HILGARDIA

A JOURNAL OF AGRICULTURAL SCIENCE PUBLISHED BY
THE CALIFORNIA AGRICULTURAL EXPERIMENT STATION

Volume 39, Number 3 • May, 1968

Effect of Artificial Leaf Coatings on Foliar Chloride Uptake During Sprinkler Irrigation

C. V. Malcolm, L. H. Stolzy, and C. R. Jensen

UNIVERSITY OF CALIFORNIA DIVISION OF AGRICULTURAL SCIENCES

Silicone and latex coatings applied to leaves have been used by other workers for the purpose of reducing transpiration of plants. The use of similar leaf coatings was studied by the authors for the purpose of reducing foliar chloride uptake from brackish water used for sprinkler irrigation. Significant reductions in foliar chloride uptake during sprinkling with NaCl solution were obtained by coating citrus leaves with acrylic polymer latex. The use of silicones to reduce foliar chloride uptake was not successful.

Filters having a maximum pore size of 0.20 microns were impregnated with a range of concentrations of latex material. The diffusion resistance of these impregnated filters to CO_2, O_2, and water vapors was studied. Concentrations of the impregnating emulsion increasing from 10 to 25 per cent caused a relatively small increase in diffusion resistance for CO_2 and O_2, but the use of 50 and 75 per cent emulsions caused a marked increase in diffusion resistance of the filter to these two gases.

THE AUTHORS:

C. V. Malcolm was André Mayer Research Fellow, Soils and Plant Nutrition, University of California, Riverside, and is Research Officer in the West Australian Department of Agriculture, Perth; L. H. Stolzy is Professor of Soil Physics, Riverside; C. R. Jensen was Research Soil Physicist, Riverside.

This work was carried out primarily during the tenure of an FAO André Mayer Research Fellowship, part of which Mr. Malcolm spent at the Department of Soils and Plant Nutrition, University of California, Riverside. Financial support was received from the Fellowship, and from the West Australian Department of Agriculture.

C. V. Malcolm, L. H. Stolzy, and C. R. Jensen

Effect of Artificial Leaf Coatings on Foliar Chloride Uptake During Sprinkler Irrigation[1]

INTRODUCTION AND REVIEW

DETRIMENTAL EFFECTS of foliar-absorbed chloride following sprinkler irrigation with brackish water have been reported by Eaton and Harding (1959),[2] Ehlig and Bernstein (1959), Harding, Miller and Fireman (1958), Heimann and Ratner (1965), Mungomery (1959), and Smith (1963). Various methods have been proposed for reducing or avoiding such damage. Chloride uptake and associated damage may possibly be reduced by sprinkling at night (Eaton and Harding, 1959; Ehlig and Bernstein, 1959; Heimann and Ratner, 1965; Malcolm, 1967; Mungomery, 1959; and Smith, 1963). This may be due to less evaporation (Eaton and Harding, 1959; Smith, 1963) or to stomatal closure (Malcolm, 1967). The method of sprinkling is also important—thus, low-angle sprinklers may be used to prevent contact of water with foliage (Jones, 1966). Where this is impractical, continuous rather than intermittent sprinklers may be used (Eaton and Harding, 1959, and Smith, 1963), or speed of rotation may be increased (Stolzy, *et al.*, 1966) thereby reducing opportunity for evaporation or perhaps decreasing the period for which the leaf is wet. Benefits have also been reported in the literature from addition of potassium to the irrigation water to achieve a more favorable ratio of Na:K in the water (Heimann and Ratner, 1965).

No previous reports are known on attemped amelioration by artificial leaf coating, although crop-growing with poor-quality water under conditions suitable for sprinkler irrigation is becoming more and more common. Additionally, increased demand for water favours the more economical usage possible with sprinklers (Frost and Rodney, 1964), the more so as yield increases in some crops are reported after changing from surface to sprinkler irrigation (Cox, 1964; Frost and Rodney, 1964). It is therefore of interest to investigate whether artificial leaf coatings will reduce foliar salt uptake, and whether some coating materials may also be useful as antitranspirants.

Mechanism of ion uptake during sprinkling. This has received scant attention. Sodium, boron, and choride are all known to be accumulated to toxic levels from waters containing relatively low concentrations (Ehlig and Bernstein, 1959; Harding, Miller and Fireman, 1958; Smith, 1963; Stolzy, Harding and Branson, 1966). Rate of uptake is roughly proportional to concentration of the sprinkling solution (Eaton and Harding, 1959; Smith, 1963) and is linear with time (Ehlig and Bernstein, 1959). Accumulation may occur against 11- to 14-fold concentration gradients; it is selective, and in some cases it may be influenced for a given ion by chang-

[1] Submitted for publication June 1, 1967.

[2] See "References" for publications referred to in text by author and date.

ing the associated cation or anion (Ehlig and Bernstein, 1959). There are considerable differences between species in ability of leaves to accumulate (or to exclude) dissolved ions; such differences are perhaps related to differences in leaf wettability (Ehlig and Bernstein, 1959). Thus it appears that foliar uptake of ions during sprinkling follows principles similar to foliar uptake of nutrients (Jyung and Wittwer, 1965).

To deduce how absorption may best be reduced or prevented, factors affecting foliar absorption of ions from solution must be closely studied. Low uptake of Na and Cl in avocado was suspected of being associated with the nonwettable nature of the leaf surface (Ehlig and Bernstein, 1959). Moreover, there are many studies reported in which surfactants were used to increase penetration of foliar-applied nutrients or herbicides (Foy, 1962; Koontz and Biddulph, 1957; Parr and Norman, 1965; Wallihan, Embleton and Sharpless, 1964). Wettability of plant leaves is associated with presence of the wax layer (Mueller, Carr and Loomis, 1954; Silva-Fernandes, 1965), its chemical nature (Brieskorn, Briner and Leiner, 1954; Fogg, 1948; Silva-Fernandes, 1964 and 1965), and its degree of roughness (Fogg, 1948; Silva-Fernandes, 1964 and 1965). These may in turn be influenced by leaf turgor (Fogg, 1947). Individual leaves vary greatly in wettability with side, age, position on the plant, and time of day (Ebeling, 1939; Fogg, 1947). Variability with age may be attributed partly to resistance of the wax layer to weathering. It has been shown (Juniper, 1959*b*) that some leaves retain nonwettability (high contact angle) until senescence, whereas others do so only for a few days. High spraying pressure (Silva-Fernandes, 1964), immersion in water (Adam, 1958; Juniper, 1959*b*), dust (Ebeling, 1939), and buffeting by wind (Hall and Jones, 1961) have been observed to make leaves more wettable (lower contact angle); the buffeting is associated with removal of wax from the dome-shaped cuticle overlying the epidermal cells. Greater transpiration during the cuticular phase was noted from clover leaves brushed to simulate wind damage (Hall and Jones, 1961); in this connection light dry-brushing or wiping with 5 per cent ether increased foliar absorption of choride by excised citrus leaves (Malcolm, 1967). Electron microscope studies (Hall and Donaldson, 1961; Juniper, 1960) indicate that only a few species are capable of regaining a high contact angle after the wax layer has been weathered.

Modification of leaf surfaces to increase contact angle could conceivably reduce foliar uptake of choride or other ions. Leaves grown in sunlight and under water stress develop more wax than do well watered shade-grown leaves (Skoss, 1955), and also develop higher contact angles. On the other hand, addition of trichloroacetic acid to soil reduces surface wax and contact angle of pea leaves (Dewey, Hartley and McLauchlan, 1962; Juniper, 1959*a*). Perhaps it may be possible to increase wax production by the use of some similar principle, but no case of this having been done is known to the authors. Breeding for nonwettability may offer promise, as it has been shown for eucalyptus (Barber and Jackson, 1957) that differences in wax coverage in different environments are highly heritable. The other possibility is to apply a water-repellant coating to leaves. Because many leaves are already highly water repellant (Juniper, 1959*b*), such coatings would need to be either of a highly structured wax layer, since smooth wax surfaces do not have exceptionally high contact angles (Adam, 1958), or of a material such as silicone, which in thin films may raise contact angles a great deal (Adam, 1958).

Wettability of the leaf is thus important in reducing contact of applied water with leaf surface. Penetration of the wax layer is facilitated by any factors which allow the contact angle to be reduced and permit the water on the leaf to come closer to the more polar (hydrophilic) cutin layer (Crafts and Foy, 1962; Hall, *et al.,* 1965). The ease with which ions may enter the leaf across the cutin layer varies with its thickness, hydration, imperfections, and composition (Jyung and Wittwer, 1965; Silva-Fernandes, 1965; Orgell, 1957), but more especially is affected by the presence or absence of stomata. Although some reports differ (Jyung, Wittwer and Bukovac, 1965), in general it appears that entry of solutes into the stomata facilitates ion uptake, presumably by presenting both a larger and a more permeable surface for absorption (Jyung and Wittwer, 1965; Silva- Fernandes, 1965; Skoss, 1955; Wallihan, Embleton and Sharpless, 1964). Moreover, in the case of plants with relatively impermeable cuticles, ion uptake occurs primarily through the sub-stomatal surfaces. Another method of reducing foliar ion uptake would therefore be to cover the leaves with a film capable of preventing entry of solution into stomata or imperfections in the cuticle. Closure of stomata with metabolically active sprays may also be effective. It has been argued (Slayter and Bierhuizen, 1964) that transpiration reduction by the closing of stomata, or use of films or other means, should be possible without seriously affecting gaseous exchange by the leaf. A recent review (Gale and Hagen, 1966) warns of the impermeability to CO_2 of film materials used as anti-transpirants. Consequently, growth effects of materials used in this study have been tested and are reported separately (Malcolm and Stolzy, 1968).

Entry of aqueous solutions into stomata and insect spiracles (Ebeling, 1939) has been represented by the formula for height of capillary rise of a liquid. The height in this expression is directly proportional to the surface tension of the liquid and the cosine of the contact angle. Therefore, wettability of the leaf will influence both the spread of irrigation water on the leaf and its entry into pores. It has been suggested (Turrell, 1947) that the raised nature of citrus stomata and the presence of resinous plugs in the stomatal openings will render entry of rainfall into citrus leaves improbable. However, the effect of raising the rim of the stomatal pit is likely to be of much less importance than contact angle.

Once ions have actually crossed the wax and cutin layers—whether via the stomata or not—there remains one means of preventing their accumulation. Diffusion gradients across the cuticle are maintained by metabolic processes which insure a sink for the particular ions within the leaf (Jyung and Wittwer, 1964); Moorby, 1964; Sargant and Blackman, 1965). These processes may be prevented and accumulation stopped by the use of metabolic inhibitors (Jyung and Wittwer, 1964). Some work has suggested that materials such as urea may increase the permeability of the cuticular membrane (Yamada, 1962), and other studies have shown absorption to be affected by pH of the sprayed solution (Orgell, 1957).

In the present study, the effect of silicones and film-forming polymer latices on foliar uptake of choride is investigated. The use of metabolic inhibitors or materials likely to affect membrane permeability has not been studied.

MATERIALS

The materials used in the studies are listed below, together with their approximate chemical nature (if available) and the name of the supplier. Each material has been given a code number which will be used throughout this publication.

Code	*Commercial name*	*Chemical composition*	*Supplier*
L1	"Bravo" floor polish	——	Johnson Bros. (USA)
L2	Rhoplex AC-22	Acrylic polymer	Rohm and Haas Company (USA)
L3	Rhoplex AC-34	Acrylic polymer (46-47% solids)	Rohm and Haas Company (USA)
L4	E216 emulsion	Vinylidene chloride co-polymer	Rohm and Haas Company (USA)
L5	Geon 650 x 1	Vinylidene chloride co-polymer	B. F. Goodrich Chemical Company (USA)
L6	Saran F-122–A20	Vinylidene chloride acrylonitrite	Dow Chemical Company (USA)
S1	Silicone HV 490	Dimethyl polysiloxane	Dow Corning (USA)

In order to insure coverage of treated plant surfaces, it has been necessary to add a surfactant to the above materials. The non-ionic surfactant used for this purpose was CS-555. Other surfactants could be used in similar studies.

METHODS

Diffusion resistance of impregnated filters. In attempting to imitate coating of a leaf in an inert system, unsatisfactory attempts were made to coat materials including cellophane paper, Saran plastic film, waxed paper, and filter paper with latex materials. Finally, 47-mm-diameter Acropor AN 200 filters were used. These filters, which have a maximum pore size of 0.20 microns, consist of an acrylic polyvinylchoride co-polymer reinforced with nylon cloth. Filters were impregnated with a range of concentrations (10, 25, 50, and 75 per cent) of material L5 by dipping, rolling out the excess on a sheet of clean glass, and hanging the filter to dry. Each filter was then placed over the opening of a specially constructed aluminum cell sealed with silicone grease and clamped in place (fig. 1). The cell was flushed with CO_2, the input port sealed, and regular measurements made of the CO_2 and O_2 in the cell as the former diffused out and the latter into the cell through the filter being tested. Beckman CO_2 and O_2 electrodes were used for the measurements.

A drop of distilled water was then placed in each cell, the electrode holes stoppered and the loss of weight with time measured with the cells standing in the fume hood. Finally, a drop of distilled water was placed on each filter and the ease of penetration noted. Equations (1) and (2) were used to calculate the diffusion resistance (R) of the filters. For derivation of equations (1) and (2) see Appendix.

For CO_2 and O_2:

$$R = -Dat/V \; ln \left(\frac{C - C_a}{C_o - C_a} \right) \qquad (1)$$

for H_2O:

$$R = Da(C_s - C_a) \; t/W_o - W) \qquad (2)$$

where V = volume of cell (cm^3)

a = cross sectional area available for diffusion (cm^2)

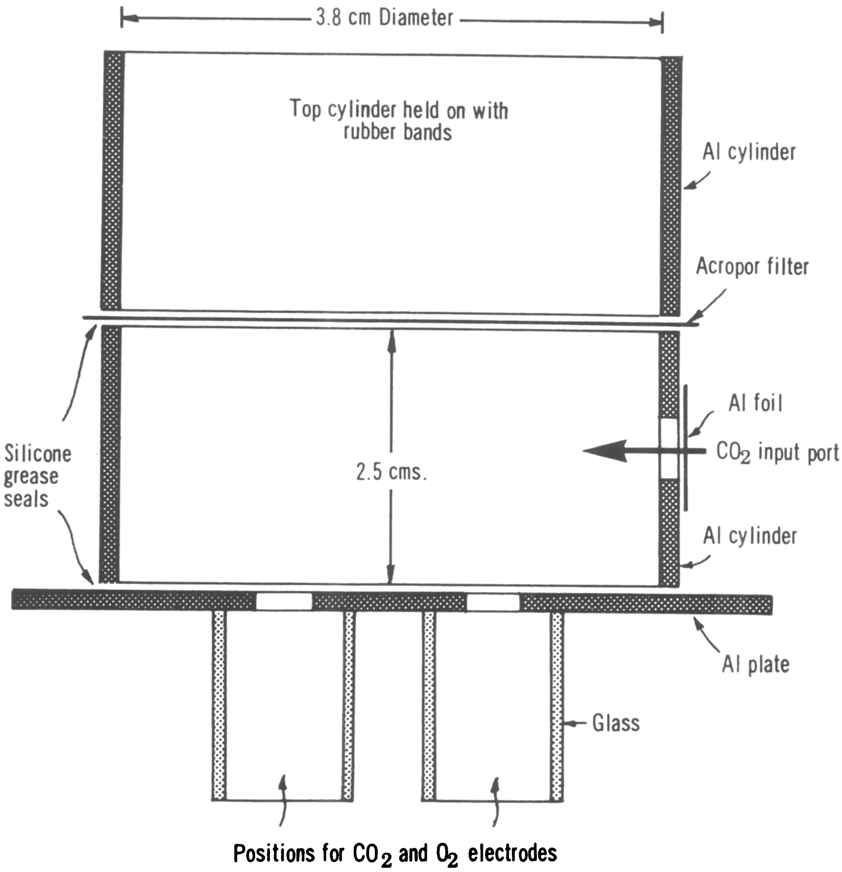

Fig. 1. Cell used for diffusion-resistance measurements on latex-impregnated filters.

D = diffusion coefficient of the gas ($cm^2 min.^{-1}$)

t = time (min.)

C_o = initial concentration ($gm\ cm^{-3}$)

C = concentration ($gm\ cm^{-3}$) at time of measurement

C_s = concentration in cell assumed saturated ($gm\ cm^{-3}$)

C_a = concentration in air ($gm\ cm^{-3}$)

W_o = initial weight (gm)

W = weight after time (gm).

Effects of artificial coatings on chloride uptake. A glass chromatography sprayer was used to apply coatings to both sides of plant leaves; test spraying was used in each case to determine minimum concentration of surfactant needed for complete wetting of leaves. Coatings were allowed to cure overnight at least. Spray irrigation was accomplished by placing plant material, with containers suitably protected, in an 8-foot-diameter tray with shielding and drainage. Spraying was from above by means of a fixed sprinkler, and irrigation water (which was 0.5 per cent NaCl solution) was recirculated. Water in the reservoir was changed at intervals for cleanliness and to avoid concentration effects. Careful arrangement of plants beneath the sprinkler ensured even water applica-

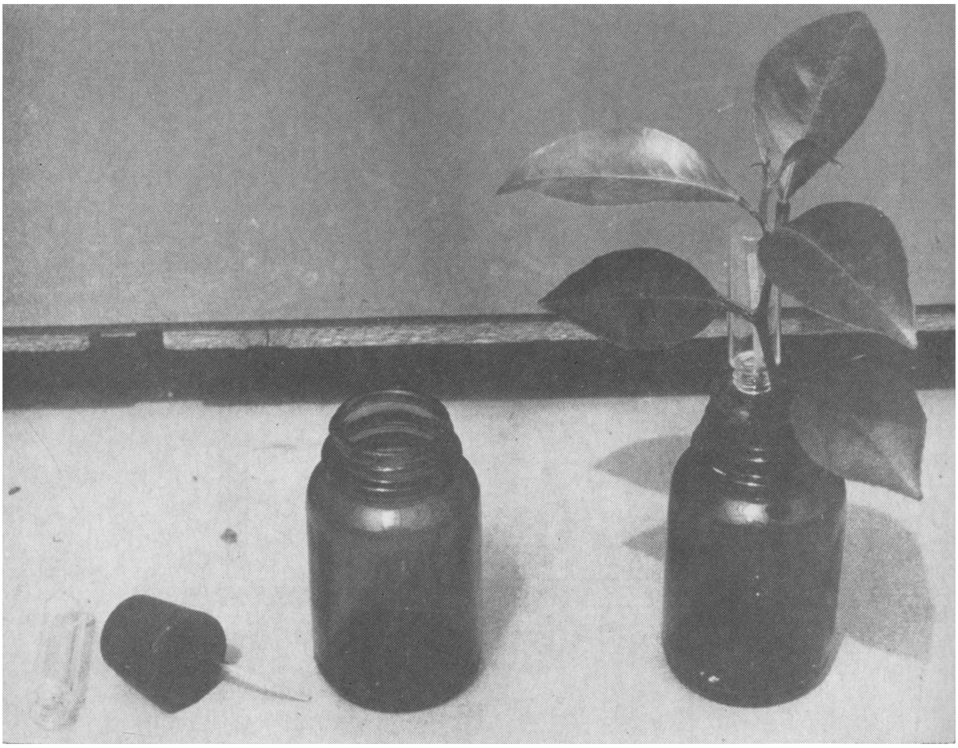

Fig. 2. Method of sealing small citrus shoot into jar (experiments 1 and 2).

tion. Except for night versus day, treatments were sprinkled simultaneously.

For rapid and satisfactory removal of nonabsorbed salt remaining on leaves after irrigation treatment, leaves were held loosely between the fingers and agitated for 10 seconds in a breaker of deionized water into which deionized water was rushing from a tap. Washed leaves were oven dried at 65°C, ground in a pestle and mortar, and allowed to stand overnight in 100 ml of 0.05 N nitric acid. Chloride was determined by titrating against silver nitrate, the end point being found potentiometrically.

Details of each experiment will be discussed in turn.

Experiment 1. Twigs having 4 to 6 leaves each were cut under water from Valencia orange trees in the orchard and placed with their stems sealed through stoppers into small bottles of deionized water (fig. 2). Eight coating materials were then applied in the morning to four replications of twigs which were then cured and sprinkler irrigated for 8 hours in the daytime. Leaves were removed, washed, and oven-dried immediately after sprinkling. Conductivity of the water in the bottles was checked to insure no salt had entered.

Experiment 2. Sweet orange seedlings were grown in the glasshouse to about 60 cm in height, and kept trimmed to a single shoot. Six replications were then coated in the morning with each of the following: S1 at concentrations of 1, 3, and 6 per cent with CS-555 at 0.88 per cent, and L2 at concentrations of 10 per cent with 1.7 per cent CS-555, and 20 and 40 per cent with 2.5 per cent CS-555; two days were allowed for curing. After removing control leaf samples, three replications were irrigated for 8 hours during the day and three for 8 hours at night. In sampling, leaves from top and bottom halves of each plant were kept separate, because they were from separate growth flushes and differed in age by several weeks. Sampling within each growth-flush was randomized to prevent age differences affecting the outcome.

Experiment 3. Twigs similar to those used in experiment 1 were used for this study. The following coatings were applied to five replications: L2 and L6 at 5 and 10 per cent, with 0.44 and 0.66 per cent CS-555, respectively. Each coating was applied once for one treatment and twice and thrice to achieve two other treatment levels, time being allowed between applications for curing. Second and third coatings were applied in the afternoon of successive days. Twigs were irrigated for 8 hours during the day.

Experiment 4. Sweet orange seedlings were grown to a height of about 60 cm as a single shoot, and then pruned back to 12 leaves each and fertilized. When all plants had initiated a shoot from the top leaf axil, S1 (3 per cent with 0.55 per cent CS-555), and L3 (10 per cent with 0.66 per cent CS-555), were each applied to 16 plants. Eight plants from each treatment and eight untreated plants were left in the glasshouse, and the same number were placed outside. Moisture usage, phytotoxic effects, and shoot growth are reported elsewhere (Malcolm and Stolzy, 1968). After 24 days, the L3-treated plants from outside were recoated using 10 per cent L3 with 1.98 per cent CS-555. Attempts to recoat either the S1-treated plants or the L3-treated plants from the glasshouse were abandoned because penetration of leaves occurred at levels of CS-555 needed for satisfactory spreading. Approximate measurements of contact angle of droplets of deionized water were made on each plant with a protractor, and a control sample of leaves was removed for choride analysis. Two samples of leaves from each plant were used for salt uptake studies by means of a dipping technique, one sample at night and one during the day. In each case, leaves were removed from the plant and quickly suspended for 8 hours in aerated 0.5 per cent NaCl solution (fig. 3). Four replications were suspended in salt solution with 0.5 per cent CS-555 and four replications without surfactant. The remaining leaves on the plant were sprinkler irrigated for 8 hours by the technique described earlier, four of the eight replications being sprinkled during the day and four at night.

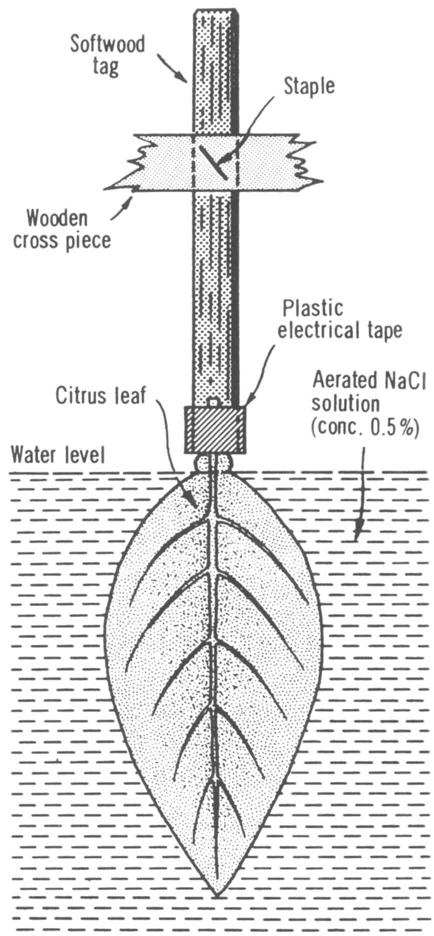

Fig. 3. Method of mounting single citrus leaves in aerated salt solution (experiment 4).

RESULTS

Diffusion resistance of impregnated filters. Table 1 shows the relative diffusion resistances of impregnated filters to CO_2, O_2, and water vapor, together with an indication of the ease with which a drop of water penetrated filters. Increasing concentration of the impregnating emulsion L5 from 10 to 25 per cent (v/v) caused a relatively small increase in diffusion resistance. The use of 50 and 75 per cent L5 emulsion caused a marked increased in diffusion resistance for CO_2 and O_2. At all concentrations liquid water placed on top of the filter penetrated to the lower side. Slowest penetration was at the 75 per cent concentration, but penetration to the lower surface even in this case occurred within 2 minutes. The high value for resistance to water vapor diffusion with 10 per cent latex impregnation indicates that the rate of diffusion of water vapor to the lower side of the filter may have been limiting in this case.

Effects of artificial leaf coatings on chloride uptake. Results here are expressed either as chloride levels occurring naturally or chloride found in the leaves after their treatments, and to appreciate the effect of treatments they must be compared with the control. In experiments 2 and 4, control samples were available from every plant treated and the amount of chloride in the control was subtracted from the level found in corresponding treated leaves at the end of the experiment. This resulted in a negative value for uptake in a few cases, but not at a significant level.

Experiment 1. In this exploratory test leaf coatings may have had a profound effect on foliar chloride uptake. Coatings of L4 and CS-555 caused significantly higher (5 per cent level) chloride levels than were found in uncoated Valencia orange leaves (tables 2, 3). No treatments produced significantly lower levels of chloride than did untreated leaves. However, results were extremely variable and it is possible that significant reductions in foliar chloride uptake could be achieved with coatings such as L1, L2, and L3, which produced lower chloride levels than did untreated leaves (though not significantly so).

Experiment 2. Chloride uptake was significantly higher (0.1 per cent level) in sweet orange leaves sprinkled during the day rather than at night (table 3). Differences were most spectacular in leaves treated with S1, but were also appreciable in L2-coated and uncoated leaves (interaction significant 0.1 per cent level). Old leaves usually took up

TABLE 1

DIFFUSION RESISTANCES OF L5—IMPREGNATED FILTERS, AND PENETRATION OF WATER*

Diffusing gas	Diffusion resistance: Concentration of impregnated emulsion (per cent v/v) 10	25	50	75	Penetration of water: Concentration of impregnated emulsion (per cent v/v) 10	25	50	75
	cm							
CO_2 (D = 10.3 cm^2 min^{-1})	4	17	113	996	Immediate	Immediate	Immediate, but some blocked pores	Delayed, but does pass through
O_2 (D = 13 0 cm^2 min^{-1})	3	7	40	278				
H_2O (D = 16.0 cm^{-2} min^{-1})	7	9	40	42				

* Acropor AN 200 filters, maximum pore size 0.2 microns.

TABLE 2

CHLORIDE LEVELS IN VALENCIA ORANGE LEAVES COATED WITH VARIOUS MATERIALS AND SPRINKLER-IRRIGATED WITH SALINE WATER (EXPERIMENT 1)

Material*	Treatment		Mean chloride level (oven-dry basis)†
	Concentration of material	Concentration of CS-555	
	per cent v/v	*per cent*	*per cent*
Control	..	..	0.018_{a}
L1	100	0	0.026_{ab}
L2	10	1.1	0.059_{abc}
L3	10	1.1	0.062_{abc}
No coating	..	..	0.072_{bc}
S1	3.3	1.1	0.080_{cd}
L5	10	0.6	0.084_{cd}
L5 and S1	10 and 1	0.6	0.093_{cd}
CS-555	0	1.1	0.118_{d}
L4	10	0.8	0.134_{d}

* See page 72 for details of coating materials.
† Subscript letters a, b, c, and d after values indicate statistical populations. Mean values are statistically significant only if they do not have a subscript letter in common after values. F value is significant at the 5% level or more.

significantly more chloride (0.1 per cent level) than did young leaves, but there was a significant interaction between leaf treatments and age. Thus, while old and young leaves coated with L2 took up roughly the same amounts of chloride in the day, S1-coated old leaves took up appreciably more than their young counterparts.

Higher concentrations of S1 and L2 spray emulsions appeared to give increased choride uptake by the leaves.

TABLE 3

FOLIAR CHLORIDE UPTAKE BY GLASSHOUSE-GROWN SWEET ORANGE SEEDLINGS TREATED WITH DIFFERENT CONCENTRATIONS OF S1 AND L2, AND SPINKLER-IRRIGATED WITH SALINE WATER (EXPERIMENT 2)

Treatment	Chloride uptake			
	Leaf type and time of sprinkling			
	Young leaves		Old leaves	
	Day	Night	Day	Night
	per cent		*per cent*	
Control*	0.014	0.014	0.030	0.026
Nil†	0.024	0.002	0.015‡	−0.003
S1 1%	0.061	0.006	0.115	−0.003
S1 3%	0.146	0.004	0.171	0.001
S1 6%	0.069	0.011	0.264	0.021
L2 10%	0.048	0.038	0.035	0.006
L2 20%	0.053	0.021	0.042	0.019
L2 40%	0.042	0.058	0.053	0.026

* Chloride values for control are over-all means of the amount in leaves removed prior to sprinkling.
† The Chloride values (per cent Cl over dry basis) for treatments other than control are the differences between treatment and control means in each case, and so represent uptake.
‡Analysis of variance indicates the following levels of significance (means are in brackets): Day [0.050] vs night [0.025] 0.1% level; Old [0.045] vs young (0.030) 0.1% level; Treatment 0.1% level; Treatments x time 0.1% level; Treatments x age 5% level.

Experiment 3. No significant differences were shown in chloride levels of Valencia orange leaves coated with different numbers of coatings of L2 or L6 (table 4). However, some leaves coated with L6 contained significantly higher levels of chloride than did those coated with L2 (5 per cent level). None of the coated leaves contained significantly less chloride than did uncoated leaves, and the majority did not differ significantly from the control (unsprinkled leaves).

TABLE 4

CHLORIDE LEVELS IN ORCHARD-GROWN VALENCIA ORANGE LEAVES COATED ONE, TWO, OR THREE TIMES WITH L2 AND L6, AND SPRINKLER-IRRIGATED WITH SALINE WATER (EXPERIMENT 3).

Material*	Treatment: Concentration of material	Treatment: Number of coatings	Mean chloride level (oven-dry basis)†
	per cent v/v		*per cent*
Control	..	..	0.038_{a}
L2	10	1	0.040_{a}
L2	5	3	0.041_{a}
No coating	..	..	0.048_{a}
L2	10	2	0.049_{a}
L2	5	2	0.050_{a}
L2	5	1	0.055_{ab}
L6	5	3	0.058_{ab}
L2	10	3	0.059_{ab}
L6	10	2	0.066_{ab}
L6	5	2	0.072_{ab}
L6	10	1	0.072_{ab}
L6	10	3	0.085_{b}
L6	5	1	0.086_{b}

* See page 72 for details of coating materials.
† Subscript letters a and b after values indicate statistical populations. Mean values are statistically significant only if they do not have a subscript letter in common after values. F value is significant at the 5% level or more.

Experiment 4. As shown in experiment 2, sweet orange leaves once again took up significantly more (0.1 per cent level) chloride during the day than at night (table 5). This was true for coated or uncoated leaves kept in the glasshouse whether they were wet by immersion or by sprinkling. Mature uncoated leaves kept outside the glasshouse for a month appeared to act in a reverse manner, and coated leaves kept outside gave smaller night-versus-day differences than did those kept in the glasshouse (interaction significant at 0.1 per cent level). Leaves kept outside took up significantly more (0.1 per cent level) chloride than those kept in the glasshouse, an effect which was much more marked for night uptake than day (interaction significant at 1 per cent

TABLE 5

FOLIAR CHLORIDE UPTAKE BY GLASSHOUSE—AND OUTSIDE—GROWN SWEET ORANGE LEAVES COATED WITH S1 AND L3 AND IMMERSED IN OR SPRINKLED WITH SALT SOLUTION (EXPERIMENT 4)

Treatment		Immersion*: Day	Immersion*: Night	Sprinkling: Day	Sprinkling: Night
		per cent		*per cent*	
Glasshouse	Nil	0.007‡	0.001	0.059	0.004
Glasshouse	S1	0.098	−0.005‡	0.221	0.014
Glasshouse	L3	0.020	−0.007	0.005	−0.005
Outside	Nil	0.010	0.058	0.086	0.089
Outside	S1	0.151	0.104	0.183	0.173
Outside	L3	0.032	0.001	0.061	0.021

* Results for similar leaves immersed in 0.5% NaCl solution containing enough CS-555 to give spreading on all leaves used were not significantly different from those in the table.
† Each figure the mean of four values for per cent Cl on oven-dry basis. Statistical analysis indicates that all treatments effects, watering method and time, leaf coating, and glasshouse vs outside are significant at the 0.1% level, as was interaction between coatings and time of watering. Other significant interactions were glasshouse-outside vs time, and glasshouse-outside vs time coating, both at the 1% level.
‡ Negative values due to control leaves analyzing higher than treatment.

TABLE 6

CONTACT ANGLES (DEGREES) AND TRANSPIRATION (GM CM^{-2}) FOR SWEET ORANGE LEAVES USED IN EXPERIMENT 4

Data	Glasshouse			Outside		
	Treatment			Treatment		
	Control	S1	L3	Control	S1	L3
	degree					
Contact angle						
Top	85†	90	63	56	97	64
Bottom	93	86	73	90	93	67
	GM CM^{-2}			*GM CM^{-2}*		
Transpiration*	5.12	4.67	3.92	5.13	4.96	4.13

* These data are for transpiration over a 20-day period prior to the sprinkler application and are extracted from another paper (Malcolm and Stolzy, 1968).
† Each figure is the mean of eight determinations.

level). Leaf coating treatments gave significant differences in chloride uptake (0.1 per cent level), S1-coated leaves being highest in every instance. However, the results for uncoated and L3-coated leaves were complicated by interaction (significant at 1 per cent level) with time of day and environment, i.e., glasshouse versus outside. In this connection the uncoated leaves kept for a month outside took up a more salt relative to the L3-coated leaves kept outside, than did coated and uncoated leaves kept in the glasshouse. Analysis of variance on the results for nil- and L3-coated glasshouse leaves indicates that coating with L3 significantly reduced chloride uptake when sprinkling in daytime (1 per cent level). Contact-angle measurements (table 6) show that being outside instead of in the glasshouse lowered the contact angle of uncoated leaves (perhaps due to dust) but the contact angle of the S5-coated leaves has been increased if anything. Contact-angle lowering of uncoated leaves was restricted to upper non-stomatal surfaces where dust accumulates.

DISCUSSION

Diffusion resistance of impregnated filters. It is surprising that a seal of 0.2μ pores in Acropor filters was not obtained in these studies, as evidenced by rapid penetration of liquid water through all treated filters. As brief studies on leaves and aluminum foil (reported in the next section) indicate that much larger pores can be bridged by latex film, it appears that other techniques for simulating leaf coating may be needed. The relatively low resistance to water vapor at 75 per cent may result from movement of water through the filter in the liquid phase. An initial lag of ½ to 2 hours in the loss of water vapor for 50 and 75 per cent concentrations was observed and indicates that water was absorbed by the filter. However, Waggoner (1965) has reported data on the resistance of 1μ-thick films of various polymers to CO_2 and water vapor diffusion. In every case, the resistance to CO_2 diffusion was reported as being much greater. Figures for 75 per cent emulsion may reflect this effect, as some of the filter pores may be sealed at this concentration—as evidenced by slow movement of liquid water into and through the filter.

Effects of artificial leaf coatings on chloride uptake. The significant reduction of foliar chloride uptake by leaf coatings of L3 in experiment 4 supports the hypothesis that foliar uptake of chloride, and perhaps other ions, can be artificially reduced. Moreover, coatings which gave these encouraging results on mature citrus leaves kept in the glasshouse were 28 days old at the time of sprinkling, and may be assumed therefore to have good durability. The same films were found also to maintain their antitranspirant efficiency over the period of 28 days, and to exercise an insignificant effect on shoot growth in the glasshouse (Malcolm and Stolzy, 1968). Results for plants kept outside during the 28-day period are less encouraging, but still suggest benefits from L3-coating in terms of less chloride taken up.

The use of silicone to reduce foliar chloride uptake has been singularly unsuccessful.

The significant increases in chloride uptake caused by silicone coating in some of the experiments may be of interest in the use of foliar sprays of plant nutrients. Similar increases in solute entry have been reported in using dimethyl sulfoxide (Leonard, 1966). The mechanism of the increase in uptake is obscure, as the contact angle of the S1-treated leaves in experiment 4 was as high as that of any treatment. Moreover, porosity of the leaves (which may be represented by the transpiration values in table 6) is, if anything, lower for S1-coated than for uncoated leaves. Time studies may reveal a change in contact angle on S1-coated leaves during sprinkling, because drop impact may cause re-emulsification of the silicone and surfactant mixture on leaf surfaces —perhaps the silicone tends to remove resinous plugs reported to occur in citrus stomatal openings (Turrell, 1947). The mechanism of reduction of uptake by coatings of L3 is presumably by actual sealing of the leaf in a continuous film, as the contact angle of L3-coated leaves was lower than that of uncoated leaves, and higher uptake would therefore be expected. But transpiration figures indicate that L3-coated leaves lost less water, and perhaps lowered permeability of the leaves to water vapor was also expressed in lowered chloride uptake. The degree to which film is not continuous (Malcolm and Stolzy, 1968) would influence its efficiency, and could be a factor in failure of other latex coatings to reduce chloride uptake. The significant increases in chloride level caused by latices L4 and L6 may be related to a combination of contact-angle lowering (perhaps due to surfactant) and faulty film formation. Work on the dipping of Sultana grapes (Chambers and Possingham, 1963) has indicated that increased water-loss rates are due to the filling of wax layers with emulsion to replace natural air spaces. A similar mechanism may explain some cases of increased chloride uptake.

Film across stomatal pit. The ability of a polymer emulsion to form a continuous film on a leaf will be affected by surface properties such as dirt and the porosity of the surface (Chatfield, 1962). Film formation from polymer emulsions occurs when evaporation of the water phase brings the minute droplets of the dispersed polymer phase into such close contact that they coalesce into a film (Chatfield, 1962). Because droplets of polymer are commonly of the order of 0.2μ diameter, any surface faults such as cracks or stomata which exceed this size could cause film faults and allow water entry. Very fine dirt may act as does paint pigment and decrease permeability of the film (Chatfield, 1962), but larger particles such as fine sand or silt may cause the film to stretch and provide weak points. Faults in latex films on leaf surfaces have been discussed by other workers recently (Waggoner, 1965, and Gale and Poljakoff-Mayber, 1967). This may be the reason for the greater chloride exclusion by 4-week-old L3-coatings on glasshouse

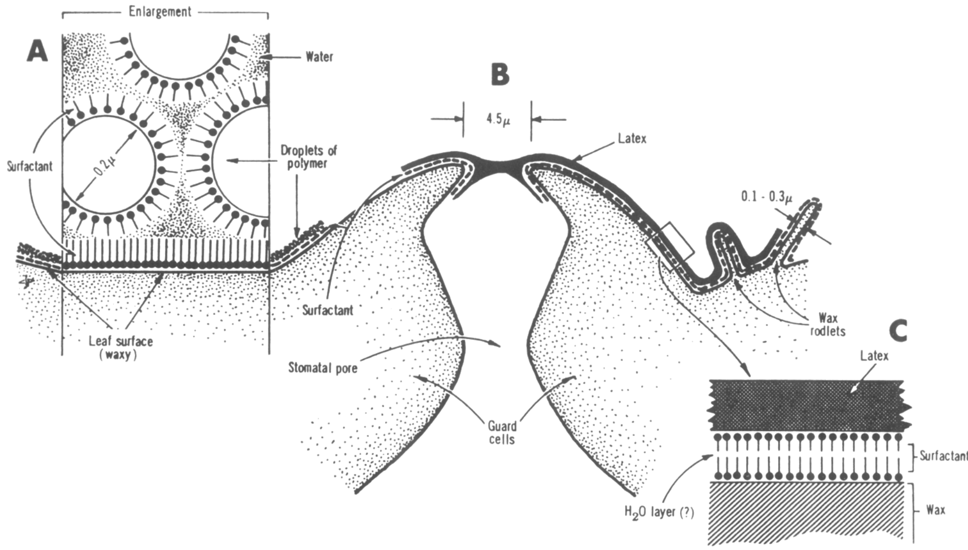

Fig. 4. Representation of polymer emulsion and latex film on surface of sweet orange leaf. (Stomate outline taken from Nadel, 1935.)

plants in experiment 4 as compared with coatings applied to the dusty plants from outside just before sprinkling. Further work is needed to demonstrate the effects of stomatal opening and dirt on film formation and chloride exclusion; however, microscopic examination of L3-coated leaves indicates that a film forms across the opening of the stomatal pit (fig. 4, B). Tests were made of the ability of L3 to form films across pinpricks in aluminum foil when applied to the raised side, to simulate domes of cuticle above stomatal pits in orange leaves (Nadel, 1935). Examination revealed that films had indeed formed across the openings, which were of the order of 250μ diameter (over 50 times that of the openings of the stomatal pits).

Surfactant in film formation. A feature of the present studies has been the very high concentrations of surfactant required to overcome the hydrophobic nature of the waxy leaf surface. The possible arrangement of surfactant molecules and polymer micelles is shown in figure 4,A. The lipophillic ends of the surfactant molecules added to the emulsion to achieve spreading would be concentrated by adsorption at the waxy leaf surface, leaving their hydrophillic ends in the water matrix. As water evaporates, any excess molecules of surfactant would combine to form micelles or adsorb onto either the leaf surface or the polymer droplets by means of their lipophillic ends. A further layer of surfactant molecules would be concentrated at the air-emulsion interface. When polymer droplets coalesce into a film, the surfactant will perhaps form a layer beneath the film, lipophillic ends outermost, and will be bonded through a water layer and a second surfactant layer to the leaf surface (as in fig. 4, C). Because surfactants are used at such high concentrations, and because they are important in film formation and adhesion, it is likely that research on a range of surfactant materials in relation to salt exclusion by films would be rewarding. Work reported elsewhere (Malcolm and Stolzy, 1968) indicates the effect of surfactant concentration on polymer films formed on perforated aluminum foil.

Night-versus-day in chloride uptake. The magnitude of the night-versus-day effects on chloride uptake in experiments 2 and 4 are apparently due to uptake through the stomata during the day and prevention of uptake at night by stomatal closure. In experiment 2 it can be postulated that the high chloride levels reached with S1-coated leaves are due to the silicone facilitating stomatal entry, as uptake at night was negligible. Penetration of stomata by silicone oils has been shown to be rapid (Leonard, 1958). However, the influence of night and day may not be restricted to movement of stomata and the possibility, for example, of changes in activity of ectodesmata (Franke, 1964) may explain day-versus-night differences. The low chloride levels obtained with night sprinkling on glasshouse-grown leaves indicate the efficiency of both the closed stomates and the cuticle in preventing uptake. On the other hand, leaves grown to maturity inside the glasshouse and then kept outside for a month took up considerable amounts of chloride during night sprinkling. The effect was more noticeable in the uncoated and S1-coated leaves than in the L3-coated leaves which were recoated a few days before sprinkling. These differences cannot be explained in terms of contact angles of the lower surface of the leaves (table 6), but perhaps outside leaves suffered mechanical damage which allowed salts to enter—strong winds towards the end of the experiment removed some leaves and caused damage to others (Malcolm and Stolzy, 1968). Apparently, effects of leaf surface permeability, stomatal or cuticular, as it may influence passive foliar uptake, and metabolic activity of the leaf—as it may influence active foliar uptake of ions—are confounded in these results.

SUMMARY

Significant reductions in foliar chloride uptake during sprinkling with NaCl solution were obtained by coating citrus leaves with an acrylic polymer latex. Other coatings including both latices and silicones caused significant increases in foliar chloride while others had no significant effect. Successful coatings may have formed a continuous film on the leaf across the raised openings of the stomatal pits. The importance of surfactants in coating leaves with latex is discussed.

Marked decreases were obtained in chloride uptake of citrus leaves by sprinkling at night, as compared with day sprinkling, when evaporation was not a factor. The efficiency of sweet orange leaves grown in the greenhouse in keeping out chloride was reduced by leaving the plants outside for 1 month prior to sprinkling.

ACKNOWLEDGMENTS

Appreciation is expressed to: FAO, Department of Soils and Plant Nutrition, University of California, Riverside; the West Australian Department of Agriculture, Perth; and to Dr. J. Letey, Jr., and Messrs. R. J. Luxmoore, N. Valoras, T. E. Szuszkiewicz, and D. Rayner for discussions and assistance. The assistance of Dr. J. Rible of the Agricultural Extension Service in making available facilities for chloride determination is greatly appreciated.

REFERENCES

ADAM, N. K.
1958. Water repellancy. Endeavour **17**:37–41.
BARBER, H. N., and W. D. JACKSON
1957. Natural selection in action in *Eucalyptus*. Nature **179**:1267.
BRIESKORN, C. H., M. BRINER, and U. LEINER
1954. Untersuchungen über die Bedeutung der Unsolsäure für die pflanzliche Kuticula. Arch. Pharm. Berlin **287**:59, 305.
CHAMBERS, T. C., and J. F. POSSINGHAM
1963. Studies of the fine structure of the wax layer of sultana grapes. Aust. J. Biol. Sci. **16**:818–25.
CHATFIELD, H. W. (Editor)
1962. The science of surface coatings. London: Ernest Benn Ltd.
COX, J. B.
1964. [Citrus] irrigation by sprinkler systems. Citrus News **40**:86–87.
CRAFTS, A. S., and C. L. FOY
1962. The chemical and physical nature of plant surfaces in relation to the use of pesticides and to their residues. Residue Reviews **1**:112–39.
DEWEY, O. R., G. S. HARTLEY, and J. W. G. MACLAUGHLAN
1962. External leaf waxes and their modification by root treatment of plants with trichloroacetate. Proc. Royal Soc. B. **155**:532.
DYBING, C. D., and H. B. CURRIER
1961. Foliar penetration by chemicals. Plant Physiol. **32**(2):169–74.
EATON, F. M., and R. B. HARDING
1959. Foliar uptake of salt constituents of water by citrus plants during intermittent sprinkling and immersion. Plant Physiol. **34**:22–26.
EBELING, W.
1939. The role of surface tension and contact angle in the performance of spray liquids. Hilgardia **12**(11):665–98.
EHLIG, C. F., and L. BERNSTEIN
1959. Foliar absorption of sodium and chloride as a factor in sprinkler irrigation. Amer. Soc. Hort. Sci. **74**:661–70.
FOGG, G. E.
1947. Quantitative studies on the wetting of leaves by water. Proc. Royal Soc. B. **134**:503.
1948. Adhesion of water to the external surfaces of leaves. Disc. Faraday Soc. **3**:162.
FOY, C. L.
1962. Absorption and translocation studies with dalapon-2-C^{14} and Cl^{36} on *Tradescantia fluminescens*. Weeds **10**:97.
FRANKE, W.
1964. Role of guard cells on foliar absorption. Nature **202**:1236–37.
FROST, K. R., and D. R. RODNEY
1964. Sprinkler versus flood irrigation of citrus. Calif. Citrog. **49**:469–74.
GALE, J., and R. M. HAGAN
1966. Plant antitranspirants. Ann. Rev. Plant Physiol. **17**:269–82.
GALE, J., and A. POLJAKOFF-MAYBER
1967. Plastic films on plants as antitranspirants. Science **156**:650-52.
HALL, D. M., and L. A. DONALDSON
1963. The ultrastructure of wax deposits on plant leaf surfaces.
1. Growth of wax on leaves of *Trifolium repens*. J. Ultrastructure Res. 9:259–67.
HALL, D. M., and R. L. JONES
1961. Physiological significance of surface wax on leaves. Nature **191**:95–96.
HALL, D. M., A. I. MATUS, J. A. LAMBERTON, and H. N. BARBER
1965. Infra-specific variation in wax on leaf surfaces. Aust. J. Biol. Sci. **18**:323–32.
HARDING, R. B., M. P. MILLER, and M. FIREMAN
1958. Absorption of salts by citrus leaves during sprinkling with water suitable for surface irrigation. Proc. Amer. Soc. Hort. Sci. **71**:248–56.
HEIMAN, H., and R. RATNER
1965. The irrigation with saline water and the ionic environment. Field experiments with groundnuts and cowpeas. Oleagineaux **20**:157–62.
JONES, J. P.
1966. Sprinklers for desert citrus. Calif. Citrog. **51**:248–49.

JUNIPER, B. E.
1959*a*. The effect of pre-emergent treatment of peas with trichloracetic acid on the submicroscopic structure of the leaf surface. New Phytol. **58**:1–4.
1959*b*. The surfaces of plants. Endeavour **18**:20–25.
1960. Growth, development, and effect of the environment on the ultrastructure of plant surfaces. J. Linn. Soc. of London (Bot.) **56**(367):413.

JYUNG, W. H., and S. H. WITTWER
1964. Foliar absorption—an active uptake process. Amer. J. Bot. **51**(4):437–44.
1965. Pathways and mechanisms for foliar absorption of mineral nutrients. Agr. Sci. Rev. **3**:26–36.

JYUNG, W. H., S. H. WITTWER, and M. J. BUKOVAC
1965. The role of stomata in the foliar absorption of Rb by leaves of tobacco, bean, and tomato. Amer. Soc. Hort. Sci. Proc. **86**:361-67.

KOONTZ, H., and O. BIDDULPH
1957. Factors affecting absorption and translocation of foliar applied phosphorus. Plant Physiol. **32**:463–70.

LEONARD, C. D.
1966. Solvent boosts impact of foliar sprays. Crops and Soils **18**:16.

LEONARD, O. A.
1958. Studies on the absorption or translocation of 2,4-D in bean plants. Hilgardia **28**(5): 115–60.

MALCOLM, C. V.
1967. Reducing salt damage from sprinkler irrigation. Calif. Citrog. **52**:122–25.

MALCOLM, C. V., and L. H. STOLZY
1968. Effect and mode of action of latex and silicone coatings on shoot growth and water use by citrus. Agronomy J. (submitted)

MOORBY, J.
1964. The foliar uptake and translocation of cesium. J. Expt. Bot. **15**:457–69.

MUELLER, L. E., P. H. CARR, and W. E. LOOMIS
1954. The submicroscopic structure of plant surfaces. Amer. J. Bot. **41**:593.

MUNGOMERY, W. V.
1959. Salt damage to citrus. Queensland Agr. J. **85**:549–52.

NADEL, MINA
1935. On the influence of various liquid fixatives on stomatal behavior. Palestine J. Bot. and Hort. Sci. **1**:22–42.

ORGELL, W. H.
1957. Sorptive properties of plant cuticle. Proc. Iowa Acad. Sci. **64**:189–98.

PARR, J. G., and A. G. NORMAN
1965. Considerations in the use of surfactants in plant systems: A review. Bot. Gaz. **126**(2): 86–96.

SARGANT, J. A., and G. E. BLACKMAN
1965. Studies on foliar penetration. II. The role of light in determining the penetration of 2,4-dichlorophenoxyacetic acid. J. Expt. Bot. **16**:24–47.

SILVA-FERNANDES, A. M. S.
1964. Leaf wax and water repellancy. Long Ashton Agr. & Hort. Res. Stn. Ann. Rept. pp. 180–82.
1965. Studies on plant cuticle. VIII. Surface waxes in relation to water repellancy. Ann. Appl. Biol. **56**:297–304.

SKOSS, J. D.
1955. Structure and composition of plant cuticle in relation to environmental factors and permeability. Bot. Gaz. **117**:55–72.

SMITH, S. T.
1963. Irrigating citrus with saline water. J. Agr. W. Aust. **4**(4th series) No. 1.

SLATYER, R. O., and J. F. BIERHUIZEN
1964. The influence of several transpiration suppressants on transpiration, photosynthesis, and water-use efficiency of cotton leaves. Aust. J. Biol. Sci. **17**:131–46.

STOLZY, L. H., R. B. HARDING, and R. L. BRANSON
1966. Foliar absorption of boron by sprinkler-irrigated citrus. Calif. Citrog. **51**: No. 5.

TURRELL, F. M.
1947. Citrus leaf stomata: structure, composition, and pore size in relation to penetration of liquids. Bot. Gaz. **108**:476–83.

WAGGONER, P. E.
1965. Decreasing transpiration and the effect upon plant growth. Iowa State Univ. Symposium on "Plant Environment and Efficient Water Use," Amer. Soc. Agron. and Soil Sci. Soc. Amer. 49–72.

WALLIHAN, E. F., T. W. EMBLETON, and R. G. SHARPLESS
1964. Response of chlorotic citrus leaves to iron sprays in relation to surfactants and stomatal apertures. Proc. Amer. Soc. Hort. Sci. **85**:210–17.

YAMADA, Y.
1962. Studies on foliar absorption of nutrients by using radioisotopes. Ph.D. Thesis, Dept. Agr. Chem., Faculty of Agr., Kyoto Univ., Japan.

APPENDIX

Derivation of equations (1) and (2)

Fick's first law of diffusion applied to a membrane of thickness $\Delta\chi$ is

$$dQ/dt = Da(C-Ca)/\Delta\chi \tag{3}$$

where dQ/dt is the rate of diffusion of a gas through the membrane and the other symbols are the same as in equations (1) and (2). Diffusion coefficient of the gas in the membrane will be less than in air, however, because only a fraction of the membrane volume consists of pores and the pathways through these pores may be tortuous. Consequently, it is necessary to multiply D by a factor of less than 1 if D is to represent the diffusion coefficient of the gas into air, thus (3) becomes

$$dQ/dt = f\ D\ a(C-Ca)/\Delta\chi \tag{4}$$

The factor f may be combined with $\Delta\chi$ to give a term, $R = \Delta\chi/f$, the diffusion resistance, which is analogous to resistance in Ohm's law. Equation (4) then becomes

$$dQ/dt = D\ a(C-Ca)/R \tag{5}$$

Although D for a given gas is explicit in (5), R will not necessarily be independent of the diffusing gas.

For a gas diffusing through a membrane into or out of a cell of limited volume V, $dQ/dt = VdC/dt$, and (5) may be written

$$dC/(C-Ca) = Da\ dt/VR \tag{6}$$

Integrating (6) yields

$$ln\ (C-Ca) = (Dat/VR) + \text{constant} \tag{7}$$

At $t = 0$, $C = Co$ and we have from (7),

$$ln\ (Co-Ca) = \text{constant}$$

Hence, (7) may be solved for the diffusion resistance, giving (1)

$$R = Dat/V\ ln\ \left(\frac{C-C_a}{C_o-C_a}\right) \tag{1}$$

In the case of water vapor diffusing out of a cell, containing liquid water, vapor concentration is assumed to be constant and the rate of diffusion is simply the rate of loss of liquid water—that is, $dQ/dt = dW/dt = (Wo-W)/t$, and (5) becomes

$$(Wo-W)/t = Da(Cs-Ca)/R$$

from which we get (2),

$$R = Da\ (Cs-Ca)\ t/\ (Wo-W) \tag{2}$$

To simplify the information, it is sometimes necessary to use trade names of products or equipment. No endorsement of named products is intended nor is criticism implied of similar products not mentioned.

4m-5,'68 (H8700) VL 141

The journal HILGARDIA is published at irregular intervals, in volumes of about 650 to 700 pages. The number of issues per volume varies.

Single copies of any issue may be obtained free, as long as the supply lasts; please request by volume and issue number from:

Agricultural Publications
University Hall
University of California
Berkeley, California 94720

The limit to nonresidents of California is 10 separate titles. The limit to California residents is 20 separate titles.

The journal will be sent regularly to libraries, schools, or institutions in one of the following ways:

1. In exchange for similar published material on research.
2. As a gift to qualified repository libraries only.
3. On a subscription basis—$7.50 a year paid in advance. All subscriptions will be started with the first number issued during a calendar year. Subscribers starting during any given year will be sent back numbers to the first of that year and will be billed for the ensuing year the following January. Make checks or money orders payable to The Regents of The University of California; send payment with order to Agricultural Publications at above address.