33 b	41 bc	72 ab	74 ab
Agri-Dex	1.0	100 a	48 b	45 b	54 de	69 abcd
MSO	1.0	100 a	29 b	41 bc	63 bcd	69 abcd
X-77	0.25	-	27 b	21 c	56 cde	65 bcd
Dyne-Amic	0.25	99 a	27 b	33 bc	53 de	59 d
Kinetic	0.25	100 a	30 b	35 bc	74 ab	79 a
Sylgard 309	0.25	100 a	76 a	90 a	79 a	76 ab
Silwet L-77	0.25	100 a	98 a	83 a	71 abc	70 abcd
Silwet 408	0.25	100 a	89 a	93 a	65 abcd	72 abc

^aMeans within a column followed by the same letters are not significantly different at the 5% level according to Duncan's Multiple Range Test.

The fact that Kinetic did not increase rainfastness of primisulfuron when simulated rainfall was applied 0.25 or 0.5 h after herbicide treatment indicated that excellent wetting does not always increase rainfastness. Other research results show that many silicone surfactants are very effective at lowering the spray solution surface tension and thus are excellent wetting agents but not all increased herbicide efficacy or rainfastness (10). Therefore, in addition to enhancing stomatal infiltration, other factors (not yet fully understood) may also subtly influence rainfastness of herbicides.

In summary, the current research indicates that organosilicone surfactants can greatly increase the rainfastness of primisulfuron in velvetleaf. The effect was immediate and dramatic, even when the simulated rainfall was applied 0.25 h after herbicide treatment. However, as the time interval between treatment and simulated rainfall was increased, the differences between organosilicone surfactants and conventional adjuvants decreased.

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CHAPTER 5. PHYSICO-CHEMICAL PROPERTIES OF SEVERAL COMMERCIAL ORGANOSILICONES, THEIR BLENDS, AND CONVENTIONAL ADJUVANTS

ABSTRACT

Adjuvants are often used to improve spray retention, wet leaf surfaces, and enhance uptake of herbicidal active ingredients. The physico-chemical properties including static surface tension, dynamic surface tension, and wetting ability of adjuvants are critical for agrochemical efficacy. A study was conducted to investigate these physico-chemical properties and the spread pattern on velvetleaf foliage of several commercial organosilicones, their blends, and conventional adjuvants. A dynamic contact angle analyzer, surface tensiometer, and goniometer were used to measure the static surface tension, dynamic surface tension, and contact angle, respectively. The progress of droplet spread of different adjuvant solutions containing fluorescent dye was recorded by videotaping and computer imaging under UV light. A logistic dose response relationship was found between adjuvant concentration and contact angle on parafilm. However, across a wide range of concentrations, there was no clear relationship between surface tension and contact angle even in a homogeneous adjuvant solution; although, at normal use rates, the lower the surface tension, the lower will be the contact angle on target surfaces. Organosilicones were superior wetting agents and showed excellent spreading patterns on velvetleaf foliage. Organosilicones not only exhibited extremely low static surface tension, but also showed superior performance in lowering dynamic surface tension. Rapidly lowering dynamic surface tension of spray droplets led to improved droplet retention on leaf surfaces, and the low static surface tension brought about complete wetting of the target surface. Consequently, herbicide efficacy was improved by bringing more of the active material into intimate contact with the target.

INTRODUCTION

Adjuvants are often used to improve retention of the spray, wet the leaf surface, and enhance uptake of the active ingredients (4, 9, 12). The physico-chemical properties of adjuvants, including static surface tension, dynamic surface tension, and wetting ability, are determined by adjuvant nature. These properties are critical for agrochemical efficacy. During the spraying process, whether droplets impacting leaves are retained or bounce off is complex and not fully understood. However, it is clear that leaf surface morphology, droplet size, impact velocity, and the dynamic surface tension of the spray solution are important factors (4, 7, 8,).

Organosilicone compounds are a class of surfactants in which an array of methyl groups bonded to silicone atoms constitute the hydrophobic part of the molecule (6). The spreading mechanism, proposed by Anathapadmanabhan *et al.* in 1990, suggests that the compact size of the hydrophobic portion of the organosilicones allows their molecules to transfer readily from the liquid/air interface of the advancing solution to the target surface. This process has been described as a unique ‘molecular zippering’ for organosilicone compounds (1).

According to Murphy *et al.*(10), a surfactant which may have low equilibrium surface tension, show excellent spreading on low energy surfaces, and ability to lower dynamic surface tension rapidly, should function as a superior adjuvant. However, there has been limited study on static surface tension, dynamic surface tension, contact angle, spread pattern, and wetting ability of different commercialized organosilicones and conventional adjuvants on waxy or biological surfaces (10, 13, 14). In the current research, an extensive study was conducted to investigate the physico-chemical properties of organosilicones and conventional adjuvants. Spread patterns of their solutions on velvetleaf foliage were also investigated. The role of these physico-chemical properties on the spreading and wetting processes are discussed.

MATERIAL AND METHODS

Chemicals.

Commercially formulated nicosulfuron, 75% water dispersible granules, was used in the test. Adjuvants used in this study are listed in Table 1.

Plants.

Velvetleaf (*Abutilon theophrasti* Medikus) seeds were placed in 15-cm pots containing a commercial potting mix, in the greenhouse with natural sunlight as the only light source. After emergence, the plants were thinned to one plant per pot. All plants were fertilized as needed with 20-20-20 water soluble N-P-K fertilizer.

Static surface tension of different adjuvant solutions and contact angle on the foliage of velvetleaf.

A Cahn Dynamic Contact Angle Analyzer with DCA software (Cahn Instruments, Inc. 16207 S. Carmenita Road, Cerritos, CA 90701-2275), based on the Wilhelmy plate technique, was used to measure the surface tension of the studied adjuvants over a range of concentrations. Solutions were prepared with distilled water (w/w). During measurement, since the receding process was more wettable and had more closely a zero contact angle on the platinum plate, the static surface tension of the fluid was taken as receding surface tension rather than advancing surface tension. After constantly obtaining very consistent results for measuring different Silwet L-77 solution with three replications, other adjuvants were measured without replication.

The instrument above was also used to measure the influence of the adjuvants on contact angles on velvetleaf foliage. Fresh leaf samples were divided longitudinally and the abaxial sides attached together with a double side tape leaving the adaxial surfaces exposed. Rectangular sections (10 by 15 mm approximately) were excised for immersion in the test fluid. In order to calculate contact angle with the equipment software (DCA software), the surface tension of the probe liquid was measured in advance, and the dimensions of the leaf sample were measured with a micrometer. Each solution was tested three times.

Table 1. Descriptions and sources of adjuvants used in the current study.

Adjuvant	Description	Source
Silwet L-77	silicone polyalkyleneoxide copolymer	OSi Company, Tarrytown, NY 10591
Silwet 408	silicone polyalkyleneoxide copolymer	OSi Company, Tarrytown, NY 10591
Sylgard 309	silicone adjuvant mixture of 2-(3-hydroxypropyl)-heptamethyltrisiloxane, ethyloxylated, acetate EO glycol, -allyl, acetate	Dow Corning Corporation, Midland, MI 48684
Kinetic	blend of polyalkyleneoxide modified polydimethylsiloxane and nonionic surfactant	Helena Chemical Company, Memphis, TN 38137
Dyne-Amic	blend of polyalkyleneoxide modified polydimethylsiloxane, nonionic surfactant and methylated vegetable oil	Helena Chemical Company, Memphis, TN 38137
X-77	a mixture of alkylaryl polyoxyethylene glycols, free fatty acids, and isopropanol	Loveland Industries, Greeley, CO 80632
MSO	methylated soybean oil concentrate	Terra Riverside, Sioux City, IA 51101
Rigo Oil Concentrate (ROC)	83% paraffin base petroleum oil and 17% nonionic surfactant/emulsifier	Wilbur-Ellis Company, San Francisco, CA 94104
Agri-Dex	83% paraffinic mineral oil and 17% polyoxyethylene sorbitan fatty acid esters	Helena Chemical Company, Memphis, TN 38137

Contact angles of different adjuvant solutions on parafilm.

A 2- μ l drop of the studied adjuvants at different concentrations was placed on parafilm (American National Can TM/ Neenah, WI 54956). Both left and right contact angles of the drop on parafilm were measured by NPI C. A. Goniometer (Model No. 100-00115, Rame-hart, Inc., 43 Bloomfield Ave. Mountain Lake, NJ). Each solution was replicated five times. During the measurement the temperature was 23.3⁰C.

Spread pattern.

To determine the droplet spreading patterns of different adjuvant solutions on velvetleaf, one fresh leaf of velvetleaf was mounted on the camera platform and a 2- μ l drop was deposited on the leaf. The progress of drop spread was recorded by videotaping and computer imaging under UV light (Spectrolite, Model ENF-260C, Spectronics Corporation, Westbury, NY).

Dynamic surface tension measurements.

A SensaDyne 6000 surface tensiometer with SensaDyne 6000 software (SensaDyne Instrument Div., Chem-Dyne Research Corp. 2855 E. Brown Rd., Suite #17. Mesa, Arizona, 85205), which is based on a refinement of the maximum bubble pressure method, was used to measure dynamic surface tension of different liquids. Adjuvant solutions were also prepared with distilled water (w/w). During measurement, nitrogen gas was bubbled slowly through two probes of different radii that were immersed in the test fluid. The bubbling of the nitrogen through the probes produces a differential pressure signal (ΔP) which was directly related to the fluid surface tension.

RESULTS

Static surface tensions and contact angles on the foliage of velvetleaf.

The static surface tension and contact angle on the foliage of velvetleaf for different adjuvants are listed in Table 2. Static surface tension of nicosulfuron solution

alone was 56.56 dyne/cm and its contact angle on the leaf sample was 95.84 degree. When the conventional adjuvants were used, the surface tension of the solution was about 28 to 36 dyne/cm and the contact angle of these solutions on the leaf of velvetleaf was 59° compared to 86° with nicosulfuron alone.

Table 2. Surface tensions of different adjuvant solutions and contact angles on the leaves of velvetleaf

Adjuvant	Concentration (w/w)	Surface tension (dyne/cm)	Contact angle (degree)
Water	-	70.21	89.0
Nicosulfuron	0.06?	56.56	95.8
ROC	1.0%	30.62	58.8
Agri-Dex	1.0%	36.71	86.51
MSO	1.0%	31.66	69.04
X-77	0.25%	28.11	59.06
Dyne-Amic	0.25%	24.81	56.20
Kinetic	0.25%	20.17	0
Sylgard 309	0.25%	21.06	0
Silwet L-77	0.25%	21.12	0
Silwet 408	0.25%	20.96	0

For the solutions of three pure organosilicone, Silwet L-77, Silwet 408, and Sylgard 309 at 0.25% (w/w), the surface tension was about 20 dyne/cm and the contact angle was equal to zero. The drops of these solutions wetted velvetleaf foliage completely.

Of the two blends, the solution of Kinetic at 0.25% (w/w) was with 20.1 dyne/cm surface tension and zero contact angle on the leaf of velvetleaf. Dyne-Amic liquid at

same concentration was with 24.8 dyne/cm static surface tension and 56.2° contact angle on the same surface.

Contact angle on parafilm.

During the modeling process, a logistic dose responding relationship between adjuvant concentration and contact angle for different adjuvants was found. Generally, as adjuvant concentration increased within a certain range, the contact angle on the parafilm was decreased. The results of contact angle measurements of different adjuvants on parafilm are shown in Figures 1 to 3. It is clearly shown that the contact angles of Silwet L-77, Silwet 408 and Sylgard 308 were dramatically decreased when the adjuvant concentration increased slightly. Complete wetting was achieved on the parafilm when the concentration of these organosilicone compounds was about 300 ppm and showed zero contact angle at about 500 ppm (Figure 1).

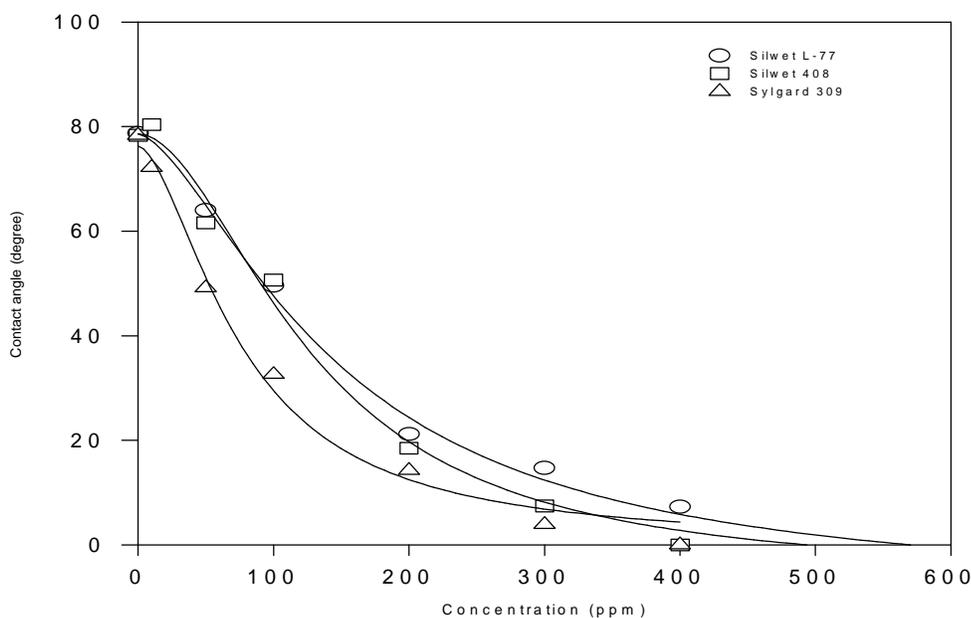


Figure 1. Contact angle vs. concentration for organosilicones. The data generated by the logistic dose responding model for each adjuvant are shown as solid lines and the actual measured data are shown as various solid or empty symbols.

Of the two blends, Kinetic completely wetted the parafilm at 1000 ppm and resulted in zero contact angle at 2500 ppm; however, the wetting ability of Dyne-Amic was more similar to conventional adjuvants (Figure 2).

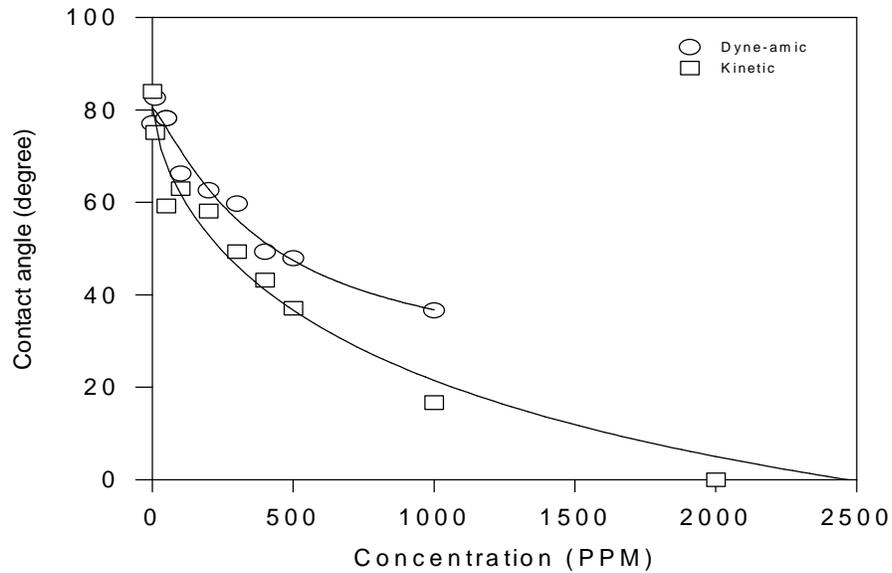


Figure 2. Contact angle vs. concentration for two blends. The data generated by the logistic dose responding model for each adjuvant are shown as solid lines and the actual measured data are shown as various empty symbols.

The minimum contact angle of Agri-Dex, MSO and ROC solutions was from 35° to 50° at 10000 ppm on parafilm. Even when the concentration of these adjuvants continuously increased above 10000 ppm (suggested applied concentration), the contact angle was not reduced further on parafilm (Figure 3).

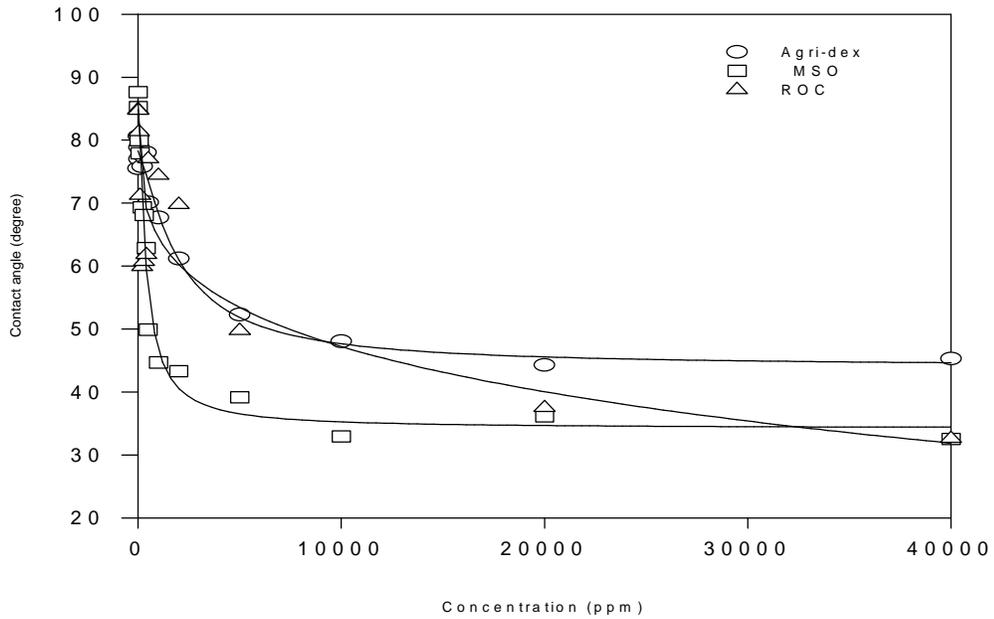


Figure 3. Contact angle vs. concentration for conventional adjuvants. The data generated by the logistic dose responding model for each adjuvant are shown as solid lines and the actual measured data are shown as various solid or empty symbols.

Spread pattern.

The spread patterns of different adjuvant solutions are shown on Figure 4 and 5.

Complete wetting of the leaf surface by Silwet L-77, Silwet 408, Sylgard 309 and Kinetic solutions at 0.25% was demonstrated under strong UV light. There were no significant differences in spreading pattern among the solutions of Dyne-Amic, Agri-Dex, ROC, MSO, X-77, primisulfuron alone, and water only. There always was a clear drop shown on the leaf which indicated that drops of these solutions or water spread only slightly.

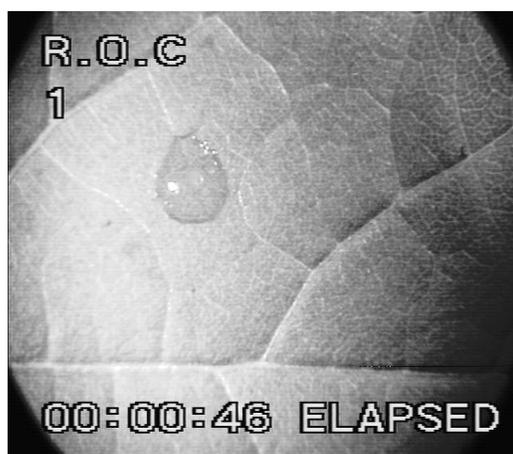
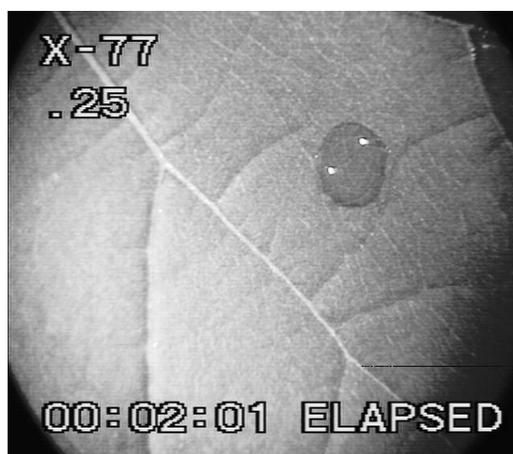


Figure 4. The distribution patterns of different solutions on velvetleaf

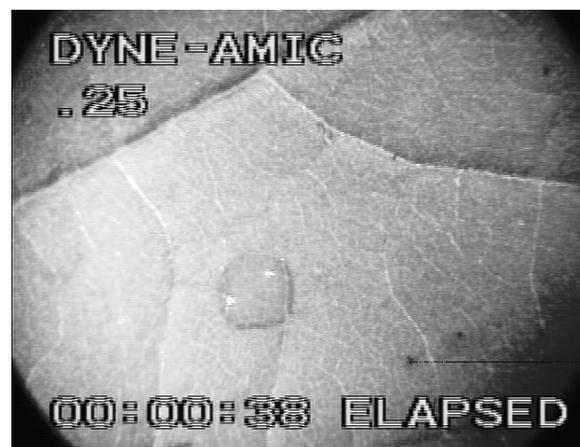
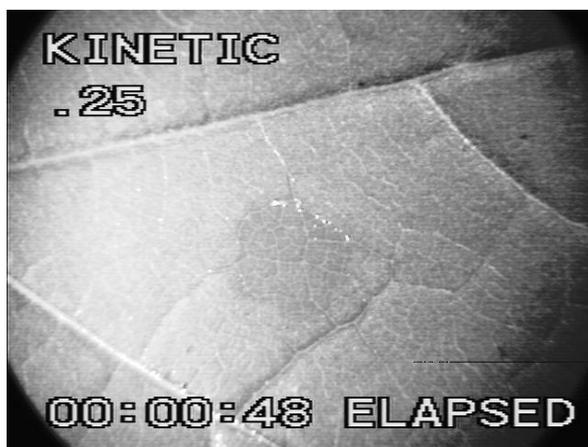


Figure 5. The distribution patterns of different solutions on velvetleaf

Dynamic surface tension.

The dynamic surface tensions of the tested adjuvants at different concentrations are shown on Figures 6 and 7. Silwet L-77, Silwet 408, Sylgard 309 and Kinetic, were fastest in reducing surface tension on the newly formed surfaces among the test adjuvants. Dyne-Amic was much slower than these adjuvants in reducing surface tension. Of the conventional adjuvants, X-77 and MSO were faster than Agri-Dex or ROC. There were no significant differences among concentrations of organosilicones and their blends in reducing surface tension on the newly formed surface between 1250 and 2500 ppm.

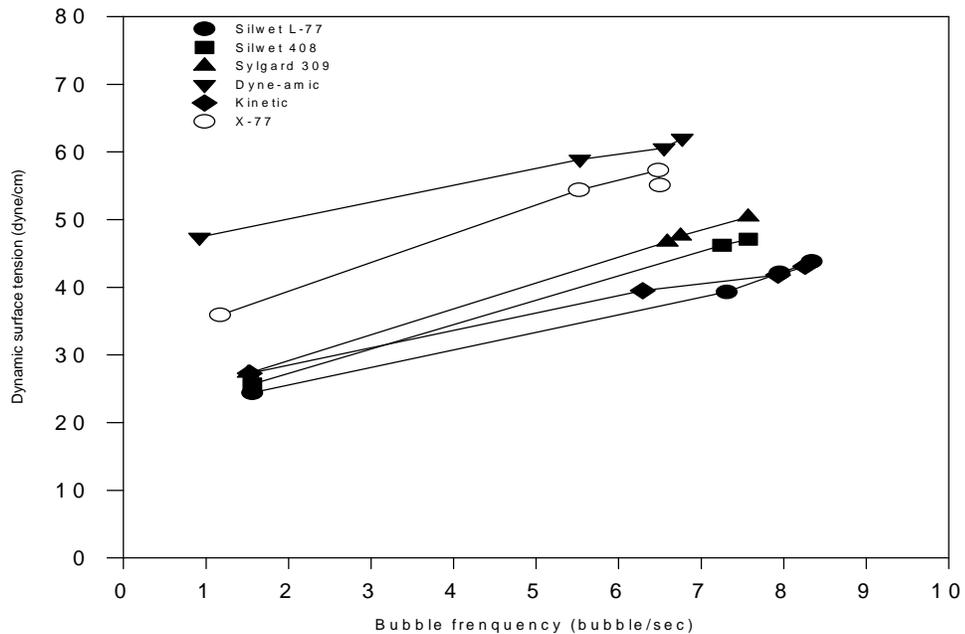


Figure 6. Dynamic surface tension of different solutions vs. bubble frequency. Silwet L-77, Silwet 408, Sylgard 309, Dyne-Amic, Kinetic and X-77 at 1250 ppm.

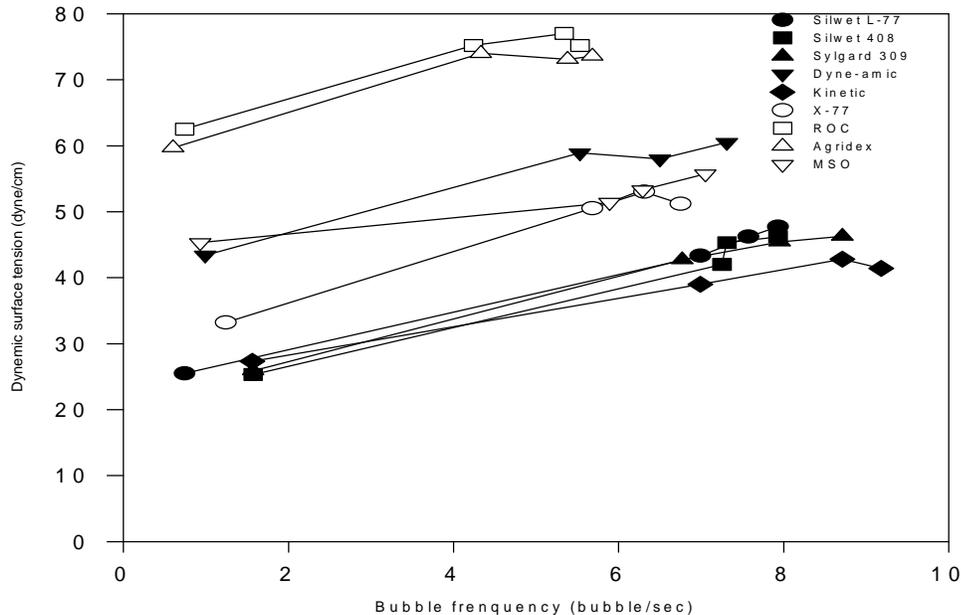


Figure 7. Dynamic surface tensions of different solutions vs. bubble frequency. Silwet L-77, Silwet 408, Sylgard 309, Dyne-Amic, Kinetic and X-77 at 2500 PPM. ROC, MSO and Agri-Dex at 10,000 ppm.

DISCUSSION

The standard of wetting capability given by Zakiewicz *et al.* (15) according to experience is that formulations with contact angle values of 50° or less are considered as having good wetting capability; complete wetting is possible if the value is 20° or less. The results of contact angle measurements on parafilm and velvetleaf foliage, and spread patterns, indicated that conventional adjuvants had poor wetting ability compared to organosilicones. Of the two blends, at relatively high concentration, Kinetic solution could completely wet the parafilm surface, but Dyne-Amic solution increased the drop size only slightly under UV light. Murphy *et al.* (10) also showed that a conventional organic hydrocarbon surfactant was not a good spreader.

The contact angle and surface tension are two important concepts in the adjuvants area. Surface tension is solely determined by the physico-chemical properties of adjuvants. Contact angle is the result of interaction between droplet and target surface.

Generally, at normal use rates, the lower the surface tension, the lower the contact angle on target surfaces; however, in the current study, across a wide range of concentrations, a clear relationship between surface tension and contact angle was not found, even in a wide range of homogeneous adjuvant solutions.

Surface tension is reduced by adsorption of surfactant molecules at air/water or water/solid interfaces. During the dynamic processes of drop spraying and wetting, the surfactant molecules in the spray solution need time to diffuse and orient at the interface. According to Anderson *et al.* (4) the speed of the diffusion and orientation at a new interface are different and depend on the type of molecule and the surrounding medium. The change in surface tension at a new interface with time is defined as dynamic surface tension, which can change dramatically in tens of milliseconds.

When the bubble formation rate increased during the dynamic surface tension measurement in this research, the time available for surfactant molecules to diffuse and orient in the newly formed surface was reduced correspondingly. As the bubble rate increased, the surfactant molecules had less and less time to lower surface tension of the newly formed interface. In the current study, dynamic surface tension for all test adjuvant solutions increased with the bubble rate. However, the organosilicones still had the lowest dynamic surface tension, regardless of the bubble rate.

It has been reported that fast dynamic surface tension lowering of spray droplets leads to improve droplet retention on leaf surfaces (2, 3, 4). When a droplet impinges on a leaf surface it undergoes an initial flattening, forming a new liquid surface, followed by recoil and bounce or retention (5). It has been thought that dynamic rather than equilibrium surface tension is important in determining spray retention (5, 7). One reason is that the droplet size is related to dynamic surface tension during the spray process. This reduction will increase retention because of the lower impacting energy of the smaller droplets (4). Improved droplet retention can, in turn, improve the efficacy of the formulation by bringing more of the active material in intimate contact with the target.

The physico-chemical properties of two blends of an organosilicone with a conventional adjuvant were significantly different. Kinetic is a blend of a nonionic surfactant with an organosilicone, its physico-chemical properties are similar to organosilicone compounds. Kinetic solution had 20.1 dyne/cm surface tension and zero contact angle on the leaf of velvetleaf at 0.25% (w/w) and showed a complete wetting process on the leaf surface under UV light. During the dynamic surface tension measurement, Kinetic solution reduced the surface tension very rapidly in the newly formed surfaces. Dyne-Amic is a blend of an oil concentrate with an organosilicone; by contrast with Kinetic, it exhibits properties that are more similar to those of the conventional adjuvants. Dyne-Amic solution had 24.8 dyne/cm static surface tension and 56.2° contact angle on the leaf of velvetleaf at 0.25% (w/w). Under UV light, the drop size of Dyne-Amic solution was only slightly increased. Dyne-Amic was much slower than Kinetic in reducing surface tension on the newly formed surface. These results did confirm that carefully selecting the co-adjuvant for organosilicone was very important to avoid ‘jamming of the molecular zipper’ which causes competition between organosilicone and conventional surfactant monomers for the interface (1, 11). Otherwise, the organosilicone surfactants’ ability of superior wetting, spreading, and inducing stomatal infiltration would be lost.

In summary, a logistic dose response relationship was found between adjuvant concentration and contact angle on parafilm. In addition to showing excellent spreading patterns on velvetleaf foliage, the tested organosilicones also showed great performance in lowering dynamic surface tension, which improved droplet retention on leaf surfaces. Consequently, herbicide efficacy was improved by bringing more of the active material into intimate contact with the target.

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CHAPTER 6. A COMPARISON BETWEEN CONVENTIONAL ADJUVANTS, ORGANOSILICONES, AND THEIR BLENDS ON THE SURFACE TENSION, WETTABILITY, FOLIAR UPTAKE, AND TRANSLOCATION IN VELVETLEAF (*Abutilon theophrasti*) AND EFFICACY WITH TWO SULFONYLUREAS IN FOUR WEED SPECIES

ABSTRACT

Static surface tension, wetting, and spreading ability of several organosilicones, their blends, and conventional adjuvants were measured. In addition, their influence on ¹⁴C-primisulfuron absorption and translocation, and the effects of the adjuvants on the activity of nicosulfuron and primisulfuron in four weed species were studied. Results showed that organosilicones, with very low static surface tension and great spreading ability, increased the uptake of primisulfuron in velvetleaf within 2 h after herbicide application. When herbicides were combined with adjuvants, weed control was significantly increased and was much more rapid than when the herbicides were used alone.

INTRODUCTION

Adjuvants were originally included in pesticide formulations added to the spray tank solutions as the wetter or as an aid to improve droplet adhesion. However, in more recent years, they have been used in larger extent and higher concentrations for enhancing the efficacy of pesticides, responding to environmental pressures, and reducing the economic cost (12). In addition to affecting retention, coverage, and the physical state of the residue on the leaf surface, adjuvants could enhance stomatal infiltration, and/or cuticular penetration by changing the structure and composition of cuticle. This could increase the diffusion coefficients in leaf surfaces and the permeability of leaf tissue, therefore improve penetration of the active ingredient (5, 7, 11, 14). The physico-chemical properties of adjuvants, including static surface tension and dynamic surface tension are critical for adjuvant efficacy. In the previous study,

the physico-chemical properties, spread patterns of several organosilicones, their blends, and conventional adjuvants were studied in detail (Chapters 3 and 5). The purpose of this research was to investigate the static surface tension and wetting ability of these adjuvants; also, their effects on foliar uptake and translocation of primisulfuron, and efficacy of nicosulfuron and primisulfuron on four weed species.

MATERIAL AND METHODS

Chemicals.

Commercially formulated primisulfuron and nicosulfuron (both 75% water dispersible granules) were used in the efficacy study. ^{14}C -primisulfuron, specific activity 52.4 $\mu\text{ci}/\text{mg}$, supplied by Ciba-Geigy Corporation (Greensboro, NC) was used in the uptake study.

Adjuvants used in this study are listed in Table 1.

Surface tension.

A Cahn Dynamic Contact Angle Analyzer with DCA software, based on the Wilhelmy plate techniques was used to measure surface tensions of the adjuvants over a range of concentrations. The solutions were prepared in distilled water (w/w). After obtaining very stable results with the series of concentrations of Silwet L-77 replicated three times, other solutions were measured without replications.

Wettability measurement.

Droplets of different volumes (2, 4, 6, 8, and 10 μl) of solutions containing organosilicone surfactants (Silwet 1-77, Silwet 408, and Sylgard 309), blends (Dyne-Amic and Kinetic) and X-77 were applied at 0.25% (v/v); the other adjuvants at, 1% (v/v) with or without nicosulfuron at 40 g ai/ha, were applied by syringe to mature foliage of velvetleaf. After the droplets reached an equilibrium state of spreading (ca. 30 s), the diameter of the spread area was measured. The spread area was calculated by the formula $S = 3.14 \times r^2$. Each treatment was replicated five times.

Table 1. Descriptions and sources of adjuvants used in the current study.

Adjuvant	Description	Source
Silwet L-77	silicone polyalkyleneoxide copolymer	OSi Company, Tarrytown, NY 10591
Silwet 408	silicone polyalkyleneoxide copolymer	OSi Company, Tarrytown, NY 10591
Sylgard 309	silicone adjuvant mixture of 2-(3-hydroxypropyl)-heptamethyltrisiloxane, ethyloxylated, acetate EO glycol, -allyl, acetate	Dow Corning Corporation, Midland, MI 48684
Kinetic	blend of polyalkyleneoxide modified polydimethylsiloxane and nonionic surfactant	Helena Chemical Company, Memphis, TN 38137
Dyne-Amic	blend of polyalkyleneoxide modified polydimethylsiloxane, nonionic surfactant and methylated vegetable oil	Helena Chemical Company, Memphis, TN 38137
X-77	a mixture of alkylaryl polyoxyethylene glycols, free fatty acids, and isopropanol	Loveland Industries, Greeley, CO 80632
MSO	methylated soybean oil concentrate	Terra Riverside, Sioux City, IA 51101
Rigo Oil Concentrate (ROC)	83% paraffin base petroleum oil and 17% nonionic surfactant/emulsifier	Wilbur-Ellis Company, San Francisco, CA 94104
Agri-Dex	83% paraffinic mineral oil and 17% polyoxyethylene sorbitan fatty acid esters	Helena Chemical Company, Memphis, TN 38137

Uptake and translocation.

A stock solution was prepared by dissolving ^{14}C -primisulfuron and technical primisulfuron in water (pH 8.5) to form a solution containing ^{14}C -primisulfuron at 0.048 $\mu\text{Ci/ml}$, 0.42 a.i. mg/ml. Solutions containing Silwet L-77, Silwet 408, Sylgard 309, Kinetic, Dyne-Amic, and X-77 at 0.25% (v/v), and Agri-Dex, MSO, and ROC at 1% (v/v) were prepared from the stock solution. The influence of adjuvants on ^{14}C uptake in velvetleaf was determined by applying ^{14}C -primisulfuron alone or with different adjuvants. Ten 1- μl drops of primisulfuron solution containing a total of 10,630 DPM were applied uniformly to the upper surface of the mature leaf nearest to the growing point. The plants were harvested 1, 2, and 24 h after application and were sectioned into the treated leaf, shoot above treated leaf, shoot below treated leaf, and roots. Unabsorbed ^{14}C -primisulfuron was removed by washing the treated leaf in 3 ml of pH 10 buffer in a scintillation vial. The ^{14}C in the wash solution was quantified by adding 15 ml of scintillation fluid and assayed using liquid scintillation spectrometry. All the harvested plant parts were oxidized to determine uptake and translocation. ^{14}C uptake into the plant was expressed as percent of applied total amount ^{14}C . The ^{14}C translocation from the treated leaf into the other parts of the plant was expressed as percent of uptake ^{14}C . Each treatment was replicated four times.

Efficacy.

Experiments were conducted in the greenhouse with natural sunlight as the only light source. Barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.], green foxtail [*Setaria viridis* (L.) Beauv.], redroot pigweed (*Amaranthus retroflexus* L.), and velvetleaf (*Abutilon theophrasti* Medikus) were seeded in 15-cm pots containing a commercial potting mix. Plants, which were fertilized as required with a 20-20-20 (N-P-K) fertilizer, were uniformly 10 to 13 cm tall at the time of treatment.

Primisulfuron at 20 and 40 g ai/ha with and without the adjuvants was applied to redroot pigweed and velvetleaf. Nicosulfuron at 17 and 35 g ai/ha was applied to barnyardgrass and green foxtail. Treatments were applied in 94 L/ha of water using a

CO₂-charged, continuous moving belt laboratory sprayer. The experimental design was a randomized block with five replications. Control ratings from 0 to 100% were made at 5-day intervals until most of the plants were killed and the fresh weights were taken. Two separate experiments were conducted. Since the same trends were shown in two separate experiments, only the data from the first experiment are presented.

Statistics.

Wettability, uptake, and efficacy.

Results of these tests were analyzed by Duncan's multiple comparison procedures with SAS Software (6.03 Edition).

Surface tension.

AsymSigR model for the log concentration versus surface tension was fitted to the data.

$$[\text{AsymSigR}] y = a + b(1 - (1 + \exp((x + \ln(2^{1/e} - 1)c)/d))^{-e})$$

where

x = log of adjuvant concentration,

a = maximum mean surface tension,

b = the difference between maximum surface tension and minimum surface tension,

c, d, e, = the factors to control the surface tension reducing speed as concentration increased,

y = mean surface tension.

RESULTS AND DISCUSSION

Surface tension.

Surface tension is defined as the energy required to create a new unit area of a new liquid-air surface, typically given in dyne/cm (6). Once spray droplets have been retained by foliage and reached equilibrium, surface tension forces of the drop solution will mainly control their degree of spreading, possible coalescence, and eventual coverage (7). Because surfactant molecules in the droplets will be strongly adsorbed at

the lipophilic leaf surface, thereby depleting the concentration at the liquid-air interface and increasing surface tension, the ultimate spreading behavior is therefore concentration-dependent, even when used at supermicellar concentrations (7). To understand the relationship between the surfactant concentration and surface tension for different adjuvants, an automated curve fitting software was used to process the data obtained from surface tension measurement with the dynamic contact angle analyzer for the best possible curve-fit equations (8). An AsymSigR relationship was found between the surfactant concentration and surface tension for all the adjuvants. The coefficient in all different models was larger than 0.99. Estimated parameters and the CMC (critical micelle concentration) for different adjuvants are shown in Table 2. Graphics describing the relationships of surface tension vs. concentrations for different adjuvant are shown in Figure 1 and 2.

Table 2. Estimated parameter and CMC for different adjuvants

Adjuvant	a	b	c	d	e	ST(min)	CMC (w/w)*
Silwet L-77	70.20	-49.06	-5.99	0.67	1.53e+14	21.14	1.5 x 10 ⁻³
Kinetic	71.15	-51.75	-5.12	1.39	3.30e+11	19.4	5.0 x 10 ⁻³
Dyne-Amic	70.85	-45.85	-5.24	1.22	28.07	25.0	1.0 x 10 ⁻²
Agri-Dex	70.21	-34.73	-3.80	0.013	0.02	35.5	4.0 x 10 ⁻²
Silwet 408	70.91	-49.94	-5.67	1.13	152.52	20.97	5.0 x 10 ⁻³
Sylgard 309	70.45	-49.67	-5.62	1.00	6.37e+09	20.78	2.5 x 10 ⁻³
MSO	70.21	-39.98	-4.85	0.19	0.27	30.37	4.0 x 10 ⁻²
ROC	70.28	-40.05	-4.747	1.07	9.83e+16	30.23	4.0 x 10 ⁻²
X-77	70.16	-42.29	-5.73	0.86	8.98e+16	27.87	7.9 x 10 ⁻³

* CMC: critical micelle concentration (w/w).

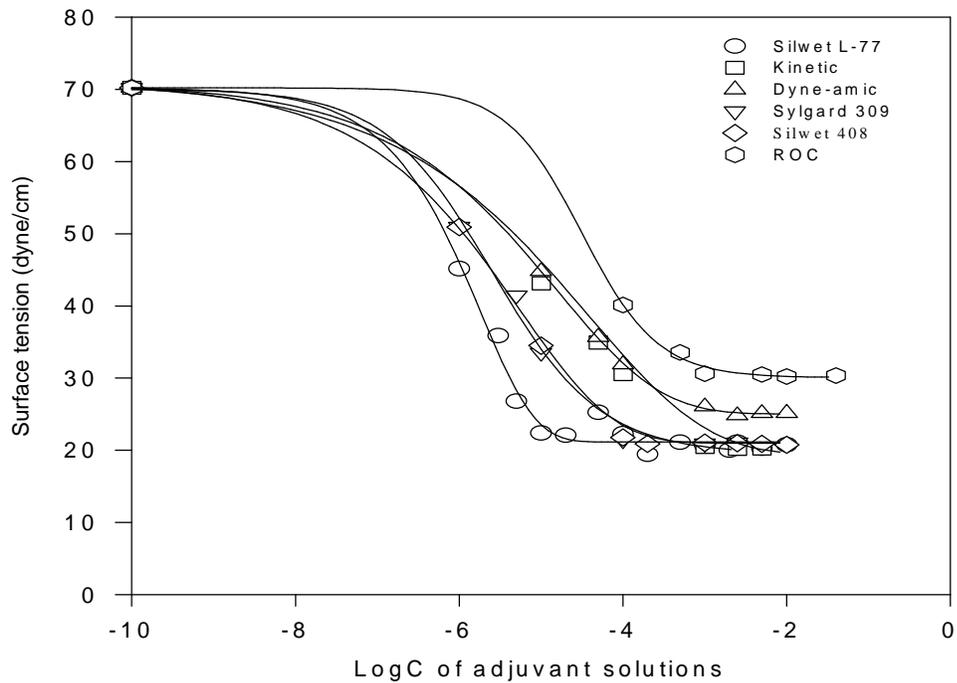


Figure 1. The relationship between surface tension and concentration for different adjuvants. Adjuvant concentrations originally prepared w/w (g/g) were transformed by log.

According to the models and Figure 1 and 2, the tested adjuvants were divided into two groups. The first group included Silwet L-77, Silwet 408, Sylgard 309, and Kinetic, which gave equilibrium surface tension values around 20 dyne/cm. These surfactants are unique in being able to cause spray liquids to spread completely over both wettable and water-repellent foliage if used at a sufficiently high concentration (1). The second group included Agri-Dex, MSO, ROC, X-77, and Dyne-Amic, which rarely reduced the surface tension of water below 28 dyne/cm, and were rarely effective spreaders on water-repellent targets.

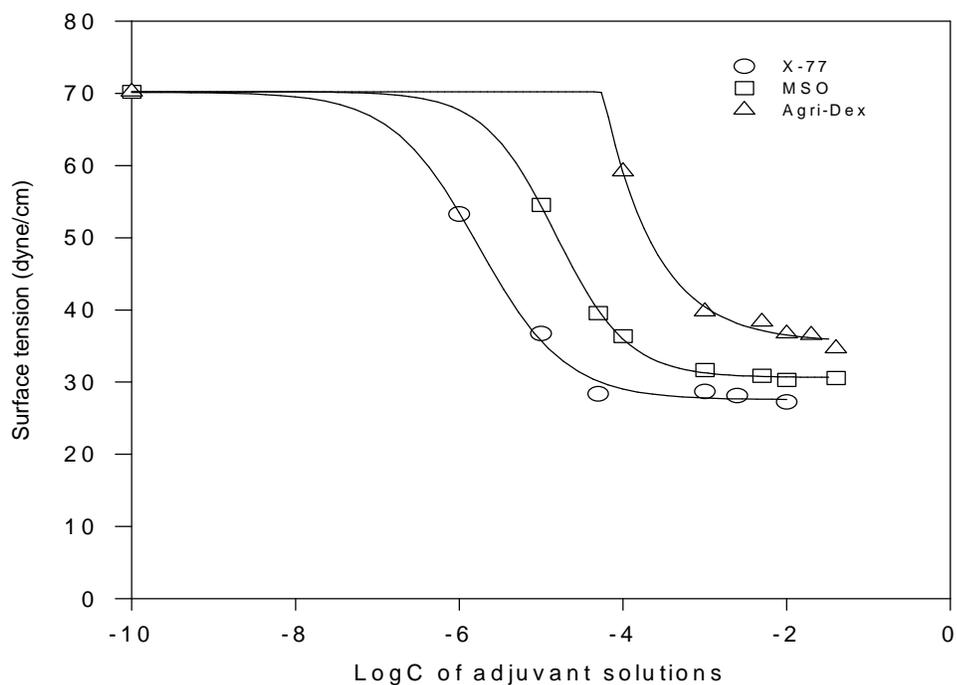


Figure 2. The relationship between surface tension and concentration for different adjuvants. Adjuvant concentrations originally prepared w/w (g/g) were transformed by log.

Wettability.

Spray droplets that hit the target can either adhere to it or bounce off. A spray droplet will be retained on the leaf surface if the adhesive force it experiences upon hitting the target is greater than the kinetic energy following the impact (2). Adjuvants that reduce the dynamic surface tension of the spray droplets, so improving the wetting of waxy leaf surfaces, are often used by mixing with the herbicide solution (3). Rapidly-absorbing adjuvant molecules may be expected to wet-out the surface microstructure of the target quickly and to spread better on the foliage of plants (7).

The spreading abilities of the tested adjuvants on the foliage of velvetleaf are shown in Figures 3 and 4. Several conclusions can be derived from the wettability

experiment. Regardless of drop volume, the spreading area of the organosilicones Silwet L-77, Silwet 408, and Sylgard 309 was always significantly higher than that of conventional adjuvants. However, there still were significantly different spreading abilities among organosilicones, which can be distinguished in the figures.

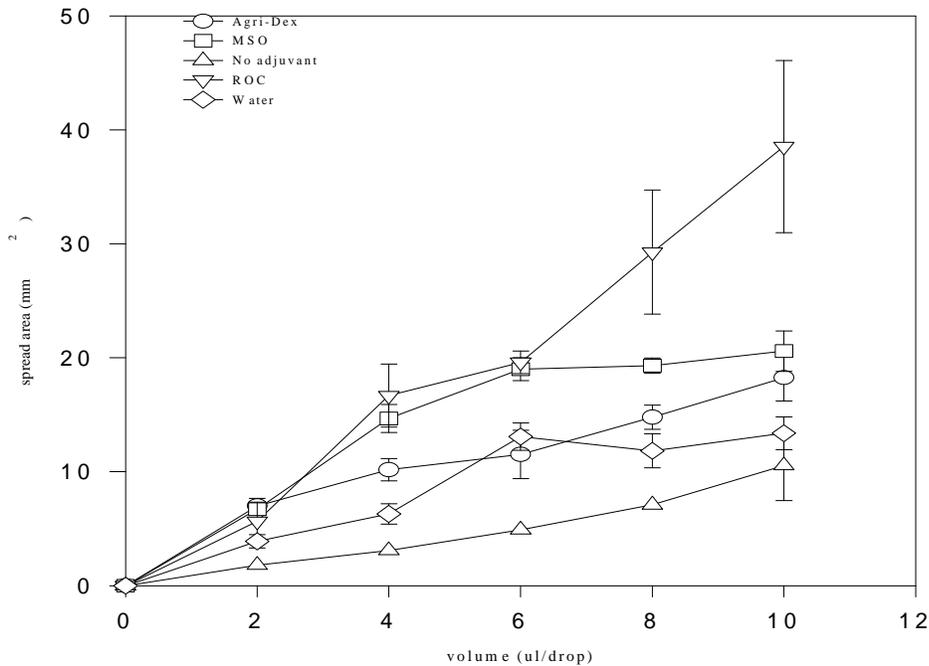


Figure 3. Wettability of different solutions on velvetleaf foliage. The vertical bars indicate the standard error of the means.

The spreading ability of Dyne-Amic, a blend of organosilicone with crop oil concentrate, was not significantly different from conventional adjuvants; however, the spreading area of Kinetic, a blend of organosilicone with nonionic surfactant, was always significantly larger than that of Dyne-Amic, except when the drop volume was 2 μ l. There was no significant difference in spreading area among conventional adjuvants, herbicide alone, and water alone. In addition, there was no effect on spreading area when conventional adjuvants were combined with herbicide, but the effect on spreading area was complicated when organosilicones were combined with

herbicide. When the drop volume was less than 8 μl , the herbicide tended to interfere with the spreading of organosilicone surfactants; the spreading area was significantly lower than (in most cases) or showed no effect compared to that of surfactants used alone. However, when the drop volume was equal to or above 8 μl , the spreading area of Silwet L-77 and Silwet 408 tended to be significantly increased by adding herbicide, and the spreading area of Sylgard 309 tended to be significantly decreased by adding herbicide.

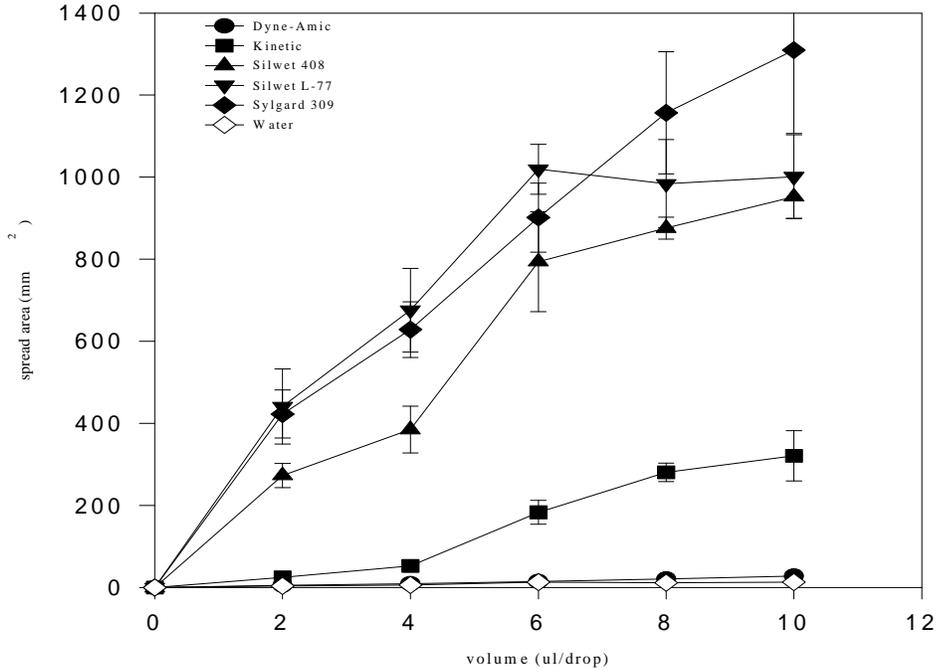


Figure 4. Wettability of different solutions on velvetleaf foliage. The vertical bars indicate the standard error of the means.

The spreading mechanism proposed for organosilicone by Ananthapadmanabhan *et al.* (1) suggests that the compact size of the hydrophobic portion of the trisiloxane allows it to transfer readily from the liquid/air interface of the advancing solution to a low energy surface, such as a waxy leaf cuticle. As a result, when organosilicone was included in the solution, the superior spreading and wetting was shown. However,

when the herbicide was added into the organosilicone surfactant solutions, the large, bulky hydrophobic group from the herbicide molecule or the surfactants added with herbicide during the formulation process, may tend to act as an obstacle for the advancing droplet, causing an interference with the spreading of the solution. This has been called the 'zipper' jam (9).

There were some differences between the two blends. Kinetic had a much lower minimum surface tension and CMC than did Dyne-Amic. In addition to differences on surface tension and wettability between Kinetic and Dyne-Amic, there were also some distinguishable differences in contact angle and spreading pattern between the two blends (Chapter 3). These results confirmed that carefully selecting the co-adjuvant for organosilicones is critical to avoid antagonism to trisiloxane and to retain its unique properties in blends (9, 10).

Uptake and translocation.

Herbicides will not begin to act until they have penetrated the target, which can be enhanced by adding adjuvants. Good leaf-wetting may increase penetration, because adjuvants may modify, and partly dissolve, the obstructing layers of wax, and cause swelling of the pathways and disruption of membranes (12). When ^{14}C -primisulfuron was combined with organosilicone or the blends of organosilicone with conventional adjuvants, the uptake of these treatments was significantly higher than that of treatments which were combined with conventional adjuvants, at 1 h after herbicide treatment (Table 3). Also, at 2 h after herbicide treatment, Silwet L-77, Silwet 408, and Dyne-Amic had significantly increased the uptake of primisulfuron more than did other adjuvants. It was reported that there was an additional site for potential enhancing action on both wettable and water-repellent targets before the spray droplets finally evaporate. The mechanism involves infiltration of the liquid containing the dissolved herbicide through stomatal pores if any are present on the adaxial surface of the leaf. The efficiency of this route of foliar entry is strongly influenced by stomatal status and organosilicone concentration (4, 15); when stomata are fully open and high

concentrations of surfactant are added (5 g/l), as much as 90% of a water-soluble herbicide may be taken up within 30 s of application to certain species, under laboratory conditions (15). Stomatal infiltration is immediate. When the active ingredient enters the plant tissue, stomatal infiltration is faster than cuticular penetration. Conventional adjuvants functioned by increasing cuticular penetration rather than stomatal infiltration. However, this is a relative slowly process comparing to the stomatal penetration. Research results have proved that the nonionic surfactants also can significantly increase the uptake of active ingredient , but the current research showed that the increase was relatively slower than with crop oil concentrate adjuvants.

Table 3. Effect of adjuvants on ¹⁴C-primisulfuron uptake in velvetleaf (% of application)

Treatment	Time after application		
	1 h	2 h	24 h
Silwet L-77	70.9 a	76.0 a	58.3 a
Silwet 408	59.4 a	74.8 a	40.3 ab
Kinetic	66.4 a	47.6 b	35.6 bc
MSO	49.1 b	41.8 b	48.6 ab
ROC	19.8c	-	19.9 cd
Agri-Dex	28.3 c	7.5 c	22.5 cd
Dyne-Amic	66.1 a	68.7 a	24.7 cd
X-77	23.4 c	12.6 c	14.4 d
Sylgard 309	69.2 a	54.3 b	44.3 ab
Check	14.4 c	11.4 c	14.0 d

When primisulfuron uptake was increased by adjuvants, the relative amount of translocation for the total uptake herbicide from treated leaf to other parts of the plant was not increased at the same time compared with herbicide used alone (data not shown). It may be suggested that when translocation was expressed as percent of uptake, the proportion of translocation to total uptake was in a certain range and not easily changed even when greater uptake occurred, at least for primisulfuron and velvetleaf. The high concentration of toxic chemical which accumulated in the treated leaf may have damaged the living cells. As a result, total translocation from the treated leaf was not significantly increased.

Efficacy.

Adjuvants are important constituents of herbicide application. When adjuvants are applied with herbicides, the efficacy of the formulation could be improved. It has been suggested that they function primarily by altering solubility relationships and therefore affect the entry of a herbicide into the plants (13). However, many research results show that the effect of adjuvants are herbicide, weed species, and even environment specific.

Table 4. Efficacy of different treatments on fresh weight (g) in four weed species (25 DAT)

Treatment	Barnyardgrass	Green foxtail	Pigweed	Velvetleaf
Check	35.38 a	36.75 a	18.16 a	25.88 a
Herbicide alone	26.90 b	2.75 bc	4.89 b	2.25 b
ROC	0.13 c	3.75 bc	3.79 b	0.76 c
Agri-Dex	0.79 c	0.00 c	1.74 b	0.86 c
MSO	0.04 c	0.25 c	1.76 b	0.25 c
Dyne-Amic	0.18 c	6.25 b	2.53 b	1.06 c
Kinetic	0.08 c	3.00 bc	4.44 b	1.35 c

Silwet L-77	0.18 c	8.25 b	4.44 b	0.81 c
Silwet 408	0.14 c	2.75 bc	2.51 b	0.98 c
Sylgard 309	0.08 c	4.50 bc	1.96 b	1.00 c

In this research, all the herbicide treatments, with or without tested adjuvants, significantly reduced the fresh weight on all four weed species compared to nontreated control (Table 4.). Since nicosulfuron and primisulfuron already showed excellent control on green foxtail or redroot pigweed respectively, the advantages of adjuvants were not readily apparent. However, with barnyardgrass, which is difficult to control by nicosulfuron alone, all the adjuvants significantly increased the efficacy of this herbicide and gave excellent control.

There was a significant difference between primisulfuron alone and with adjuvants; According to fresh weight measurement, even primisulfuron alone controlled velvetleaf acceptably. However, the growth points of the plants were not completely dead, and there was a possibility for regrowth. On the other hand, the treatments with adjuvants killed all growth points.

CONCLUSIONS

An AsymsigR relationship was found between the surfactant concentration and surface tension for all the adjuvants. According to the surface tension and wettability measurement, the tested adjuvants were divided into two groups, organosilicone group included Silwet L-77, Silwet 408, Sylgard 309, and Kinetic, which gave equilibrium surface tension value around 20 dyne/cm and showed great spreading ability on the foliage of velvetleaf. Second, the conventional adjuvants group, which included Agri-Dex, MSO, ROC, X-77, and Dyne-Amic, which surface tension was rarely below 28 dyne/cm and showed a very limited spreading ability on the foliage of velvetleaf. When ¹⁴C- primisulfuron was combined with organosilicone or the blends of organosilicone with conventional adjuvants, the uptake of ¹⁴C- was significantly higher

than with treatments which were combined with conventional adjuvants, at 1 or 2 h after herbicide application. The herbicidal efficacy of nicosulfuron and primisulfuron was significantly increased by adjuvants when tested for control of marginally susceptible weed species.

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SUMMARY AND CONCLUSIONS

Adjuvants are defined by Weed Science Society of America as any substance in a herbicide formulation or added to the spray tank to improve herbicidal activity or application characteristics (Hodgson, 1982). It has long been recognized, in a general way, that surfactants may facilitate and accentuate the emulsifying, dispersing, spreading, wetting, solubilizing, and/or bring about enhancement of foliar penetration and herbicidal action (Foy, 1989). In 1992, of the 485 pesticide formulations, 49% were recommended to be used with adjuvants, including 71% of all herbicide formulations (Foy, 1993).

Recently, organosilicone adjuvants have become widely used with different agrichemicals, especially with herbicides, and attracted much attention because of their unique physical-chemical properties (Knoche, 1994; Stevens, 1993). The current project was focused on the enhancement mechanisms of organosilicone compounds on sulfonylurea herbicide activity as compared to conventional adjuvants. Several research objectives were established for this study.

1. Examine and compare physical-chemical properties between organosilicones and conventional adjuvants (referred to as non-silicone adjuvants in this study). These physical-chemical properties included: static surface tension, dynamic surface tension, contact angle on both leaf surface and parafilm, wettability, and spreading pattern on leaf surface.
2. Investigate the similarity and differences of several structurally related organosilicones.
3. Analyze the effect of organosilicones on herbicide uptake and translocation with radiolabelled herbicide.
4. Study the effect of organosilicones on herbicide rainfastness.
5. Explore the effect of organosilicones on herbicide efficacy.

Two sulfonylurea herbicides, primisulfuron and nicosulfuron, and four weed species, barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.], green foxtail [*Setaria viridis* (L.) Beauv.], redroot pigweed (*Amaranthus retroflexus* L.), and velvetleaf (*Abutilon theophrasti* Medikus), were included in the study. The tested adjuvants included three pure organosilicones, Silwet L-77, Silwet 408, and Sylgard 309; two blends of an organosilicone with conventional adjuvants, Kinetic and Dyne-Amic; four conventional adjuvants, Agri-Dex, Rigo oil concentrate, methylated soybean oil, and X-77.

Physico-chemical properties

Static surface tension is the energy required to create a new unit area of a new liquid-air surface, typically given in dyne/cm (Hermansky and Krause, 1995). Contact angle is the angle formed between the baseline of the drop and the tangent at the drop boundary. These two terms are very important concepts in the adjuvants field. Surface tension is solely determined by the physical-chemical properties of adjuvants; however, contact angle reflects the interaction between droplet and target surface. At adjuvant practical use rates in agriculture, the lower the surface tension, the lower is the contact angle expected on target surfaces.

The static surface tension over a wide range of adjuvant concentrations was measured by a Cahn Dynamic Contact Angle Analyzer with DCA software. The principle of this equipment is based on the Wilhelmy plate technique, which is a universal method for measuring static surface tension. In this method, a vertical platinum plate of known perimeter is attached to a balance, and the force due to wetting is measured when the plate is inserted into the test solution (Anonymous, 1992). A goniometer which measures an optical contact angle between a liquid droplet and a solid surface, was used to investigate the contact angle on parafilm. To better understand the relationship between the static surface tension or contact angle and adjuvant concentration, an automated curve fitting software Table curve 2 D (Anonymous, 1994) was used to process the data obtained for the best possible fitting model. AsymsigR (Anonymous, 1994) relationship was found between static surface

tension and adjuvant log concentration; and a typical logistic relationship (Anonymous, 1994) was found between contact angle and adjuvant concentration on the surface of the parafilm. The regression coefficient in all adjuvant models was larger than 0.99. These results indicated that the static surface tension and contact angle were highly concentration dependent and there was a narrow concentration range in which a slight change in adjuvant concentration could cause a sharp alteration in both static surface tension and contact angle. However, when the adjuvant concentration reaches a certain point, the static surface tension will result in the minimum value. The effect of adjuvant concentration on contact angle was the same as that on static surface tension. However, since surface absorption of surfactant molecules would occur, even for the same adjuvant, the concentration value required to reach equilibrium for both static surface tension and contact angle could be quite different. Compared to conventional adjuvants which required about 2500 ppm to reach the minimum contact angle on the parafilm, the concentration for organosilicones was about 500 ppm.

Dynamic surface tension is defined as the change in surface tension at a new interface with time (Anderson *et al.*, 1983). Surface tension is reduced by adsorption of surfactant molecules at air/water or water/solid interfaces. During the dynamic processes of drop spraying and wetting, the surfactant molecules in the spray solution need time to diffuse and orient at the interface. The time required for different adjuvants is different (Anderson *et al.*, 1983). A SensaDyne 6000 surface tensiometer with SensaDyne 6000 software was used to measure dynamic surface tension of different liquids. This equipment is based on a refinement of the maximum bubble pressure method which measures surface tension within the body of a test fluid by blowing a bubble of gas inside the fluid body and measuring the maximum bubble pressure of this bubble.. An inert process gas (nitrogen or dry air) is bubbled slowly through two probes of different radii that are immersed in a test fluid. The bubbling of the nitrogen through the probes produces a differential pressure signal which is directly

related to the fluid surface tension. The differential pressure at certain bubble rate transducer outputs a “sawtooth” voltage waveform signal that is peak detected, filtered, and amplified, then scaled and offset by the computer program in relation to a previously determined calibration curve. The final output is displayed in dynes/cm on the computer video monitor screen. Concurrently, a temperature probe monitors the fluid temperature and this is also output on the computer screen in degrees Centigrade, along with bubble frequency information (Anonymous, 1990).

The results showed that Silwet L-77, Silwet 408, Sylgard 309, and Kinetic were fastest in reducing surface tension on the newly formed surfaces among the test adjuvants. It has been reported that fast dynamic surface tension lowering of spray droplets leads to improve droplet retention on leaf surface (Anderson and Hall, 1985). One reason is that the droplet size is related to dynamic surface tension during the spray process. The reduction of dynamic surface tension will increase retention because of the lower impacting energy of the smaller droplets. Improved droplet retention can, in turn, improve the efficacy of the formulation by bringing more of the active material in intimate contact with the target.

Generally, if the solution has the lower static surface tension and contact angle on the leaf surface, better spreading and wetting are expected. However, the properties of the target surface are also an important factor during the wetting process. In measuring the adjuvant effect on wettability, regardless of drop volume, the spreading area of the organosilicones was always significantly higher than that of conventional adjuvants on parafilm. Under UV light, the droplets containing the solutions of Silwet L-77, Silwet 408, Sylgard 309, and Kinetic showed complete distribution patterns. However, the droplets containing the solutions of Agri-Dex, Rigo oil concentrate, methylated soybean oil, and Dyne-Amic exhibited clear drop patterns.

Comparing the two blends, Kinetic is a blend of an organosilicone with a nonionic surfactant; its properties were more like pure organosilicones. Kinetic solution had 20.1 dyne/cm static surface tension and zero contact angle on the both parafilm and

leaf surface at 0.25% (w/w) and showed complete wetting on the leaf surface under UV light; but the spreading area was significantly smaller than that of pure organosilicones. In measuring dynamic surface tension, Kinetic solution reduced the surface tension as fast as pure organosilicone in the newly formed surface. Dyne-Amic is a blend of an oil concentrate with an organosilicone; unlike Kinetic, it had properties more like the conventional adjuvants. Dyne-Amic solution had about 25 dyne/cm static surface tension and 56.2° contact angle on the leaf surface at 0.25% (w/w). Under UV light, Dyne-Amic showed a clear drop distribution pattern which was similar to that of conventional adjuvants. Dyne-Amic was much slower than Kinetic in reducing dynamic surface tension on the newly formed surface. These results did confirm that carefully selecting the co-adjuvant for organosilicone was very important to avoid 'jamming of the molecular zipper' which causes competition between organosilicone and conventional surfactant monomers for the interface (Murphy *et al.*, 1991; Policello *et al.*, 1991). Otherwise, the organosilicone surfactants properties of superior wetting, spreading, and inducing stomatal infiltration would be lost.

Effect of organosilicones on herbicide uptake, rainfastness, and efficacy

Herbicides will not begin to act until they have penetrated the target, which can be enhanced by appropriate adjuvants. Good leaf-wetting may increase penetration, because adjuvants may modify, and partly dissolve, the obstructing layers of wax, and cause swelling of the pathways and disruption of membranes (Seaman, 1982). When ^{14}C - primisulfuron was combined with organosilicone or the blends of organosilicones with conventional adjuvants, ^{14}C uptake was significantly higher than when combined with conventional adjuvants at 1 or 2 h after herbicide treatment. However, as the time interval increased to 24 h after herbicide application, the difference in herbicide uptake between organosilicones and conventional adjuvants decreased.

In addition to cuticular penetration, it was reported that there was an additional site for potential enhancement of action on both wettable and water-repellent targets before the spray droplets finally evaporate (Knoche, 1994; Stevens, 1993). The mechanism

involves infiltration of the liquid containing the dissolved herbicide through stomatal pores, if any stomata are present on the adaxial surface of the leaf and the static surface tension of spray solution is equal to or less than the critical surface tension of the leaf surface, which ranges from 20 to 30 dyne/cm. Since the surface tension of organosilicone solutions is always below this range, stomatal infiltration may be expected to occur (Knoche, 1994; Stevens *et al.*, 1991). The solution that enters into the substomatal cavity by stomatal infiltration provides easier diffusion of the active ingredient into the adjacent cells. In addition, stomatal infiltration is immediate. As a result, herbicide rainfastness is expected to be improved. In the current study, organosilicone surfactants greatly increased the rainfastness of primisulfuron on velvetleaf. The effect was immediate and dramatic, even when simulated rainfall was applied 15 min after herbicide treatment. As the time interval between treatment and simulated rainfall was increased, the differences between organosilicone surfactants and conventional adjuvants decreased.

In the greenhouse efficacy study, there was no significant difference among the adjuvants. It confirmed the result of uptake with radiolabelled herbicide which did not show any significant difference between organosilicones and conventional adjuvants 24 h after herbicide applications. In the efficacy study, all the herbicide treatments, with or without tested adjuvants significantly reduced the fresh weight on all four treated weed species compared with nontreated control. Since nicosulfuron and primisulfuron already showed excellent control on green foxtail or redroot pigweed, respectively, the advantages of using adjuvants were not apparent. However, barnyardgrass was difficult to control by nicosulfuron alone, and all the adjuvants significantly increased the efficacy of this herbicide on barnyardgrass. All treatments gave excellent control, but no significant difference was found among the adjuvants. This result showed that when the herbicide was tested with adjuvants to control marginally susceptible weed species, herbicide efficacy was significantly increased.

Structurally-related organosilicone surfactants

Four structurally related organosilicone surfactants were evaluated. These surfactants were based on a trisiloxane containing a polyether with approximately 7.5 EO (ethylene oxide). All of these materials were prepared from the same batch of polyether and trisiloxane intermediates. The tested end groups in the hydrophobic part of the organosilicone were methyl, hydrogen, ethyl, and propyl, respectively. On the basis of the present studies, it appears that the end group on the hydrophilic portion of trisiloxane surfactants has little or no effect on surfactant physical-chemical properties, including static surface tension, contact angle, and spread pattern, nor on uptake and translocation, and efficacy of primisulfuron. Small observed differences did not change the behavior of the organosilicones when they were used as adjuvants with primisulfuron on velvetleaf. It may be suggested that there is no need for a strict requirement to purify the end group during the synthesis process, which is time consuming and expensive.

In conclusion, organosilicone surfactants showed extremely low static surface tension, complete wetting ability on both parafilm and leaf surface, fast reducing dynamic surface tension. In biological studies, organosilicones increased the short-term herbicide uptake; as a result, rainfastness of the herbicide was greatly improved. However, a very complicated relationship exists between herbicides and adjuvants. The enhancement effects of adjuvants are often herbicide specific, weed species specific, and even environment specific. No one type of adjuvant functions well in all circumstances. Therefore, there is a need to understand the properties and functions of each class of adjuvants and locate the 'right' niche for each individual adjuvant.

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APPENDIX

Table 1. Effect of adjuvants on translocation of ¹⁴C-primisulfuron from treated leaf in velvetleaf at different times postapplication after application (% of uptake).

Treatments	Time after application		
	1 h	2 h	24 h
Primisulfuron	37.0 a	9.5 b	36.2 a
Silwet L-77	8.8 b	15.6 b	16.5 a
Silwet 408	38.2 a	43.8 a	11.6 a
Sylgard 309	15.1 b	8.1 b	10.42 a
Kinetic	21.7 ab	10.4 b	18.3 a
Dyne-Amic	4.1 b	11.2 b	14.3 a
MSO	10.9 b	16.3 b	5.92 a
ROC	16.7 b-	32.6	40.55 a
X-77	18.1 ab	41.1 a	38.47 a
Agri-Dex	14.6 b	9.5 b	26.1 a

Note: Means within a column followed by the same letters are not significantly different at $p = 0.05$ level according to Duncan's multiple range test.

Table 2. Effect of adjuvants on uptake of ¹⁴C-primisulfuron into the treated leaf in velvetleaf at different times postapplication after application (% of uptake).

Treatments	Time after application		
	1 h	2 h	24 h
Primisulfuron	63.0 b	90.5 a	63.9 a
Silwet L-77	85.9 ab	77.4ab	72.9 a
Silwet 408	61.8 b	56.3 b	88.4 a
Sylgard 309	84.9 ab	91.9 a	89.6 a
Kinetic	66.3 b	85.9 ab	66.8 a
Dyne-Amic	94.3 a	86.5 ab	75.0 a
MSO	89.1 a	83.7 ab	94.1 a
ROC	60.7 b	66.3 b	59.5 a
X-77	81.9 ab	58.9 b	61.5 a
Agri-Dex	85.4 ab	82.7 ab	73.9 a

Note: Means within a column followed by the same letters are not significantly different at p = 0.05 level according to Duncan's multiple range test.

Table 3. Effect of adjuvants on translocation of ¹⁴C-primisulfuron into shoot above treated leaf in velvetleaf at different times after application (% of uptake).

Treatments	Time after application		
	1 h	2 h	24 h
Primisulfuron	12.0 a	0.2 b	3.7 b
Silwet L-77	1.1 a	6.3 ab	5.1 b
Silwet 408	6.0 a	16.3 a	0.5 b
Sylgard 309	7.6 a	1.7 ab	4.7 b
Kinetic	7.4 a	0.4 b	2.1 b
Dyne-Amic	0.4 a	4.9 ab	1.2 b
MSO	6.1 a	11.1 ab	1.8 b
ROC	2.3 a	0.1 b	25.8 a
X-77	2.0 a	24.1 a	2.1 a
Agri-Dex	4.6 a	0.1 b	7.8 b

Note: Means within a column followed by the same letters are not significantly different at p = 0.05 level according to Duncan's multiple range test.

Table 4. Effect of adjuvants on translocation of ¹⁴C-primisulfuron into shoot below treated leaf in velvetleaf at different times after application (% of uptake).

Treatments	Time after application		
	1 h	2 h	24 h
Primisulfuron	22.9 a	7.2 a	29.0 ab
Silwet L-77	5.3 ab	7.1 a	10.6 ab
Silwet 408	12.9 ab	17.8 a	9.4 ab
Sylgard 309	5.3 ab	3.0 a	3.0 b
Kinetic	12.0 ab	3.7 a	15.0 ab
Dyne-Amic	2.0 b	2.4 a	10.6 ab
MSO	3.0 ab	3.1 a	4.1 ab
ROC	3.8 ab	13.5 a	11.3 ab
X-77	13.3 ab	13.2 a	34.4 a
Agri-Dex	6.0 ab	7.8 a	13.1 ab

Note: Means within a column followed by the same letters are not significantly different at $p = 0.05$ level according to Duncan's multiple range test.

Table 5. Effect of adjuvants on translocation of ¹⁴C-primisulfuron into root in velvetleaf at different times after application (% of uptake).

Treatments	Time after application		
	1 h	2 h	24 h
Primisulfuron	2.0 a	2.1 a	3.2 a
Silwet L-77	2.3 a	2.2 a	0.8 a
Silwet 408	1.9 a	9.6 a	4.5 a
Sylgard 309	2.2 a	3.5 a	2.7 a
Kinetic	2.2 a	6.4 a	1.2 a
Dyne-Amic	2.2 a	5.5 a	2.6 a
MSO	1.8 a	2.1 a	0.0 a
ROC	7.0 a	4.1 a	1.6 a
X-77	2.9 a	3.8 a	1.9 a
Agri-Dex	4.0 a	1.5 a	5.1 a

Note: Means within a column followed by the same letters are not significantly different at p = 0.05 level according to Duncan's multiple range test.

VITAE

Jinxia Sun, daughter of Changlin Sun and Xiulin Guo, was born, on April, 15, 1965 in the beautiful middle sized city, Louyang, which served as the capital for nine dynasties in the history of China. She graduated from high school at Louyang Number 3 middle school in 1981. After that, she went straight to Shenyang, which is located in the northeast of China, and lived in this city for twelve years. She earned her B.S. degree in Plant Protection in July, 1985 at Shenyang Agricultural University, and continued her graduate study at the same university. She received her M.S. degree in Weed Science in June, 1988, and then served as an instructor and researcher in the Plant Protection Department at this university for another four years. At the end of this time, she decided to pursue her Ph. D. She came to America in July, 1992 and began to study at Virginia Polytechnic Institute and State University.

Currently she is a member of the Northeastern Weed Science Society, Southern Weed Science Society, and Weed Science Society of America. She also is a member of the honor societies of Phi Kappa Phi, Gamma Sigma Delta, and an associate member of the honor society Sigma Xi. She received the Arthur J. Webber 'Outstanding Graduate Student' award in the Department of Plant Pathology, Physiology, and Weed Science at Virginia Polytechnic Institute and State University in 1995.