Reduction in Gas Exchange of Citrus Fruit by Wax Coatings

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Grapefruits and oranges were coated with various fruit waxes. Compared to control, internal CO_2 concentration was markedly higher and weight loss markedly lower for coated fruit. Resistance of coated fruit to passage of CO_2 and water vapor was shown to be influenced by permeability of the coating but more so by the degree to which the coating seals openings in the fruit epidermis. For restriction of CO_2 exchange the coating thickness and surface tension of liquid coating were of less importance than type of wax. Critical surface tension of grapefruit and orange peel, after washing, was 23 dyn/cm. Shellac coatings adversely affected fruit flavor.

Citrus fruit is commonly coated with so-called fruit waxes that reduce the gas exchange between fruit and atmosphere, resulting in reduced respiration rate and weight loss and elevated internal CO_2 concentration (Hasegawa and Iba, 1980; Farooqi et al., 1988; Meheriuk and Porritt, 1972; Durand et al., 1984).

Reduced gas exchange of coated fruit might be accounted for in two quite different ways: the coating forms an additional barrier through which the gas must permeate, or the coating plugs openings in the peel. Which mechanism prevails depends on what is the main pathway for gas exchange in the uncoated fruit. By comparison, both pathways are important for a leaf: when stomata are open, the only important pathway is air diffusion through these (Meidner and Mansfield, 1968). However, when pores are closed, permeance through the cuticle becomes an important pathway for the gases (Nobel, 1974).

The two pathways for gas exchange (permeance and viscous flow) differ in selectivity. Permeance of a barrier is highly selective, depending as it does on a mechanism by which gas molecules dissolve in a polymer barrier, move through it in stepwise fashion by lodging in temporary holes formed by thermal agitation of polymer chains, and desorb from the barrier. Viscous flow (free diffusion, bulk flow), on the other hand, is nonselective; gases flow through permanent holes without intimate contact with the barrier material.

The two modes of gas movement also differ in another respect. Viscous flow is highly dependent on hydrostatic pressure difference across the barrier, whereas permeance is not (Lebovits, 1966). Thus, hydrostatic pressure is used in this work to detect viscous flow.

How a coating restricts the air exchange of fruit can be expected to depend not only on separate properties of fruit and coating but also on how the coating is distributed over the surface of the fruit, especially whether it forms a continuous layer or penetrates into pores. For the uncoated fruit the holes associated with lenticels, stomata, stem scars, and injuries are probably the main pathway for gas exchange (Burg, 1990). For the coated fruit, on the other hand, it is possible that these holes are filled or bridged over by the coating.

This paper shows how coatings of differing surface tensions restrict gas exchange and how this is related to blockage of pores in the fruit epidermis.

MATERIALS AND METHODS

Fruit was harvested by clipping the stems, Marsh grapefruit from two trees in one grove and Valencia oranges from three trees in another. Fruit was washed with rotary brushes, made of triangular polypropylene bristles of medium stiffness (Industrial Brush Corp., Eaton Park, FL), using an o-phenylphenate detergent (SOPP Soap from American Machinery Corp., Orlando, FL).

Coatings were applied with brushes made of 50% polyethylene and 50% horsehair (American Machine Corp.), prewetted with 250 mL of wax formulation/m of brush length. To determine the amount of wet coating applied, the fruit were weighed within 5 s before and after waxing (six samples). The coatings were dried under a 2 m/s flow of ambient air for several minutes over fruit rotating in a metal cage at 1.3 rpm. Coated fruit and controls were stored at ambient conditions of 21 °C and 50% average relative humidity.

Air Flux. The air flux through whole fruit was determined with an apparatus (Figure 1) similar to the viscous flow porometer developed in 1911 for leaves (Meidner and Mansfield, 1968). An 18-gage side-port syringe needle, inserted 2 cm into the blossom end, was sealed against the fruit epidermis with a 1-2-cm-diameter flange of 5-min epoxy. To ensure that the needle tip was not in a juice sac, about 3 mL of air was pulled into a syringe; the test was aborted if any liquid was withdrawn. To monitor pressure inside the fruit, the syringe was removed and the needle connected by tubing to a manometer. Through a septum fitted into that tubing, enough air was injected into the system to give an initial hydrostatic pressure of approximately 0.08 bar inside the fruit. Air flux at ambient temperature was measured by 1-5-cm movement of meniscus after steady-state flow conditions were achieved (time of 2 min or flow of 2 mL, whichever occurred first). Finally, the fruit was submerged and pressure-tested to verify the integrity of the epoxy seal and also to detect lesions in the peel.

Valencia oranges were used to determine effects of differing conditions during measurement. Mean applied pressure during the test was typically 75 cm of water (0.074 bar); however, to determine pressure dependence, flux was determined for two oranges at 12 different pressures ranging from 0.01 to 0.09 bar. Additionally, although fruit was normally not submerged under water for the test, that was done for six oranges-taking care to correct for the back-pressure exerted by the water. Further, measurements of air flux were normally under fluorescent lights; however, air flux was measured 1 day after harvest after 1 h of exposure to daylight, in darkness after 1 h, again in daylight, and so on, for six observations on each of two pieces of fruit. Finally, although air flux was routinely measured with greater pressure inside the fruit than outside, the pressures were reversed once then again for four pieces of fruit. Air flows in this case were corrected for pressure difference. Except for these variations in conditions of measurement, each piece of fruit was used for only one measurement of air flux. Localized air flux through 8-cm² sections of the peel was measured by replacing the syringe with a metal lid sealed with epoxy glue to the fruit epidermis. This made it possible to determine the magnitude of air flux through different sections of the fruit peel.



Figure 1. Apparatus (not to scale) for measuring (A) air flux of whole fruit and (B) localized flux through 8-cm² section of fruit surface.

Internal CO_2 concentration was determined by gas chromatography with a polystyrene column (Hagenmaier and Shaw, 1992). A 3-mL gas sample was withdrawn by syringe from the internal cavity of the fruit, at blossom end.

Respiration rate (RR) was determined at 50% relative humidity and 21 °C for 1.5 kg of fruit held in metal vessels of 8-L capacity. Relative humidity, monitored by passing exit gas over a hygrometer, was controlled with chilled water coils. Another set of coils controlled internal temperature, monitored with thermocouple. Respiration rate was determined after 6 h from flow rate (about 80 mL/min) and CO₂ concentration (typically 0.2– 0.4%).

Liquid-vapor surface tension (γ) was measured at 24-26 °C by the drop-weight method. Drops fell from a separatory funnel with Teflon stopcock, whose exit tube has been replaced with 0.3 cm o.d. glass tubing cut to a clean edge. Drops were collected in a receiving vessel placed on an electric balance. Weight was determined after each drop, corrected for evaporative loss from measurement of rate of weight loss of receiving vessel with no drops falling. Drop weight was corrected to infinite drop time using the factor of Jho and Burke (1983). Reported values of γ are means of two trials, each based on the weight of eight drops.

Surface wetting was determined by whether or not receding drops left behind a visually wetted surface. Ten seconds after each liquid drop was put on the surface, it was made to recede by tilting the surface and touching the bottom edge of the drop with absorbant paper. The surface was not wetted if any of three drops left behind a dry surface.

Values of advancing equilibrium contact angles (Θ) were determined with a goniometer (Model 100, Rame-hart, Inc., Mountain Lakes, NJ). Drop size was 20-30 μ L. Right and left angles were read 30-60 s after drop formation, for three separate drops. Values of Θ on fruit epidermis were measured within 3 min after sections of it were sliced from the fruit. The paraffin surface was Parafilm (American Can Co., Greenwich, CT).

Critical surface tension (γ_c) is defined as

$$\gamma_c = \lim \gamma as \, \theta \to 0 \tag{1}$$

Wu (1980) reported that γ_c is equivalent to the maximum value of the function $\gamma(1 + \cos \theta)^2/4$, here designated γ_{WU} . For our purposes, the mean of the two largest values of γ_{WU} is taken as an estimate of γ_c .

Weight loss was determined for fruit stored at 21 °C and ambient relative humidity (35-65%). For each treatment, 10 individual fruits were weighed daily.

Liquid Coating Formulations. Polyethylene wax coatings were water dilutions of a microemulsion consisting of 26% highdensity polyethylene wax (Epolene E-20, Eastman Chemical Products, Inc., Kingsport, TN), 4.6% oleic acid, and 3.9% morpholine. Undiluted E-20 was designated PEWAX26; once diluted it was PEWAX14 or PEWAX05, according to percentage of polyethylene. Shellac was Mantrolac R-49, a refined, dewaxed, bleached food-grade product (Mantrose-Haeuser Co., Westport. CT), dissolved with 0.16 g of morpholine/g of shellac. Shellac solutions were designated according to shellac and 2-propanol content, e.g., shellac 14-16 had 14 g of shellac (dry basis)/100 mL of a solvent made up of 16% 2-propanol and 84% water. The coating formulation resin was an aqueous solution of 13.5%Resinall 807A, a modified maleic wood resin (Resinall, Hattiesburg, MS) and 3.9% morpholine. Carnauba was an anionic carnauba-wax microemulsion with 20% total solids, made by water dilution of 62125-AM (Michelman, Inc., Cincinnati, OH). Also used were three commercial citrus waxes. Johnson was a water-based formulation containing carnauba wax, shellac, and

 Table I.
 Contact Angle,^s Wettability, and Critical Surface

 Tension^b of Grapefruit and Orange Epidermis

		grapefruit		orange		paraffin	
probe liquid	$\gamma,$ dyn/cm	θ, deg	γwu, dyn/cm	θ, deg	γ _{wU} , dyn/cm	θ, deg	γ _{wυ} , dyn/cm
water	71.0	99	13	100	12	111	7
glycerin	63.3	93	14	98	12	95	13
formamide	57.2	86	16	89	15	92	13
ethylene glycol	47.0	73	20	72	20	81	16
methyl sulfoxide	43.1	57	26	60	24	72	19
1-propanol	23. 8	0°	24	04	24	30	21

^a Standard error (SE) = 0.3 dyn/cm. ^b SE = 3° for fruit and 1.0° for paraffin. ^c Receding liquid wetted the surface.

fatty acid amines (Primafresh HS from Johnson Wax, Racine, WI; diluted to 80% strength before use). Another water-based formulation, *citrus wax*, contained shellac, wood rosin, ethanol, NH4OH, KOH, and fatty acids. Finally, *solvent wax* contained coumarone-indene resin in a solvent consisting of xylene and petroleum naphtha.

Multiple Regression. Multiple linear regression was used to fit the following equation for both CO_2 and water vapor

$$r = \text{constant} + Sr_{\text{cost}} - N(\text{flux ratio})$$
 (2)

where r is gas resistance of the fruit, S and N are coefficients (selective and nonselective), and flux ratio is the air flux of the treated sample divided by air flux of uncoated control. The values for constants and coefficients are calculated by least-squares analysis (Statistix 3.1, Analytical Software, St. Paul, MN).

Values of $r_{\rm coat}$ were from mean values of coating thickness and published values of permeability at 30 °C. For example, polypropylene wax has a CO₂ permeability of 135 000 mL(STP) mil/(m² day atm) (Hagenmaier and Shaw, 1991). A coating of thickness 0.15 mg/cm², equivalent to 0.06 mil thick, has resistance (calculated as thickness/permeability) of 352 s/cm, giving due consideration to differences in units. Values of permeability of *resin*, Johnson, citrus wax, and solvent wax were those reported for samples 5, F, P, and G, respectively, in Hagenmaier and Shaw (1992).

Resistance of the coated fruit to CO₂ was calculated from

$$r_{\rm CO_2} = K(\Delta\% \ {\rm CO_2})/{\rm RR} \tag{3}$$

where r_{CO_2} is fruit CO₂ resistance in units of s/cm, K is a constant determined by weight and surface area of the fruit, $\Delta\%$ CO₂ is the CO₂ level inside the fruit minus its value outside, and RR is respiration rate. For example, a 320-g grapefruit with surface area 230 cm² has K = 47 200. With RR of 9.5 mg of CO₂/(kg h) and internal CO₂ of 5.4%, the value for $r(CO_2)$ is 27 000 s/cm. Similar calculations apply to $r(H_2O)$, the resistance of water vapor. The calculations were performed separately for grapefruit and oranges.

Flavor was determined by taste panel evaluation on 1–9 hedonic score of juice extracted from the fruit, using 16 experienced but untrained panelists.

RESULTS AND DISCUSSION

Surface Properties. The values of θ for reference solvents on citrus epidermis tend to be slightly lower than their values on paraffin (Table I), indicating that if a coating spreads on paraffin (a readily available surface), it will also spread on citrus fruit. The value of θ for water on citrus epidermis is similar to those of water on leaf-wax constituents (Holloway, 1969).

None of the reference solvents wetted paraffin, and only 1-propanol, which had the lowest value of γ (23.8 dyn/ cm), wetted citrus epidermis. For shellac coatings, γ of 29.2 dyn/cm was sufficiently low to wet the surface of grapefruit (Table II). For uniform coating of fruit surfaces, wettability would seem a more applicable property than contact angle, since coatings are applied to fruit surfaces by brushing rather than by spontaneous spreading.

Table II. Properties of Marsh Grapefruit, Harvested December 2, Coated with Shellac Solutions of Differing Surface Tension (Coated Fruit Was Stored for 2-5 Days at 21 °C, 50% Relative Humidity)

coating type	γ,ª dyn/cm	⊖,⁵ deg	coat thickness, ^c mg/cm ²	RR ^d	% CO₂⁰	wt loss, %/h
uncoated control			0	10.8	0.9	0.030
shellac 14-0	41.5	59	0.26	6.4	8.4	0.018
shellac 14-10	36.5	51	0.22	7.7	6.7	0.019
shellac 14-25	29.2	48 ª	0.26	7.2	9.5	0.021

^a SE = 0.3 dyn/cm. ^b SE = 3°. ^c Means for six fruit per trial. SE = 0.01 mg/cm². ^d In units of (mg of CO₂)/kg h. Two trials. SE = 0.5. ^e Internal CO₂. Means for six fruit per treatment. SE = 6% of mean. ^f Ten fruit per treatment. SE = 0.002%/h. ^g The surface of the fruit was wetted by receding drop.

Table III. Marsh Grapefruit Harvested December 13, Coated with Waxes of Differing Permeability and Same Surface Tension (Application Rate for Both Waxes Was 0.17 mg/cm², Dry Basis)

coating type	θ⁰	γ, ^b dyn/cm	RR¢	$\overset{\%}{\mathrm{CO}_{2^{d}}}$	wt loss," %/h	flavor score
uncoated control			10.6	2.0	0.032	5.7
shellac 14-16	53 ^e	33.4	6.3	9.3	0.017	4.6
PEWAX14	56 ^g	33.4	9.0	3.7	0.013	5.4

 a SE = 0.3 dyn/cm. b Contact angle. SE = 3°. c Units are (mg of CO₂)/kg h. Three trials. SE = 0.4. d Internal CO₂ after 3–6 days for eight fruit per treatment. SE = 0.6. The means after 18 days of storage were 2.0, 11.1, and 3.8%, respectively. e Weight loss from third to eighth day of storage at 21°C, 50% relative humidity. Ten fruit per treatment. SE = 0.002%/h. $^/$ Hedonic score of juice from fruit stored for 2 weeks, 16 panelists. s Fruit surface was wetted by coating formulation.

Influence of γ on coating performance was tested using liquid coating formulations with the same coating solids but varying alcohol contents and by assuming all formed coatings of the same permeability after solvent evaporation. Contact angles and wettability were markedly dependent on alcohol content (Table II). The coating formulation without alcohol had higher γ than water-based commercial coating formulations, eight of which had γ of 31-35 dyn/cm-values between those of our formulations with 10 and 25% alcohol. Despite differences in γ of the liquid formulations, the coated grapefruit had virtually the same RR, internal CO_2 , and weight loss (Table II). In addition, flux through an 8-cm² section of peel was reduced to less than 5% of control for all three treatments (three trials each). The γ of coating formulations was apparently not important to performance of the coating.

Values of γ_{WU} for different liquids indicate that γ_c was approximately 23 dyn/cm for grapefruit and orange peel. The measured value for paraffin was 20 dyn/cm, which agrees with reported values of 15–22 dyn/cm (Kaelble, 1970). Values of 25–28 for γ_c were reported for leaf surfaces of soybean, corn, and wheat (McKay et al., 1985).

For the coating formulations used in this study, all values of Θ were less than 90° (Tables II, III, and V), which suggests these coating formulations could enter cylindrically shaped pores (Adamson, 1990). However, because stomata are not cylindrically shaped, it has been proposed that only those liquids with γ below γ_c can penetrate stomata (Schonherr and Bukovac, 1972). Of the coating formulations used in this study, only the nonaqueous formulation (Table IV) could enter stomata by Schonherr's criterion.

Air Flux, Preliminary Observations. Results of air flux measurement under different test conditions were used in developing the method. First, at 0.01–0.09 bar the air flux was proportional to pressure difference (correlation coefficient = 0.999). Second, air flux measured at 0.074 bar decreased from 0.94 ± 0.4 to 0.06 ± 0.01 when fruit was submerged under water (95% confidence intervals). In further tests with submerged fruit the air flux increased approximately 10-fold when pressure was subsequently raised to about 0.25 bar, with air bubbles appearing fairly uniformly over the peel. Taking pressure as 2γ /radius and assuming that the bubbles, at time of initiation, have radius equal to that of the exit holes, we find at 0.074 bar that air can exit holes as small as 0.002-cm radius and at 0.25 bar as small as 0.0006-cm radius, about the size of the over 200 000 stomata on a citrus fruit (Albrigo, 1972; Turrell and Klotz, 1940). All other values of air flux reported herein were at mean pressure of 0.06–0.08 bar, using fruit not submerged in water.

Third, air flux was 7% higher for fruit exposed to sunlight, compared to darkness (SE = 2%). This suggests that the main pathway for viscous flow is not through active stomata, leaving as possibilities lenticels (which remain open in dark and light (Pantastico, 1975) or inactive stomata. Fourth, air flux was 5% lower with the fruit with excess pressure inside the fruit compared to that with negative pressure inside (SE = 2%).

Steady-state air flux was achieved within 1 min; thereafter, flow held steady for 3 h. Now, the volume of air flowing through uncoated citrus fruit each hour was roughly equal to the total volume of the fruit. Maintenance of such values of air flow for long periods indicates that what was measured was not air flowing into the fruit and building up pressure there. Nor do such magnitudes seem possible from selective permeation. A barrier with gas resistance of 10000 s/cm and area of 200 cm² (the size of an orange surface) would exhibit a permeance of 0.001 mL/min at 0.07 bar, less than 1% of the observed values of air flux.

Mean air flux of field-run grapefruit was 6.2 mL/min, sd = 5.5 mL/min; 95% of values were in the range 1.6-10 mL/min. For washed grapefruit the mean was 4.5 mL/min, sd = $4.9 \text{ cm}^3/\text{min}$; 90% had values in range 1.6-10 mL/min. Thus, washing of the fruit did not significantly change air flux (Student's t, p = 0.05), and the observed values cannot be attributed to damage caused by washing. Data are for 57 washed and 23 field-run Marsh grapefruit, mean weight 320 g, mean surface area 230 cm², 1 week after harvest.

Air flux decreased to 1.6 mL/min for five very shriveled grapefruit stored for 8 weeks (SE = 0.7%). Mean weight loss amounted to 30%. All other values reported in this paper were determined after no more than 10 days of storage.

Air Flux of Coated Fruit. For uncoated grapefruit only about 5% of the air flow was through the area near the stem (Table VI). For coated fruit, on the other hand, the stem region was a major pathway for air flow, indicating that wax coatings are more efficient at blocking holes in the peel than in the stem region.

Coating thickness was not a critical factor in determining air flux of whole fruit (Table IV). However, the type of coating was critical. For coatings of similar thickness (0.2- $0.5 \text{ mg/cm}^2)$ the air flux was lowered 92-98% for resinous coatings (shellac, wood rosin, or coumarone-indene resin; Tables II, IV, and V). By contrast, wax microemulsions reduced air flux by only 78-83\%. A possible explanation is that the dried emulsions retain some of the globule structure, making these somewhat porous.

Coating Thickness vs Coating Type. Compared to polyethylene wax, grapefruit coated with shellac had CO_2 resistance about 4 times as high (Table IV). Fruit with

Table IV. Marsh Grapefruit, Harvested January 8, Coated with Waxes of Various Concentrations, and Stored at 21 °C for 2-5 Days

coating type	$\gamma,^a \mathrm{dyn/cm}$	coat thickness, ⁶ mg/cm ²	RR¢	% CO2 ^d	wt loss," %/h	air flux,/ mL/min	<i>r</i> _{CO₂} , ^g s/cm
uncoated control		0	14.6	2.4	0.023	3.8	6 500
shellac 25-16	33.1	0.47	6.6	16	0.014	0.1	110 000
shellac 14-16	33.5	0.28	8.1	17	0.015	0.1	100 000
shellac 05-1	32.9	0.09	8.2	11	0.016	0.4	60 000
PEWAX26	32.9	0.53	10.2	5.7	0.011	0.7	25 000
PEWAX14	33.3	0.15	9.5	5.4	0.012	0.9	25 000
PEWAX05	35.2	0.10	11.7	4.7	0.014	0.8	17 000

 a SE = 0.3 dyn/cm. b SE = 6% of mean. c Units of (mg of CO₂)/kg h. Three trials, 2–7 days of storage. SE = 0.4. d After 2–7 days of storage. Means of six fruit. SE = 7% of mean. e From third to fifth day of storage. SE = 0.002 %/h. / Measured 1–2 days after coating. SE = 27%. Four fruit per treatment. e Calculated per eq 3.

Table V. Valencia Oranges Coated with Different Waxes [Coated Fruit Are Ranked According to Decreasing $r_{coat}(CO_2)$]

coating type	γ,° dyn/ cm	₽⁵	coat thickness ^c mg/cm ²	R R ^d	wt loss,e %/h	% CO₂∕	air flux,/ mL/mir
uncoated control			0	19.6	0.049	4.5	1.2
shellac 14-16	33.5	54^{h}	0.31	13.3	0.030	18.6	0.05
resin	35.6	46 ^h	0.22	15.8	0.028	16.0	0.10
citrus wax	34.5	47^{h}	0.25	10.2	0.026	11.1	0.09
carnauba	28.8	46 ^h	0.46	14.6	0.013	7.6	0.27
solvent wax	22.7	0^h	0.21	12.5	0.020	9.5	0.05
Johnson	30.8	49 ^h	0.22	12.8	0.024	9.4	0.21
PEWAX14	33.3	59 ^h	0.23	14.5	0.025	6.2	0.24

^a SE = 0.3 dyn/cm. ^b SE = 3°. ^c SE = 0.04 mg/cm². ^d SE = 1.0 mg of CO₂/(kg h). Three trials per treatment. ^e There were four fruit per treatment. SE = 0.03%/h ^f N = 6, Se = 12% of mean. ^g N = 6, Se = 23% of mean. ^h The peel was wetted by the wax.

Table VI. Air Flux of Coated and Uncoated Grapefruit

	local	ized flu	ıx, mL/r	whole fruit air flux ^c		
$peel^a$ stem end ^b		end^b	mL/1	nL/min		
coating type	mean	CV ^d	mean	cv	mean	CV
control ^e	0.24	1.1	0.23	0.3	4.5	1.1
shellac 14-16	0.005	0.6	0.05	1.0	0.07	0.7
PEWAX14	0.03	0.5	0.2	0.3	0.9	0.8

^a Flux through a 8-cm² section of epidermis midway between stem and blossom end, at pressure of 0.074 bar; 5 fruit per treatment.^b Air flux of 8-cm² area over the stem. ^c For entire fruit; 57 samples for control, 4 each for the waxed fruit. ^d Coefficient of variation. ^e All fruit were washed; control was not waxed.

thick coatings tended to have higher $r_{\rm CO_2}$ than those with thin coatings, though these differences were not as large (Table IV). Indeed, the fruit with thinnest shellac coating (0.09 mg/cm²) had $r_{\rm CO_2}$ double that of fruit with thickest wax coating (0.53 mg/cm²). The conclusion for CO₂ exchange is that coating type is far more important than coating thickness. In general, high values of $r_{\rm CO_2}$ resulted from use of resinous coatings and low values from waxy coatings.

The same conclusion does not apply to resistance to water vapor. There, coating thickness seems as important as type.

Coating formulations from four commercial suppliers, applied per manufacturer recommendations, would have given coatings of mean weight 0.22 mg/cm^2 , equivalent to 0.08- μ m thickness, near the middle values of Table IV, far below the 20 μ m reportedly necessary to completely cover stomatal pores (Brusewitz and Singh, 1985).

Regression Analysis. From mere inspection of the data (Tables IV and V) it is not readily apparent just why resinous coatings cause fruit to have higher r_{CO_2} values, since—compared to waxy coatings—these have two different properties that would tend to inhibit air exchange:

Table V	VII.	Regression	Coefficients
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gas	fruit	constant, s/cm	S^b	-N,ª s/cm
CO ₂	orange ^b	33 000 ± 600	0.5 ± 0.1	28 000 ± 1 000
	grapefruit ^c	35 000 € 800	0.8 ± 0.1	31 000 ± 17 000
H ₂ O	orange ^b	92 ± 5	0.6 € 0.1	37 € 12
	grapefruit ^c	154 ± 12	1.0 € 0.4	46 € 23

 a For eq 1. The values after \pm signs are standard errors. b Constant and coefficient fitted from data of Table VI. c From data of Table V.

first, the resinous coatings are more effective at sealing holes in the fruit epidermis; second, they have lower permeability (Hagenmaier and Shaw, 1991, 1992).

The relative importance of these two properties is shown by regression analysis (Table VII), especially if a numerical example is used as illustration. Consider a coating with $r_{\rm coat}({\rm CO}_2) = 20\,000\,{\rm s/cm}$. Suppose a grapefruit with this coating has air flux of 0.3 mL/min, compared to 3.8 mL/ min for uncoated control. The values of N and S from Table VII predict that as a result of coating the fruit, $r_{\rm CO_2}$ would rise 29 000 s/cm from sealing pores [calculated as $-31000 \times -3.5/3.8$] and 16 000 s/cm from reduced permeance [calculated as 20000×0.6). Similarly calculated, water vapor resistance would rise 46 s/cm from sealing pores and 14 s/cm from reduced permeance. For this example, increase in resistance to passage of both CO_2 and water vapor is caused more by sealing pores than reducing permeance. The same conclusion seems to hold in general, except for coatings with very high resistance.

It is not possible, however, to predict reliably any numerical values of coated-fruit resistance from the fitted equations, for several reasons. First, the coating resistance and pore-blocking ability are linked, since gas exchange is partly determined by the permeance of the material that is sealing openings in the peel. Second, the fitted equations are based on values of coating permeability not determined at the same conditions of temperature and relative humidity used in the present work. Third, fruit resistance is not expected to be linearly dependent on air flux, considering that laminar air flow through an orifice is proportional to r^4 (Poiseuille's law), whereas diffusion through apertures varies with the first power of radius (Stefan's law). Hence, air flux overrates the importance of large holes, probably more so for coated fruit because large holes would presumably be the last to be blocked by coating.

Despite our inability to predict numerical values, it seems an important conclusion that gas resistance of coated fruit is strongly influenced by the coating's ability to block pores on the surface of the fruit. This means that changes in formulation to reduce hole blockage may improve the performance of the coating. For example, wax microemulsions that have larger globule size might not be so effective in sealing pores.

Flavor. Juice from shellac-coated grapefruit had poorer flavor than fruit coated with polyethylene wax (p = 0.99, Table III). Poor flavor has also been correlated to elevated internal CO₂ of citrus fruit by others (Cohen et al., 1990).

LITERATURE CITED

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- Adamson, A. W. Physical Chemistry of Surfaces; Wiley: New York, 1990; pp 12, 392, 496.
- Albrigo, L. G. Ultrastructure of cuticular surfaces and stomata of developing leaves and fruit of the Valencia orange. J. Am. Soc. Hortic. Sci. 1972, 97, 761-765.
- Brusewitz, G. H.; Singh, R. P. Natural and applied wax coatings on oranges. J. Food Process. Preserv. 1985, 9, 1-9.
- Burg, S. P. Theory and practice of hypobaric storage. In Food preservation by modified atmospheres; Calderon, M., Barkai-Golan, R., Eds.; CRC Press: Boca Raton, FL, 1990.
- Cohen, E.; Shalom, Y.; Rosenberger, I. Postharvest ethanol buildup and off-flavor in Murcott Tangerine fruits. J. Am. Soc. Hortic. Sci. 1990, 115, 775-779.
- Durand, B. J.; Orcan, L.; Yanko, U.; Zauberman, G.; Fuchs, Y. Effects of waxing on moisture loss and ripening of Fuerte avocado fruit. *HortScience* 1984, 19, 421-422.
- Farooqi, W. A.; Salih Ahmad, M.; Zain-ul-Abdin. Effect of waxcoatings on the physiological and bio-chemical aspects of Kinnow Fruit. Pak. J. Sci. Ind. Res. 1988, 31 (2), 142-145.
- Hagenmaier, R. D.; Shaw, P. E. Permeability of coatings made with emulsified polyethylene wax. J. Agric. Food Chem. 1991, 39, 1705–1708.
- Hagenmaier, R. D.; Shaw, P. E. Gas permeability of fruit coating waxes. J. Am. Soc. Hortic. Sci. 1992, 117 (1), 105-109.
- Hasegawa, Y.; Iba, Y. The effects of coating with wax on citrus fruit. I. Characteristics of various wax coatings. Kaju Shikenjo Hokoku B 1980, 7, 85–97.
- Holloway, P. J. Chemistry of leaf waxes in relation to wetting. J. Sci. Food Agric. 1969, 20, 124-128.

- Jho, C.; Burke, R. Drop weight technique for the measurement of dynamic surface tension. J. Colloid Interface Sci. 1983, 95 (1), 61-71.
- Kaelble, D. H. Dispersion-polar surface tension properties of organic solids. J. Adhes. 1970, 2, 66-81.
- Lebovits, A. Permeability of polymers to gases, vapors and liquids. Mod. Plast. 1966, 43 (3), 139–213.
- McKay, B. M.; Koch, R.; Herbert, R. M. Selection of Wetting Adjuvants. Pesticide Formulations and Application Systems. ASTM Spec. Tech. Publ. 1985, 875, 27-31.
- Meheriuk, M.; Porrit, S. W. Effects of waxing on respiration, ethylene production, and other physical and chemical changes in selected apple cultivars. *Can. J. Plant Sci.* 1972, 52 (3), 257-259.
- Meidner, H.; Mansfield, T. A. Physiology of Stomata; McGraw-Hill: New York, 1968.
- Nobel, P. S. Biophysical Plant Physiology; Freeman: San Francisco, 1974; p 325.
- Pantastico, E. B. Structure of fruits and vegetables. In Postharvest Physiology, Handling and Utilization of Tropical and Subtropical Fruits and Vegetables; Pantastico, E. B., Ed.; AVI: Westport, CT, 1975.
- Schonherr, J.; Bukovac, M. J. Penetration of stomata by liquids. Plant Physiol. 1972, 49, 813-819.
- Turrell, F. M.; Klotz, L. J. Density of stomata and oil glands and incidence of water spot in the rind of Washington Navel orange. *Bot. Gaz.* **1940**, *101*, 862–871.
- Wu, S. Surface tension of solids: generalization and reinterpretation of critical surface tension. *Polym. Sci. Technol.* 1980, 12A, 53-65.

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