NEW FORMULATION TECHNOLOGY - SILWET® ORGANOSILICONE SURFACTANTS HAVE PHYSICAL AND PHYSIOLOGICAL PROPERTIES WHICH ENHANCE THE PERFORMANCE OF SPRAYS

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Summary. Solutions containing Silwet organosilicone surfactants have exceptionally low surface tensions. This assists the retention of spray droplets on leaf surfaces and markedly increases their coverage. A substantial quantity of spray solution can infiltrate the stomata of the target foliage, making the a.i. rainfast and reducing other weathering processes. Rapid uptake of formulants can cause contact phytotoxicity, limiting translocation of the a.i. However, Silwets are less phytotoxic than most surfactants and have been shown to increase the systemic activity of some herbicides. The properties and behaviour of Silwets are reviewed and presented in comparison with "conventional" surfactants to show why they enhance spray performance.

INTRODUCTION

The potential value of organosilicone surfactants as adjuvants for herbicides was first reported in 1973 (11). Recently, Silwet L-77 (Union Carbide) has been introduced as a commercial spray adjuvant (Pulse; Monsanto) in Australia, New Zealand and SE Asia and has already gained label recommendations for use with the herbicides Roundup (glyphosate; Monsanto) and Escort (Ally, Brushoff: metsulfuron-methyl; Du Pont). Only in the last few years has a substantial scientific database relating to the use of L-77 and other Silwets in agriculture been published. In many respects, the behaviour of these adjuvants is markedly different from that of "conventional" (non-organosilicone) surfactants, thus providing new technology for the formulation of sprays. The physical and physiological properties of Silwets are reviewed here, in combination with some previously unreported data, to illustrate how these surfactants can be used to enhance the performance of sprays.

METHODS

Surfactants. Silwets L-77 (Pulse, Silwet M) and L-7607 (polyalkyloxylated dimethylpolysiloxane; Union Carbide)
Agral 90 (nonlyphenoxypolyethoxyethanol mean EO 9 with 10% propan-2-ol; ICI)
Triton X-45 (octylphenoxypolyethoxyethanol mean EO 4.5; Rohm and Haas).

Calcium in apples. Three applications of calcium nitrate (6 g/L) followed by 8 applications of calcium chloride (3.6 g/L) were made to apple trees (*Malus pumila* cv. Cox's orange pippin) during the course of the growing season. Spray volumes were 2000 L/ha without and with Pulse (0.05% and 0.1%) and 1000 L/ha with Pulse (0.1%), the latter incorporating doubled concentrations of calcium nitrate or calcium chloride as appropriate. At harvest 2 fruit from each of 10 trees (4 replicates) within each treatment were picked, bulked and analysed for calcium by the NZ Apple and Pear Marketing Board.

Hygroscopicity of surfactants. Surfactants (*c.* 100 mg) were weighed (± 0.1 mg) into petri dishes (5 replicates) and held in desiccators at varying humidities provided by saturated aqueous solutions of salts at 20°C (20). The dishes were removed and reweighed at intervals until constant weight was achieved. Hygroscopicity was calculated as percent weight of water gained.

Spreading and drying of aqueous surfactants. Five droplets (1 µl) of aqueous surfactant, incorporating Blankophor P (1% w/v; Bayer), were applied to each of 2 microscope slides coated with gorse (*Ulex europaeus*) wax (40 µg cm^{-2}). The weight (± 0.1 mg = 1% of total weight of droplets) of the slides (5 replicates) was recorded at 1.5s intervals by interfacing an electronic balance with a micro-computer. Measurements were conducted in a controlled environment facility (19° to 20°C; 60% to 75% relative humidity). Evaporation rates were determined by linear regression of weight versus time. Spread areas of the dried deposits were determined by image analysis under u.v. illumination.

Statistical analyses. Comparisons between treatments were made by analysis of variance in combination with least significant differences tests. Hygroscopicity data required a log transformation, while spreading and drying data required square root transformations for variance stabilisation prior to analysis.

RESULTS AND DISCUSSION

The aqueous surface tension of sprays incorporating conventional surfactants is typically around 30 mN/m or higher. In contrast, addition of Silwets L-77 and L-7607 to water produces aqueous surface tensions in the low 20's (19). These greater reductions in surface tension assist the retention of spray droplets on the hydrophobic surfaces of foliage; 0.25% Silwet M (Silwet L-77) provided equivalent retention of a Roundup spray on bracken to that provided by 0.5% Triton X-45 (15). The effects of Silwets and other surfactants on spray retention are currently being investigated in detail at the Forest Research Institute.

The wetting and spreading characteristics of aqueous Silwets are exemplary, exceeding even those of fluorocarbon surfactants with lower surface tensions (9). Silwet L-7607, and particularly Silwet L-77, provided lower contact angles and greater spreading of droplets on bean, citrus and eucalypt leaves than did either Agral 90 or Triton X-45 (21). The spreading provided by Silwet L-77 has been employed to improve the coverage of low-volume CDA sprays (12) but can be detrimental to high-volume sprays as a result of runoff. The addition of Silwet L-77 at 0.1% to sprays applying calcium to apple trees in a volume of 2000 L/ha had no effect on the concentration of this mineral in the fruit at harvest (Table 1). That this lack of effect was attributable to runoff of spray is demonstrated by the increased calcium when either the concentration of Silwet L-77 or the spray volume was halved.

Table 1. Effect of Pulse (Silwet L-77) concentration and spray volume on calcium concentration in apple fruit tissue at harvest.

Pulse (% v/v)	Volume (L/ha)	Calcium (mg/100 g fresh wt.)
0	2000	2.20
0.1	2000	2.19
0.05	2000	2.41
0.1	1000	2.38
l.s.d. (p = 0.05)		0.21

The very low surface tension produced by Silwet L-77 enables spray solutions to infiltrate the stomata of the target foliage (13). The a.i. taken up in this manner is immediately made rainfast, reducing the critical rainfall period (5). Additionally, volatilisation and photodegradation, which contribute to the weathering of pesticide deposits on the exterior foliage, are attentuated. The contribution of Silwet L-77 induced stomatal infiltration can be substantial and levels of uptake of 50% into bean, 35% into oat and 20% into wheat have been observed within ten minutes of application (18). Although Silwets provide excellent wetting and spreading at concentrations of 0.05% and less (21), the infiltration of stomata seems to require higher concentrations (*c.* 0.2%), particularly because the formulants of some pesticide antagonise the effects of Silwets (18).

The a.i. which is not introduced into the leaf interior via stomata must penetrate the cuticle covering the foliar surfaces. Although there is little evidence that surfactants increase the rate of cuticular penetration *per se*, Silwets can increase the proportion of a.i. ultimately taken up via this pathway (18). This is probably associated with the hygroscopicity of Silwets which, at high humidity, results in the retention of more moisture within visibly dried spray deposits than when conventional surfactants are used (Table 2). Hygroscopic water retention has been correlated with the enhancement of foliar uptake by surfactants (17). Uptake is thus likely to be increased by Silwets in humid conditions, as are prevalent in the tropics and often elsewhere early in the morning and in the evening. Foliage which has received sprays incorporating Silwet L-77 has been observed to be readily rewetted several days post-application (unpublished). The rewetting of spray deposits can considerably increase the uptake of a.i. (2).

Table 2. Hygroscopic water retention of Silwet and conventional surfactants at various humidities.

	Relative humidity (%)					
	66	79.5	84	90	95	100
	% weight of water					
Silwet L-7607	3.0	8.4	10	23	100	190
Silwet L-77	6.1	5.9	7.3	19	91	180
Agral 90	1.6	4.4	6.4	15	54	73
Triton X-45	4.9	8.9	10	13	48	58

l.s.d. ($p = 0.05$) Log (%) ±0.06

The extensive spreading of Silwets may be of some detriment to uptake because of the increased rate of drying of spray (Table 3). The rate of non-stomatal uptake of pesticides into foliage can be 100 to 1000 fold faster from wet than from dry deposits (16). There is evidence that rapid drying contributes to the antagonism of Silwet L-77 to glyphosate uptake in certain grasses (6). It is possible this may be exploited in the future as a basis for selectivity.

Significant quantities of surfactant, as well as a.i., enter foliage either by cuticular penetration (17) or particularly by stomatal infiltration (18). The phytotoxicity of surfactants is well established (14) and may restrict translocation of the a.i. Silwets have been shown to be less phytotoxic than conventional surfactants (4). Thus, the translocation of a model a.i. was increased by L-77 because stomatal infiltration deposited the a.i. within the leaf in close proximity to the vascular tissues (18). Deleterious effects on translocation appear to be attributable to the phytotoxic effects of pesticide formulants, which are manifest when their uptake is enhanced by adjuvants (7). Foliage age, and thus "hardiness", is also a factor in this interaction (8). When used at sufficient concentration to promote stomatal infiltration, Silwet L-77 may be of benefit with systemic but not with contact herbicides because the advantage of increased uptake of the latter is offset by localised scorch (12).

Table 3. Spreading and rate of evaporation of droplets of aqueous Silwet and conventional surfactants on a plant wax surface.

% w/v	Agral 90	Triton X-45	Silwet L-7607	Silwet L-77
	Spread area (mm^2)			
0.05	ND	ND	ND	14
0.1	ND	ND	4.7	30
0.2	3.4	4.1	4.6	56
0.5	3.2	4.0	6.1	104
	l.s.d. ($p = 0.05$) $\sqrt{\text{mm}^2} \pm 0.06$			
	Evaporation rate (% of initial weight/min.)			
0.05	ND	ND	ND	7.9
0.1	ND	ND	5.4	14
0.2	4.8	4.1	5.4	21
0.5	4.7	3.8	5.9	27
	l.s.d. ($p = 0.05$) $\sqrt{\%} \pm 0.35$			

ND not determined

In summary, it is apparent that the physical properties of Silwet surfactants enable greater retention and coverage of sprays on foliage. Uptake of a.i. into the plant is also increased and a substantial proportion of the pesticide can be rendered rainfast almost immediately by infiltration of stomatal pores. Silwets are physiologically relatively benign and thus may enhance the translocation, and hence systemic activity, of pesticides. These effects have already been recognised as benefiting various herbicides for control of the scrubweeds gorse (22), bracken (15) and pampas grass (7) as well as weeds of cereal crops (12) and for overcoming seasonal herbicide tolerance in perennial ryegrass (3). The value of Silwets as adjuvants is not restricted to herbicides but has also been exploited with insecticidal (1), growth regulatory (10) and nutritional (13) sprays.

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