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Volatile Response of Four Apple Varieties with Different Coatings during Marketing at Room Temperature

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Five experimental coatings with different resistance to gas exchange were used with freshly harvested and 20-week commercially stored apples of Delicious, Fuji, Braeburn, and Granny Smith varieties. The coated or noncoated apples were held at 20 °C for up to 4 weeks. The gas partial pressures inside the fruits with the various coatings ranged from 1 to 25 kPa CO_2 and from 20 to 1 kPa O_2. Volatile evaporation rates were measured, as also were the volatiles compositions in the fruit. The coatings with intermediate gas resistance (carnauba–shellac mixture and candelilla) gave intermediate values of CO_2 and O_2 in the internal atmosphere in Delicious, Fuji, and Braeburn apples and the highest concentrations of butyl acetate and 2-methylbutyl acetate in the fruits. The coatings with the highest gas resistance (shellac and shellac–protein) caused high internal CO_2 and low O_2, resulting in anaerobic fermentation in Braeburn and Granny Smith apples and relatively high amounts of low-molecular-weight ethyl esters trapped within the fruit. A small portion of the alcohols were evaporated from fruits compared to esters, this attributed to their high Henry's law coefficients.

KEYWORDS: **Apple; coating; volatile; ester; alcohol; internal gas; modified atmosphere; variety**

INTRODUCTION

Although it is well known that the flavor of apples is an important quality factor (*1–3*) and can be significantly affected by the kind and amount of coating applied (*4–6*), it nevertheless often happens that coatings are selected mostly for their affect on the fruit's appearance (*7*). Coatings affect postharvest physiological and quality changes by making the fruit skin more of a barrier to gas exchange. The pioneering work of Burg and Burg (*8*) showed that the O_2 and CO_2 partial pressures inside the fruit are determined by the barrier properties of the skin, which are, in turn, affected by the gas permeability of the coating and how the coating blocks the hole (lenticels, stomata, lesions, etc.) in the skin (*4*, *9*, *10*).

Thus, fruit coatings result in elevated internal CO_2 and reduced internal O_2 concentrations such as those found in controlled atmosphere (CA) storage and modified atmosphere (MA) packaging. In both cases, the elevated CO_2 concentration or low O_2 concentration, or a combination of the two, inside the fruit or the package retards the reopening and senescence, which in turn can affect concentrations of flavor volatiles. In addition, fruit coatings might help to trap volatiles inside the fruit (*5*).

Modified atmosphere storage of apples, despite its wide usage to help preserve quality, does result in a decrease in major apple esters and some risk of hypoxia and fermentative metabolism (*11–20*). An interactive effect occurs as increased CO_2 decreases the tolerance of fruit to low O_2, and vice versa CO_2 (*19*, *21*). Under fermentative metabolism, ethanol synthesis increases, and therefore ethyl esters are competitively produced in fruit. As a result, the balance among the volatiles, many of which are important aroma components, is distorted, leading to unnatural flavor or off-flavor, depending on the CO_2 and O_2 concentrations (*14*, *16*, *22*).

The purpose of this work was to investigate the influence of the experimental coatings with different gas resistance on the amounts of flavor volatiles in four varieties of apples.

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MATERIALS AND METHODS

Fruit. Freshly harvested and 20-week commercially stored Delicious, Fuji, Braeburn, and Granny Smith apples were obtained from Publix Supermarket after having been shipped from Washington to Florida in refrigerated trucks overnight. The freshly harvested apples arrived on Oct 25, 2000, and were stored at 3 °C until coating application on Nov 10; the 20-week-stored (by Yakima Fruit & Cold Storage Co, Yakima, WA) apples arrived on March 15, 2001, and were stored at 3 °C until coating application on March 20. The basic attributes of the fruit and storage conditions are shown in **Table 1**. Delicious, Fuji, and Granny Smith apples were stored in the optimal CA conditions at 1 °C, respectively. However, Braeburn apples were stored in regular atmosphere at 3 °C instead of CA, because they are sensitive to high CO_2 (*23*, *24*).

Coatings. The experimental coatings, made in our laboratory, had the following formulations. Polyethylene: 18.6% oxidized polylethylene (AC680, AlliedSignal Inc., Morristwon, NJ), 3.4% food-grade oleic acid (Emersol 6321, Henkel, Cincinatti, OH), 2.8% mopholine, and 0.01% polydimethylsiloxane antifoam (SE21, Wacker Silicones Corp., Adrian, MI); here and in all cases the balance was water. Candelilla:

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Table 1. Attributes of Apples and Storage Conditions Used in This Research

	freshly harvested			20-week stored					
							storage conditions[a]		
variety	weight	Brix	TA ($g \cdot 100\ g^{-1}$)	weight	Brix	TA ($g \cdot 100\ g^{-1}$)	CO_2 (kPa)	O_2 (kPa)	temp (°C)
Delicious	197	13.0	0.13	235	12.8	0.10	2	8	1
Fuji	204	14.2	0.14	247	15.4	0.10	1.8	1.8	1
Braeburn	222	12.8	0.24	247	12.0	0.17	regular atmosphere		3
Granny Smith	201	11.6	0.36	231	12.4	0.19	1.7	2	1

[a] Storage conditions during the 20-week storage preceding application of coatings.

18.3% candelilla wax (type SP 75, Strahl & Pitsch Inc., West Babylon, NY), 2.1% oleic acid, 2.4% morpholine, and 0.02% polydimethylsiloxane antifoam. Carnauba−shellac: 9.5% shellac (type R52, Mantrose Haeuser Co., Attleboro, MA), 8.3% carnauba wax (No. 1, Strahl & Pitsch), 3.3% morpholine, 1.7% oleic acid, 0.17% NH_3, and 0.01% polydimethylsiloxane antifoam. Shellac: 19% shellac, 1.0% oleic acid, 4.4% morpholine, 0.3% NH_3, and 0.01% polydimethylsiloxane antifoam. Shellac−protein: 13.3% shellac, 3.0% whey protein isolate (BiPRO, Davisco Foods International, Inc., Le Sueur, MN), 3.1% morpholine, 0.7% oleic acid, 0.2% NH_3, and 0.01% polydimethylsiloxane antifoam. All of the other coatings were used on both freshly harvested fruit and 20-week-stored fruit, except for shellac−protein, which was only used on freshly harvested fruits, and because its effect on apples was similar to that of shellac coating on freshly harvested fruits, it was not used in later experiments.

Processing. Apples were washed with standard packinghouse-type rotary brushes (polyethylene, Industrial Brush Co., Eaton Park, FL). The fruits were soaked in 5% commercial cleaner (Fruit & Vegetable Kleen 241, ELF Atochem North America, Inc., Monrovia, CA) for 30 s prior to being put on the brush line. The brush diameter was 12 cm, and rotation was 22 rpm. The line included 20 rotaries, and the fruit stayed on the line for about 2 min. Washed fruit was rinsed through a top shower rotary and then dried for 5 min at 50 °C using a pilot-plant-scale conveyor dryer (Central Florida Sales and Service, Inc., Auburndale, FL). Coating was applied by spreading 1.0 mL of liquid coating over the fruit surface using latex-gloved hands. Instead of coating, water was used for noncoated control. Coated fruit were dried for 5 min at 50 °C in the same pilot plant as described above. After application of the coatings, the apples were stored at 20 °C and 70% relative humidity for up to 4 weeks. The mean amount applied was 0.6 g of liquid coating per apple.

Ethylene Production and Volatiles Evaporation. The ethylene production and volatiles evaporation rates were measured at 20 °C by putting six apples in a 3.9-L container, which was then flushed with humidified air at 21 $mL \cdot min^{-1}$ for at least 15 h, which was determined to be a sufficient time to achieve steady-state partial pressure flowing out of the containers, and measurements were taken twice for each container. Three replicates (containers) were applied for each treatment. The measurements were made at week 1 and week 3 after coating for freshly harvested apples and were made only at week 1 for 20-week-stored apples, because of the quality deterioration of most of the varieties except Fuji.

Ethylene partial pressures were measured with a gas chromatograph (GC, model 8500, Perkin-Elmer, Norwalk, CT) equipped with an activated alumina column and a flame ionization detector.

Volatile esters and alcohol concentrations in the exhaust gases from the containers were measured with a GC (Perkin-Elmer Autosampler) equipped with a flame ionization detector. The column was Stabilwax, 0.53 mm × 60 m carbowax capillary (2.0-μm film thickness, Restek, Bellefonte, PA). The oven temperature was 115 °C. Peak identities were confirmed by matching the retention times of sample peaks with those of standards on the Stabilwax column and with those on medium- and low-polarity columns. The low-polarity column was DB5, 0.32 mm × 60 m (5%-phenyl)-methylpolysiloxane capillary (1.0-μm film thickness, J&W Scientific, Folsom, CA), used at 60 °C for 0.1 min, ramped at 7 $°C \cdot min^{-1}$ to 140 °C, and held there for 4 min. The intermediate polarity column was EC20, 0.32 mm × 30 m 20% phenyl−80% methylpolysiloxane (0.25-μm film thickness, Alltech Associates, Inc., Deerfield, IL), used at 50 °C for 0.1 min, ramped at 5 $°C \cdot min^{-1}$ to 90 °C, and held.

Internal Gases. Samples for internal gas measurement were obtained from the seed cavity of fruit under submerged conditions (*25*). Ten replicate fruits were applied for each treatment. The measurements were made at week 0 (initial), week 2, and week 4 after coating for freshly harvested apples and were made only initially and at week 2 for 20-week-stored apples, because of the quality deterioration of most of the varieties except Fuji.

The CO_2 and O_2 partial pressures were analyzed by using a GC (HP 5890A, Hewlett-Packard, Avondale, PA) equipped with a CTR 1 column and a thermal conductivity detector (*4*). Ethylene partial pressures were analyzed using GC as described above.

Volatiles Concentration. For volatiles analysis (*4*), three samples, each consisting of 50-g apple slices (core tissue removed) pooled from six apples, were homogenized with 25 mL of deionized water and 25 mL of saturated NaCl solution. Two milliliters of homogenate was then placed into a 6-mL vial sealed with a crimp-top and Teflon−silicone septum, flash frozen in liquid nitrogen, and stored at −80 °C prior to analysis. For GC analysis, sample vials containing homogenate were thawed under running tap water, heated rapidly to 80 °C, and incubated for 15 min by using a Perkin-Elmer HS-6 headspace sampler heating block before the headspace was pressurized and injected onto the GC column. The analysis was carried out using a gas chromatograph (Perkin-Elmer model 8500) equipped with a 0.53-mm × 30-m polar Stabilwax capillary column (1.0-μm film thickness, Restek) and a flame ionization detector. The oven temperature was held at 40 °C for 6 min and then raised to 180 °C at a rate of 6 $°C \cdot min^{-1}$. The compounds were identified by comparison of their retention times with those of standards and by enrichment of apple homogenate with authentic samples. The concentrations of volatiles in the homogenates were calculated from the peak height of headspace samples, using the regression equations, determined by injecting five different concentrations of each standard to obtain a peak height calibration curve (*26*). The standard homogenates were prepared by adding 4 μL of an aqueous ethanolic solution of the standard volatiles to 2 mL of a bland homogenate which had been stripped of flavor volatiles by refluxing at 100 °C for 10 h. Identification of volatiles was periodically checked by spiking the homogenate with standards. The volatile components that were analyzed were those found to be abundant or reported to be significant for apple (*6*, *27*), including ethanol, ethyl acetate, ethyl butyrate, ethyl hexanoate, butanol, butyl acetate, 2-methylbutyl acetate, and 2-methylbutyl 2-methylbutanoate.

The measurements of volatile concentration were made at week 0 (initial), week 2, and week 4 after coating for freshly harvested apples and were made initially and at week 2 for 20-week-stored apples.

Volatiles Accumulation. The accumulation rate of volatiles, namely the volatiles increase rate in fruit, was calculated by

$$\text{accumulation rate } (\text{nmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}) = (C - C_0)/(\text{weight} \times \text{time})$$

where C was the measured volatiles concentration in flesh at week 2 and C_0 the initial concentration during holding at 20 °C. Except for

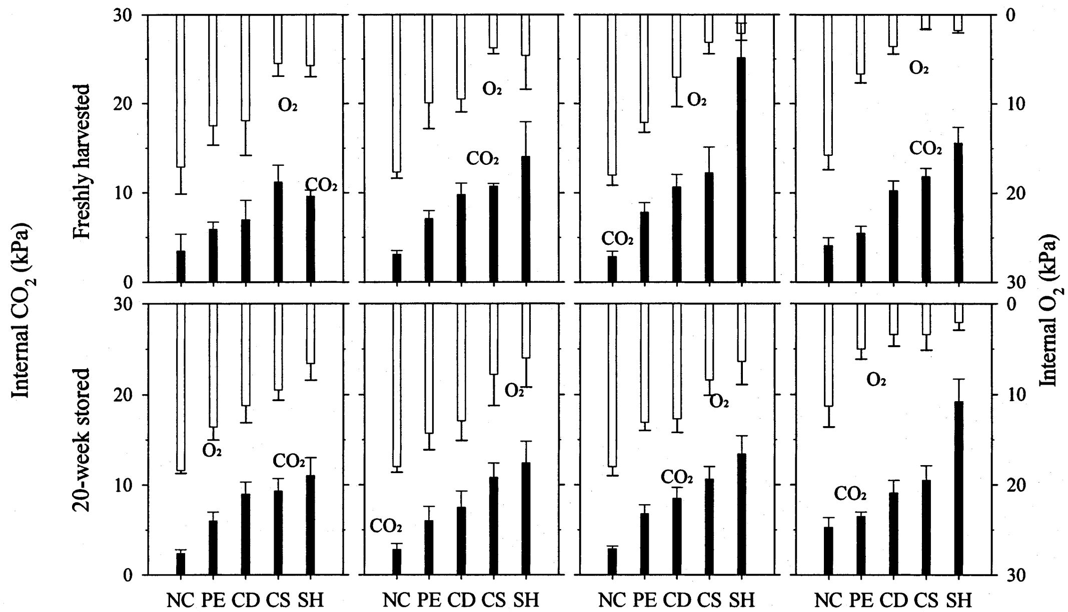

Figure 1. Internal CO_2 and O_2 partial pressures of apples with different coating treatments at 20 °C. Freshly harvested or 20-week commercially stored apples of four varieties were coated with five coating treatments and held at 20 °C for 2 weeks. Commercial storage conditions are shown at **Table 1**. Abbreviations for coating treatments: NC, noncoated; PE, polyethylene; CD, candelilla; CS, carnauba–shellac; and SH, shellac.

Table 2. *F*-Values and Significant Levels from Analysis of Variance Performed on Some Major Volatiles of Four Apple Varieties for Two Prestorage Durations, Six Coating Treatments, and Three Marketing Durations[a]

source	DF	1-butanol	butyl acetate	butyl butanoate	2-ethylbutyl acetate	2-methylbutyl 2-methylbutanoate	ethanol	ethyl acetate	ethyl butanoate	ethyl hexanoate	total
variety (V)	3	55.53**	128.72**	30.38**	115.5**	21.82**	20.51**	42.72**	55.89**	4.24**	15.81**
prestorage duration (P)	1	66.20	1.69	94.07**	0.11	0.05	0.36	56.45**	2.39	4.69*	3.83
coating (C)	5	3.94**	12.87**	2.22	14.87**	11.67**	37.84**	61.95**	31.73**	0.95	59.07**
marketing duration (M)	2	1.29	1.37	2.58	10.76**	12.68**	10.31**	8.64**	16.49**	253.8**	11.73**
V × P	3	28.10**	7.77**	23.24**	4.50**	6.70**	8.37**	9.25**	19.51**	22.89**	13.23**
V × C	15	1.41	5.59**	0.84	3.34**	1.25	4.84**	14.94**	3.46**	0.15	5.51**
V × M	6	0.39	1.12	0.32	6.36**	5.73**	1.83	3.41**	1.91	22.27**	1.02
P × C	4	1.26	0.71	0.68	2.55*	1.03	0.39	5.25**	2.35	0.71	0.34
P × M	2	3.52*	3.47*	21.04**	0.87	1.41	0.18	1.68	13.09**	193.14**	0.61
C × M	5	0.22	0.78	0.52	1.32	0.55	0.39	0.88	2.07	0.55	0.42
V × P × C	10	1.22	0.91	0.32	1.38	1.31	2.18*	0.26	1.06	1.06	2.09*
V × P × M	3	0.73	0.68	0.04	2.45	1.94	1.49	0.76		49.67	2.51
V × C × M	10	0.11	0.91	0.18	0.9	1.05	1.09	1.32	1.28	0.21	0.96
P × C × M	4	1.25	0.31	2.01	0.76	0.61	0.24	0.33	7.56**	3.49*	1.03
mean peak height		1075	2289	1048	2635	571	21298	6609	1949	903	50200

[a] Varieties are Delicious, Fuji, Braeburn, and Granny Smith; coating treatments are noncoated, polyethylene, candelilla, carnauba–shellac, shellac, and shellac–protein; prestorage durations are freshly harvested (0 week) and commercial prestorage for 20 weeks; and marketing durations are 0, 2, and 4 weeks at 20 °C after coating. Statistical analysis was based on FID response in peak height: *, $p < 0.05$; **, $p < 0.01$.

ethylene, the amounts of volatiles in the headspace were ignored in the calculation of accumulation rates. Ethylene concentration in the flesh was not measured, but rather estimated from the internal pressure and its Henry's law constant, assuming 200 mL of gas phase per kilogram of fruit.

Statistical Test. PROC GLM of SAS Version 8 (SAS Institute, Cary, NC) was used for analysis of variance. Mean separation was determined by the Scheffe's test.

RESULT AND DISCUSSION

Interior Gases. The internal CO_2 partial pressures ranged from 1 to 25 kPa, and O_2 partial pressures ranged from 20 to 1 kPa, depending on the apple varieties and coating treatments (**Figure 1**). In general, the internal CO_2 was lower and internal O_2 was greater in the order noncoated (NC), polyethylene (PE), candelilla (CD), carnauba–shellac (CS), and shellac (SH). With the same coating, the grade of gas modification increased in the order Delicious, Fuji, Braeburn, and Granny Smith (**Figure 1**). Using shellac to coat Braeburn and Granny Smith apples caused excessive modification of internal gas (**Figure 1**) and led to physiological disorder and even flesh browning (*28*).

Concentrations of Volatile Components. Analysis of variance (**Table 2**) showed that 1-butanol, butyl acetate, butyl butanoate, 2-methylbutyl acetate, 2methylbutyl 2-methylbutanoate, ethanol, ethyl acetate, ethyl butanoate, ethyl hexanoate, and total volatiles were significantly different with respect to apple varietiy, coating, and marketing duration. Most of the interactions between variety and other factors (storage duration, coating, and marketing duration) were significant for the

Table 3. Delicious Apple: Concentration (mol·L^{-1}) of Selected Volatiles in Homogenate of Fruits That Were Freshly Harvested or 20-Weeks-Stored, Coated with Five Coating Treatments, and Held at 20 °C for 2 or 4 Weeks[a]

			coating				
compound	duration of storage + holding (weeks)[b]	initial[c]	NC[d]	PE	CD	CS	SH
ethanol	0 + 2	116.6 e[e]	326.3 d	367.5 d	2319.0 c	6835.1 b	6677.0 b
	0 + 4		1926.9 c	119.8 e	160.1 e	454.8 d	11423.8 a
	20 + 2	14.6 f	122.7 e	184.7 de	235.1 de	67.3 ef	1976.0 c
ethyl acetate	0 + 2	0.8 c	1.0 c	0.6 c	53.9 b	137.0 a	146.8 a
	0 + 4		3.4 c	0.8 c	1.4 c	15.9 b	154.4 a
	20 + 2	tr[f]	1.8 c	0.4 c	1.1 c	0.1 c	14.3 b
ethyl butanoate	0 + 2	tr	1.1 bc	0.3 c	3.6 b	15.9 a	15.3 a
	0 + 4		3.9 b	1.3 bc	3.5 b	12.0 a	9.7 a
	20 + 2	tr	1.7 bc	0.2 c	0.9 bc	0.1 c	0.9 bc
ethyl hexanoate	0 +2	4.3 a	0.6 b	0.8 b	0.9 b	0.7 b	0.4 bc
	0 + 4		0.7 b	0.8 b	0.6 b	0.8 b	0.8 b
	20 + 2	0.2 c	1.1 b	0.4 bc	0.8 b	0.3 bc	0.8 b
1-butanol	0 + 2	9.0 bc	11.7 b	13.1 b	17.1 ab	24.2 a	8.5 bc
	0 + 4		7.7 c	10.9 b	17.4 ab	25.6 a	14.0 b
	20 + 2	3.4 c	13.7 b	5.2 c	12.1 b	6.6 c	8.6 bc
butyl acetate	0 + 2	15.7 a	3.3 bc	4.2 bc	6.5 b	7.5 b	2.1 bc
	0 + 4		2.0 bc	2.4 bc	7.8 ab	14.2 a	3.9 bc
	20 + 2	0.1 c	3.9 bc	1.7 bc	4.3 bc	0.5 c	1.8 bc
2-methylbutyl	0 + 2	6.0 bc	5.1 bc	5.2 bc	8.3 ab	15.9 a	3.9 bc
	0 + 4		2.4 c	3.5 c	6.5 bc	15.0 a	4.2 bc
	20 + 2	3.7 c	9.7 a	5.2 bc	12.3 a	5.9 bc	8.2 ab
2-methylbutyl	0 + 2	0.4 ab	0.2 b	0.4 ab	0.6 ab	0.8 ab	0.1 b
	0 + 4		0.1 b	0.2 b	0.3 b	1.7 a	0.2 b
	20 + 2	tr	0.2 b	0.1 b	0.2 b	0.1 b	0.2 b

[a] Commercial storage conditions: 2 kPa CO_2 + 8 kPa O_2, 1°C. [b] Duration of storage and holding times for all samples except the initial. [c] Noncoated apple sampled on day of coating application (zero holding time). [d] NC, noncoated; PE, polyethylene; CD, candelilla; CS, carnauba–shellac; and SH, shellac. [e] Mean values ($n = 3$) for the same compound not followed by the same letter are significantly diffierent ($p < 0.05$). [f] tr, trace.

Table 4. Fuji Apple: Concentration (mol·L^{-1}) of Selected Volatiles in Homogenate of Fruits That Were Freshly Harvested or 20-Weeks-Stored, Coated with Five Coating Treatments, and Held at 20°C for 2 or 4 Weeks[a]

			coating				
compound	duration of storage + holding (weeks)[b]	initial[c]	NC[d]	PE	CD	CS	SH
ethanol	0 + 2	141.5 d[e]	1717.5 c	1067.8 c	2062.1 c	7419.0 b	29494.6 a
	0 + 4		1794.7 c	3319.1 bc	2626.3 bc	5254.6 b	17375.2 a
	20 + 2	199.0 d	4423.4 bc	1539.6 c	1699.4 c	3366.6 bc	26625.1 a
ethyl acetate	0 + 2	0.1 e	8.7 cd	6.6 c	23.6 c	75.1 b	193.9 a
	0 + 4		8.8 d	20.7 c	19.5 c	57.1 bc	133.9 a
	20 + 2	3.7 d	5.7 cd	5.1 cd	7.9 cd	22.2 c	107.8 a
ethyl butanoate	0 + 2	tr[f]	3.8 c	2.1 c	5.3 c	15.7 ab	12.2 ab
	0 + 4		7.5 b	7.6 b	7.2 b	12.7 ab	15.1 ab
	20 + 2	1.2 d	6.5 bc	5.4 c	6.0 bc	10.9 b	23.6 a
ethyl hexanoate	0 + 2	2.8 a	0.4 b	0.3 b	0.3 b	0.6 b	0.5 b
	0 + 4		0.5 b	0.4 b	0.3 b	0.3 b	0.3 b
	20 + 2	1.5 a	1.9 a	1.4 a	1.4 a	1.5 a	0.9 ab
1-butanol	0 + 2	18.6 cd	16.6 d	13.0 d	21.5 cd	39.2 b	20.3 cd
	0 + 4		20.7 cd	20.5 cd	21.8 cd	28.1 c	28.0 c
	20 + 2	78.5 a	42.9 b	44.6 b	43.7 b	64.0 a	66.2 a
butyl acetate	0 + 2	31.9 a	1.2 c	1.1 c	3.3 c	9.4 b	1.2 c
	0 + 4		0.7 c	1.9 c	1.4 c	3.7 c	1.9 c
	20 + 2	10.9 b	2.4 c	2.3 c	4.2 bc	8.9 b	5.7 bc
2-methylbutyl	0 + 2	4.9 ab	3.0 b	2.0 c	3.4 b	12.1 a	3.6 b
	0 + 4	2.3 bc	2.3 bc	2.0 c	3.4 b	1.8 c	2.3 bc
	20 + 2	8.4 a	3.6 b	2.9 b	3.9 ab	7.0 a	4.8 ab
2-methylbutyl	0 + 2	0.2 b	0.4 ab	0.4 ab	0.4 ab	0.5 ab	0.5 ab
	0 + 4		0.5 ab	0.4 ab	0.3 ab	0.3 ab	0.3 ab
	20 + 2	1.1 a	0.1 b	0.1 b	0.2 b	0.3 ab	0.4 ab

[a] Commercial storage conditions: 2 kPa CO_2 + 8 kPa O_2, 1 °C. [b] Duration of storage and holding times for all samples except the initial. [c] Noncoated apple sampled on day of coating application (zero holding time). [d] NC, noncoated; PE, polyethylene; CD, candelilla; CS, carnauba–shellac; and SH, shellac. [e] Mean values ($n = 3$) for the same compound not followed by the same letter are significantly diffierent ($p < 0.05$). [f] tr, trace.

volatiles, indicating the need to select coating, storage duration, and marketing duration according to variety.

The amounts and kinds of volatile components of freshly harvested, noncoated fruit were different from those of 20-week-stored apples (**Tables 3−6**). Freshly harvested Braeburn apples contained the most (total 34) different volatile components, and their total of all volatiles was highest of all samples, including this same variety after 20 weeks of storage. By comparison, Delicious apples had only 30 and 26 detectable components for freshly harvested and 20-week-stored apples, respectively,

Table 5. Braeburn Apple: Concentration (mol•L^{-1}) of Selected Volatiles in Homogenate of Fruits That Were Freshly Harvested or 20-Weeks-Stored, Coated with Five Coating Treatments, and Held at 20 °C for 2 or 4 Weeks[a]

compound	duration of storage + holding (weeks)[b]	initial[c]	coating NC[d]	PE	CD	CS	SH
ethanol	0 + 2	16.9 e[e]	341.1 d	2543.0 c	474.7 cd	3685.2 c	43301.4 a
	0 + 4		2994.2 c	1636.0 c	1608.6 c	10774.8 b	20175.4 a
	20 + 2	637.3 cd	987.1 c	122.5 d	148.5 d	2669.3 c	15241.5 ab
ethyl acetate	0 + 2	tr[f]	1.1 d	0.2 d	39.7 c	148.9 ab	462.1 a
	0 + 4		3.4 d	2.4 d	28.7 c	98.3 b	385.7 a
	20 + 2	2.6 d	1.7 d	1.6 d	2.8 d	39.0 c	318.3 a
ethyl butanoate	0 + 2	tr	tr	tr	7.7 b	12.9 a	15.0 a
	0 + 4		tr	tr	4.3 b	10.2 ab	29.9 a
	20 + 2	0.5 c	1.2 c	1.6 c	2.0 bc	3.3 bc	13.0 a
ethyl hexanoate	0 + 2	3.5 a	0.5 b	0.4 b	0.3 b	0.3 b	0.5 b
	0 + 4		0.5 b	0.3 b	0.2 b	0.3 b	0.2 b
	20 + 2	tr	0.4 b	0.2 b	0.2 b	tr	tr
1-butanol	0 + 2	24.6 a	25.3 a	19.3 ab	25.6 a	32.5 a	17.5 b
	0 + 4		27.7 a	21.1 ab	29.8 a	29.7 a	18.4 b
	20 + 2	40.5 a	24.8 a	28.8 a	39.1 a	31.5 a	21.1 ab
butyl acetate	0 + 2	18.3 b	19.6 ab	19.3 ab	26.9 a	22.2 ab	3.0 c
	0 + 4		16.2 b	21.3 ab	32.4 a	30.4 a	13.0 b
	20 + 2	20.8 ab	11.9 b	14.1 b	15.4 b	19.2 ab	5.3 c
2-methylbutyl	0 + 2	29.3 a	17.7 ab	7.4 c	20.8 ab	31.9 a	9.6 bc
	0 + 4		15.0 b	9.0 bc	12.2 b	19.3 ab	11.5 b
	20 + 2	16.2 ab	11.0 b	9.1 bc	13.3 a	15.4 b	4.4 c
2-methylbutyl	0 + 2	1.4 a	0.4 ab	0.5 ab	0.9 a	1.2 a	0.1 b
	0 + 4		0.2 b	0.4 ab	0.6 ab	1.3 a	0.5 ab
	20 + 2	1.8 a	0.2 b	0.4 ab	0.5 ab	1.5 a	0.2 b

[a] Commercial storage conditions: 2 kPa CO_2 + 8 kPa O_2, 1°C [b] Duration of storage and holding times for all samples except the initial. [c] Noncoated apple sampled on day of coating application (zero holding time). [d] NC, noncoated; PE, polyethylene; CD, candelilla; CS, carnauba–shellac; and SH, shellac. [e] Mean values ($n = 3$) for the same compound not followed by the same letter are significantly diffierent ($p < 0.05$). [f] tr, trace.

Table 6. Granny Smith Apple: Concentration (mol•L^{-1}) of Selected Volatiles in Homogenate of Fruits That Were Freshly Harvested or 20-Weeks-Stored, Coated with Five Coating Treatments, and Held at 20°C for 2 or 4 Weeks[a]

compound	duration of storage + holding (weeks)[b]	initial[c]	coating NC[d]	PE	CD	CS	SH
ethanol	0 + 2	33.9 e[e]	690.1 d	1434.9 c	10871.4 b	10756.7 b	21632.8 b
	0 + 4		3136.6 c	389.1 d	1268.5 c	17959.2 b	44498.3 ab
	20 + 2	132.1 e	287.9 de	2886.2 c	30325.0 b	46394.5 ab	75682.7 a
ethyl acetate	0 + 2	tr[f]	tr	tr	tr	tr	14.8 ab
	0 + 4		tr	tr	tr	7.3 b	20.9 ab
	20 + 2	0.3 c	0.9 c	1.4 c	10.7 b	13.9 ab	35.2 a
ethyl butanoate	0 + 2	tr	tr	tr	0.4 bc	1.4 b	1.9 ab
	0 + 4		tr	tr	tr	2.7 ab	2.9 ab
	20 + 2	0.1 c	0.8 b	0.5 b	2.4 ab	3.2 a	4.6 a
ethyl hexanoate	0 + 2	8.3 a	0.7 b	0.3 c	0.3 c	0.3 c	0.3 c
	0 + 4		0.8 b	0.7 b	0.3 c	0.2 c	0.4 c
	20 + 2	0.2 c	0.3 c	0.5 bc	0.8 b	0.5 bc	tr
1-butanol	0 + 2	3.4 ab	2.6 ab	1.6 b	2.6 ab	3.2 ab	2.9 ab
	0 + 4		4.0 a	3.8 a	2.0 b	3.7 a	4.5 a
	20 + 2	0.4 c	3.4 ab	2.7 ab	3.4 ab	4.6 a	3.0 ab
butyl acetate	0 + 2	22.8 a	0.7 bc	0.4 c	0.9 b	1.5 b	1.3 b
	0 + 4		1.0 b	1.3 b	0.7 bc	0.8 bc	1.3 b
	20 + 2	0.2 c	0.1 c	0.2 c	0.2 c	0.3 c	0.1 c
2-methylbutyl	0 + 2	0.5 a	0.2 a	0.2 a	0.2 a	0.2 a	0.2 a
	0 + 4		0.3 a	0.3 a	0.2 a	0.1 b	0.2 a
	20 + 2	tr	0.2 a	0.1 a	0.1 a	0.1 a	0.1 a

[a] Commercial storage conditions: 2 kPa CO_2 + 8 kPa O_2, 1°C [b] Duration of storage and holding times for all samples except the initial. [c] Noncoated apple sampled on day of coating application (zero holding time). [d] NC, noncoated; PE, polyethylene; CD, candelilla; CS, carnauba–shellac; and SH, shellac. [e] Mean values ($n = 3$) for the same compound not followed by the same letter are significantly diffierent ($p < 0.05$). [f] tr, trace.

with a greater decrease in amount during 20-week CA storage at 1 °C. In Fuji apples, the total amount of volatiles increased slightly, and the number of components remained constant after 20-week CA storage at 1 °C. Of all the varieties tested, the amount of volatiles in Granny Smith apples decreased the most during CA storage, although the number of components detected did not decrease.

With regard to amounts of volatile components, there were significant differences between coatings for all varieties (**Tables 2−6**). Even so, the important apple character compounds butyl acetate and 2-methylbutyl acetate (*16*, *29*) were not significantly different between fresh and 20-week-stored fruits (**Table 2**). It is possible, however, that the levels may have been different at some time during the 20 weeks of storage; Saftner (*6*) found a

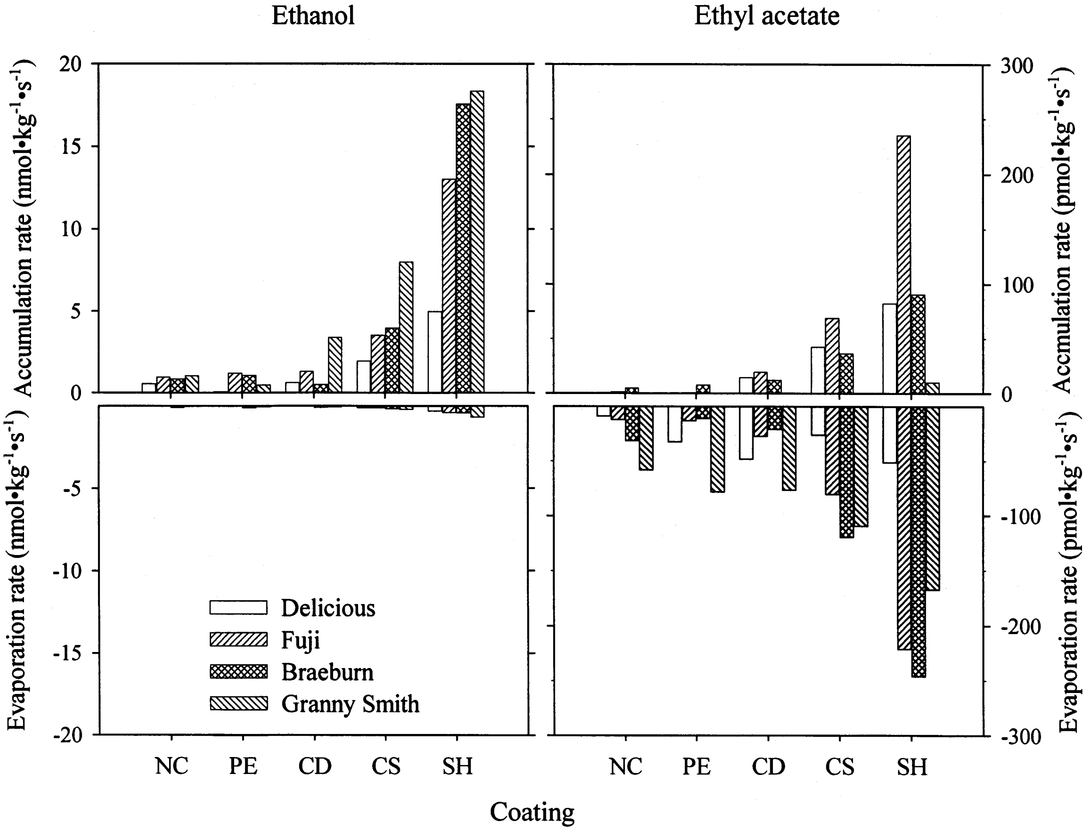

Figure 2. Accumulation and evaporation rates of ethanol and ethyl acetate in freshly harvested apples with different coating treatments at 20 °C within 2 weeks. The evaporation rate was measured at week 1. Abbreviations for coating treatments: NC, noncoated; PE, polyethylene; CD, candelilla; CS, carnauba–shellac; and SH, shellac.

3-month increase followed by a decrease of total volatiles content during 6 months of storage at 0 °C for noncoated and coated Golden Delicious and Gala apples.

The combined effect of variety and cold storage duration showed strong relationships (**Tables 2−6**). See, for example, the large decreases in control apples during 20 weeks of cold storage of butyl acetate in Granny Smith and Delicious apples (**Tables 3** and **6**), the increase of 1-butanol in Fuji apples (**Table 4**), and the decrease of ethanol in Delicious apples (**Table 3**).

Coating influenced most of the volatiles concentrations significantly (**Table 2**). Generally, the ethanol concentrations increased with elevated internal CO_2 and lower internal O_2 partial pressures in the order NC, PE, CD, CS, and SH. Ethanol increases were particularly high with the shellac coating, amounting, for example, to increases of 57-, 208-, 638-, and 2562-fold for freshly harvested Delicious, Fuji, Granny Smith, and Braeburn apples, respectively, after 2 weeks at 20 °C (**Tables 3−6**). The highest ethanol concentrations were observed with Granny Smith and Braeburn apples, and these had the most anaerobic conditions (**Figure 1** and **Tables 3−6**). On the other hand, Delicious apples had the lowest ethanol content and the most aerobic interior atmosphere (**Figure 1** and **Tables 3−6**). Bai et al. (*28*) reported that shellac coatings developed for Delicious apples may cause anaerobic metabolism when used for other varieties.[5]

All of other coatings also increased ethanol concentration, except for polyethylene, which modified the internal atmosphere less than other coatings (**Figure 1** and **Tables 3−6**). In fact, polyethylene-coated Fuji and Delicious aples had even lower average ethanol concentrations than noncoated control (**Tables 3** and **4**). This is consistent with the finding by Ueda et al. (*16*) that a slightly modified environment (lower O_2 and higher CO_2

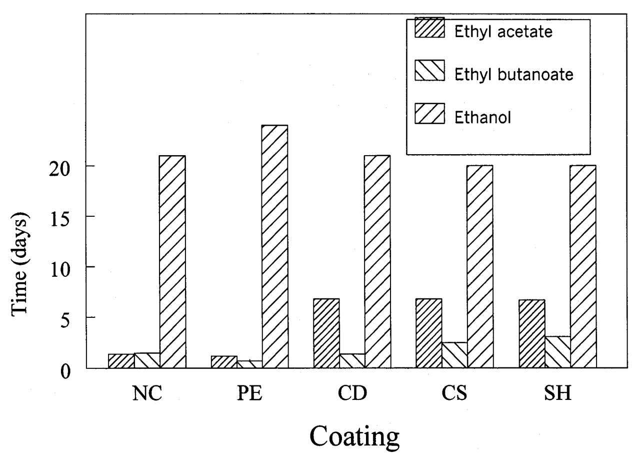

Figure 3. Equivalent time within which the accumulated volatile compounds in the first 2 weeks would be completely released from apples with different coating treatments through evaporation at 20 °C. Calculation used the average evaporation rates of Delicious, Fuji, Braeburn, and Granny Smith apples at week 3. Abbreviations for coating treatments: NC, noncoated; PE, polyethylene; CD, candelilla; CS, carnauba–shellac; and SH, shellac.

than the ambient atmosphere) would not stimulate fermentation but rather would decrease ethanol production of apples.

As ethanol increased, so did the concentrations of ethyl esters of acetic and butanoic acids (**Tables 3−6**), presumably as a result of ethanol competing with other alcohols in ester formation (*30*). However, ethyl hexanoate did not increase with increasing ethanol concentration (Tables 3−6), possibly an indication that the hexanoic acid concentration is rate-limiting.

For all varieties except Granny Smith, the highest butanol concentration generally occurred under intermediate partial

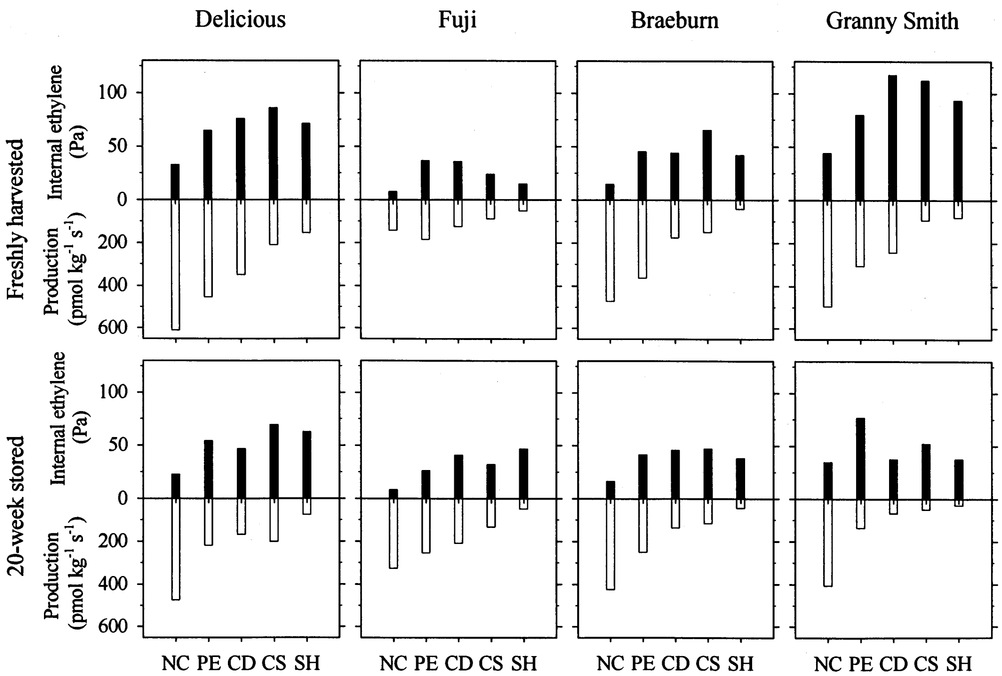

Figure 4. Internal partial pressure and production rate of ethylene in apples with the different coating treatments. Freshly harvested or 20-week commercially stored apples of four varieties were coated with five coating treatments and held at 20 °C for 2 weeks. The commercial storage conditions are shown in **Table 1**. Abbreviations for coating treatments: NC, noncoated; PE, polyethylene; CD, candelilla; CS, carnauba–shellac; and SH, shellac.

pressures of O_2 and CO_2 with the candelilla or carnauba−shellac coatings (**Figure 1** and **Tables 3−5**). Butyl acetate and other esters with higher molecular weight had a tendency similar to that of butanol (**Tables 3−5**). High levels of butyl acetate and 2-methylbutyle acetate tend to contribute to better fruit-like and apple-like aroma (*14*, *16*, *30*, *31*). For Granny Smith apples, the concentrations of esters with butyl or higher molecular weight alcohol moieties were significantly lower than those in other varieties and were about the same as those for different coating treatments (**Table 6**).

Holding the apples at 20 °C caused a marked increase in ethanol and ethyl esters, although most of the other esters decreased (**Tables 2−6**).

Accumulation and Evaporation of Esters, Alcohols, and Ethylene. The volatiles concentrations just described refer only to the components that accumulated in the flesh of the apples and do not include any lost by evaporation. As described, the evaporation rate of ethanol was measured from the concentration of gases flowing from a container of apples. Very little of the ethanol evaporated (**Figure 2**). Most ethanol stayed in the fruits, presumably because of its greater water solubility, reflected in its relatively high Henry's law coefficients (**Table 7**). This is in agreement with the relatively low ethanol concentration of headspace gases noted by Saftner et al. (*6*).

Relatively more esters (which have much lower Henry's law coefficients than alcohols, **Table 7**) evaporated from the fruit (**Figure 2**). The proportion of ethyl acetate that evaporated depended very much on the resistance of the coating. Those coatings in which CO_2 accumulated also tended to accumulate ethyl acetate (**Figures 1** and **2**). A high proportion of the ethyl butanoate evaporated from fruit with all coatings (data not shown).

Stated in different terms, the mean concentration of ethyl acetate found in the four varieties amounted to the amount produced in about 1 day for noncoated and low-resistance formulation (polyethylene) coated fruit, and in about 7 days for candelilla-, carnauba−shellac-, and shellac-coated fruits (**Figure 3**). For ethyl butanoate, these amounted to 1 day's and 3 days' production. The amount of ethylene found in noncoated fruit, calculated from measured values of internal ethylene concentration (**Figure 4**), amounted to what was produced in only about 2 h. The ethylene in apples for treatments PE, CD, CS, and SH amounted to 7, 12, 17, and 25 h of the production means for all varieties, respectively.

Table 7. Estimated Proportion of Several Volatile Compounds in Gas Phase and Flesh of Different Varieties of Apple Fruit, Assuming Henry's Law Distribution

component	k_H ($mol·kg^{-1}·bar^{-1}$)[a]	distribution (%)[b]	
		in gas phase	in flesh
ethanol	120–230	0.004–0.006	99.994–99.996
1-butanol	110–140	0.006	99.994
acetaldehyde	9.8–17	0.05–0.07	99.93–99.95
ethyl acetate	4.7–8.9	0.1–0.2	99.8–99.9
butyl acetate	2.1–3.6	0.2–0.4	99.6–99.8
ethyl butanoate	2.8	0.3	99.7
ethylene	0.0047–0.0049	63	37

[a] Values cited from http://webbook.inst.gov/chemistry (2001). [b] Calculated distribution with 200 mL of gas phase per kilogram of fruit and the same gas solubility in flesh as in water.

The ethylene production rate tended to be lower for the apples with higher internal CO_2 and lower O_2 (**Figures 1** and **4**), as might be expected. The internal ethylene concentration, however, tended to be highest at intermediate values of internal CO_2 and O_2 partial pressures. Note that this is possible because in general the difference in gas partial pressures across a barrier is expected to be the product of flux times resistance times area. The various treatments affected gas resistance of the skin, evident from the different values of internal CO_2 and O_2, and therefore it is understandable that the same treatment that gives maximum ethylene production may not give maximum internal ethylene partial pressure. Ethylene has a relatively low solubility (**Table 7**).

A Note on Calculations. In addition to conclusions about how apples' volatiles are affected by coatings, these results show that interpretation of data to calculate production rates of various components needs to take some consideration of component solubility. Ethylene has very low water solubility (low Henry's law coefficient, **Table 7**); therefore, emitted ethylene seems a good estimate of its production rate. The esters were more soluble (higher Henry's law coefficients, **Table 7**), but evaporation rates were still relatively large (**Figure 2**); therefore, the accumulation rates are similar to but somewhat short of production rates. For alcohols, the evaporation rate was very much less than the production rate because very little is found in the vapor phase (**Figure 2**).

Therefore, for the determination of production rates of different flavor volatiles, somewhat different measurements are needed for esters and alcohols. For esters, the measurement of evaporation rates suffices to get approximate values of production rates. However, for alcohols, measurements of juice volatiles seems necessary, and therefore alcohol production rates calculated from evaporation rates are probably not correct (*1*, *6*, *27*, *32*, *33*).

Conclusion. There were significant differences for the abundant or characteristic apple volatiles among varieties, coatings, and holding time at marketing temperature. The Granny Smith and Braeburn varieties were more sensitive to high gas resistance coatings than Fuji and Delicious. A wax coating with intermediate gas resistance gave increased fruit-like and apple-like volatiles concentrations while averting excessive accumulation of fermentation products. The coatings affected flavor by regulating the rates at which the apples synthesized the various flavor volatiles and also by the restricting the rates at which they were lost by evaporation from the fruit.

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