Proc. Fla. State Hort. Soc. 115:303-308. 2002.

STORAGE OF 'MARSH' GRAPEFRUIT AND 'VALENCIA' ORANGES WITH DIFFERENT COATINGS

ROBERT D. HAGENMAIER[1] AND KEVIN GOODNER
U.S. Citrus and Subtropical Products Laboratory
USDA, ARS, SAA
600 Avenue S, N.W.
Winter Haven, FL 33881
E-mail Hagenmaier@usda.citrus.gov

RUSSELL ROUSSEFF AND HUATING DOU
Citrus Research and Education Center
700 Experiment Station Road
Lake Alfred, FL 33850

Additional index words. oranges, grapefruit, cold storage, quality, permeability, electronic nose, chilling injury

Abstract. **'Valencia' oranges and 'Marsh' grapefruit with three different coating treatments (high-gloss shellac, wax, or non-coated) were kept in cold storage for 1 - 5 months, oranges at 1 °C and the grapefruit at 3 or 7 °C. Oxygen permeabilities of the coatings were measured. Stored fruit were analyzed for flavor, ethanol content, Brix-acid ratio, chilling injury and electronic nose response. The ethanol content of oranges and grapefruit with high-gloss shellac coating both increased substantially during cold storage. Fruit with wax coatings had little increase in ethanol. Chilling injury of grapefruit was the most extensive for non-coated fruit and lowest with the high-gloss shellac coating. Electronic nose response was significantly different for grapefruit with different coatings, but did not separate the treatment with best sensory panel flavor, which was that stored at 3 °C with the wax coating.**

Citrus fruit tends to develop off-flavor when stored at about 20 °C after application of coating with low O_2 permeability that overly restrict the exchange of O_2 and CO_2 between atmosphere and fruit to the extent that internal O_2 concentration becomes too low to support aerobic respiration (Baldwin et al., 1995; Hagenmaier, 2000, 2002; Hagenmaier and Baker, 1994; Shaw et al., 1991). Others have found flavor changes during cold storage of citrus.

Mention of a trademark or proprietary product is for identification only and does not imply a guarantee or warranty of the product by the U.S. Department of Agriculture. The U.S. Department of Agriculture prohibits discrimination in all its programs and activities on the basis of race, color, national origin, gender, religion, age, disability, political beliefs, sexual orientation, and marital or family status.

[1]Corresponding author. e-mail: hagenmaier@usda.citrus.gov

Under refrigerated conditions, flavor also deteriorates. 'Valencia' oranges stored at 3 °C developed high ethanol and off flavor after 10 weeks if coated, but not if wrapped in polyvinyl chloride or left non-coated (Jiminez-Cuesta et al., 1983). The flavor of 'Clementine' decreased after 25 d at 4 °C (Cuquerella-Cayuela et al., 1983). Ethanol content of 'Murcott' tangerines increased and flavor decreased after 4 weeks at 5 °C for fruit with two coatings of wax (Cohen et al., 1990a). Ethanol content of lemons, taken as an indicator of quality, increased markedly at 2 °C storage (Cohen et al., 1990b).

However, little information is available to show how coating permeability affects flavor quality during refrigerated storage of citrus fruit, which is what the present study aims to do.

Materials and Methods

'Valencia' oranges [*Citrus sinensis* (L.) Osbeck cv. Valencia] and 'Marsh' grapefruit [*Citrus paradisi* Macf.] were harvested at various times near Winter Haven, Fla. (Table 1). On the day after harvest, the fruit were washed on rotary brushes with Decco Fruit and Vegetable Keen 241 (Elf Atochem, Monrovia, Calif.), sprayed with 1000 mg·kg^{-1} imazalil, (Fungaflor 500EC, Janssen Pharmaceutical, Titusville, N.J.), passed through a hot-air drier (residence time 5 min at 50. °C), divided into four subsamples: fruit sampled on day one, fruit not coated and fruit for each of the two coatings. Coatings were applied manually, using rubber gloves and the fruit again passed though the drier, same temperature and holding time. The amount of liquid coating applied to oranges was 0.3 g per orange and 0.4 g per grapefruit. Within three hours of application of the coatings, the fruit were put into cold storage (1 °C, 97% R.H for Valencia oranges; and 3 °C, 70%RH or 7 °C, 75% RH for the 'Marsh' grapefruit.

Coating treatment A consisted of Brogdex 555 with 1000 mg·kg^{-1} TBZ. This is a commercially available, high-gloss coating not unlike other shellac-resin based coatings used in the citrus industry. Coating treatment B was an experimental coating made in our laboratory, consisting of 12.0% polyethylene (AC673 or AC 316, Allied Signal), 4.0% candelilla wax, 3.2% oleic acid, 0.8% myristic acid, and 0.9% NH_3, with 500 mg·kg^{-1} TBZ.

Coating permeability was measured with coatings of approximately 20 μm thickness prepared by uniformly spreading the liquid formulations on low-density polyethylene film, drying and storing for about 1 month at 50% RH. The O_2 fluxes through coated and non-coated films were measured at 30 °C in a 100 cm^2 permeability cell (Mocon, Minneapolis, MN) by passing air on one side and N_2 on the other, at flow rates of 10 and 3 mL·min^{-1}, respectively, until the O_2 content of the N_2 stream reached steady-state O_2 concentration. Coating thickness was determined from weights and also by measurement of thickness to 1 μm accuracy (n = 6) with a micrometer (model μMaxμm, Federal Products Co. Providence, R.I.). Coating permeance was calculated as 1/((permeance of coated film)$^{-1}$ - (permeance non-coated film)$^{-1}$).

Table 1. 'Valencia' harvest dates.

'Valencia' experiments and harvest dates		'Marsh' experiments and harvest dates	
V1	April 28, 2000	M1	Jan. 25. 2001
V2	April 28, 2000	M2	Jan 30, 2001
V3	May 4, 2000	M3	Feb. 8, 2001
V4	May 4, 2000	M4	Feb. 21, 2001
V5	May 16, 2000	M5	Mar 21, 2001[a]
V6	May 19, 2000	M6	Mar 21, 2001[a]
V7	May 19, 2000		
V8	May 26, 2000[a]		
V9	May 26, 2000[a]		
V10	May 26, 2000[a]		

[a]Fruit harvested on the same day was from different groves.

Table 2. Oxygen permeability of the coatings, measured at 30 °C.

	Permeability	
Coating	mol/m^{-1}s^{-1}Pa^{-1}	mol/m^{-1}s^{-1}Pa^{-1}
High-gloss shellac	(1.4 ± 0.2) • 10^{-16}	1,100 ±160
Wax	(17 ± 5) • 10^{-16}	21,000 ± 3700

Respiration rates of non-coated fruit at 21 °C were measured from the increase in CO_2 concentration (measured in the same manner as internal CO_2) of air flowing at 15 mL·min^{-1}

Ethanol content of juice was determined on pooled juice from 4 pieces of fruit extracted with the FMC Multi-juicer. The samples were spiked with 1000 mg·kg^{-1} n-propanol as internal standard, centrifuged and injected into a gas chromatograph fitted with a FFAP column (Hewlett Packard) and flame ionization detector. Column flow was 4 mL·min^{-1}. Column temperature was 55 °C for injection, increased 3 °C·min^{-1} to 70 °C and held at that temperature 1 min.

Samples for internal O_2 and CO_2 were withdrawn with a syringe (previously flushed with N_2 to remove traces of oxygen) from fruit that were submerged in water. The O_2 and CO_2 concentrations were measured with a Hewlett Packard 5890 gas chromatograph fitted with a CTR-1 column (6 ft long, 1/inch and 1/8 inch diameter, outer and inner columns, respectively, Alltech, Deerfield, Ill.). Samples were applied with a 250 μl loop injector. Column flow rate was 140 mL·min^{-1}. Temperatures were 40 °C and 120 °C, respectively, for the column and thermal conductivity detector. Peak areas obtained from standard gas mixtures were determined before and after analysis of the samples. Oxygen concentration was calculated from the O_2-Ar peak area after correction for 0.93% Ar in the atmosphere.

The Nordic electronic nose (Applied Sensor Inc., Parsippany, NJ) was used for comparison of volatile gases from the 'Marsh' grapefruit juiced on June 14. Samples were held at 8 °C until 15 min before sampling, then heated to 30 °C for 5 min and 40 °C for 5 min before a 30 s sample flush and measurement of signal with 22 sensors. Samples were run in random order, 2 samples of 4 fruit each per treatment, each sample run four times. Every fifth sample was air at 15 °C.

Brix was determined with a Leica Abbe Mark II plus Refractometer. Acidity was determined by titration to a phenolthalein endpoint.

Hedonic flavor of 'Valencia' was the mean score of 15 experienced panelist using a 1-15 scale, dislike-like. Flavor quality and off flavor of 'Marsh' were the mean readings of 7 experienced panelist using 1-5 scales, with descriptors of poor - excellent and weak - strong, respectively.

Chilling injury was rated 0 for none, 1 for collapsed area of peel < 5% of surface area, 2 for 5%<area<25% and 3 for area >25% for 20 fruit/treatment after storage for 50-140 days.

Table 3. Internal CO_2 and O_2 of 'Valencia' Oranges and 'Marsh' Grapefruit after Storage. Oranges were stored 47-163 d at 1 °C and grapefruit for 47-103 d at 3 or 7 °C.

	Internal CO_2 (kPa)			Internal O_2 (kPa)		
	High-gloss	Wax	No coating	High-gloss	Wax	No coating
'Valencia'	8.4 a	3.3 b	2.3 b	9.8 a	15.7 b	17.5 c
'Marsh' at 3 °C	8.9 a	2.5 c	1.7 c	7.9 a	17.2 c	16.0 c
'Marsh' at 7 °C	7.3 b	2.2 c	1.6 c	11.8 b	16.6 c	16.2 c

Mean values for internal CO_2 or O_2 not with the same letter are significantly different ($p < 0.05$, Tukey).

Statistical treatment of data used Statistix for Windows (Analytical Software, Tallahassee, Fla.) or Statistica (Hallogram Pub. Co., Aurora, Colo.). Separation of means used Tukey statistic at $p < 0.05$.

Results

Internal gases. The high-gloss coating had only about 5% the permeability of the wax coating (Table 2), and is use resulted lower internal O_2 and higher CO_2 than fruit with the wax coating, which in turn was about the same as non-coated fruit (Table 3). Internal gases did not change with storage time. In previous studies with 'Valencia' oranges and 'Marsh' grapefruit stored at 20-25 °C with shellac coatings the internal O_2 was 1-2% and ethanol accumulated rapidly; the internal O_2 with wax coatings was roughly 10% and ethanol accumulated much more slowly (Hagenmaier, 2000; Hagenmaier and Baker, 1994). In the present study the internal O_2 with the shellac coating was 8- 12% (Table 3), roughly the same as that found previously with wax coating at 20-25 °C storage.

Ethanol. For the present study the ethanol contents of 'Valencia' oranges with the lower permeability high-gloss shellac coating increased markedly during storage (Fig.1, Table 4). The same data plotted against juicing date shows less scatter, suggests that date of making the juice may be more important than storage time, especially for fruit kept in storage after about Sept. 1 (Fig. 2). In contrast, the ethanol content with wax coating or no coating did not increase during storage (Fig. 3). The mean ethanol content of juice from freshly harvested 'Valencia' oranges (not stored, harvested April 28-May 26) was 536 ± 110 mg·kg^{-1}.

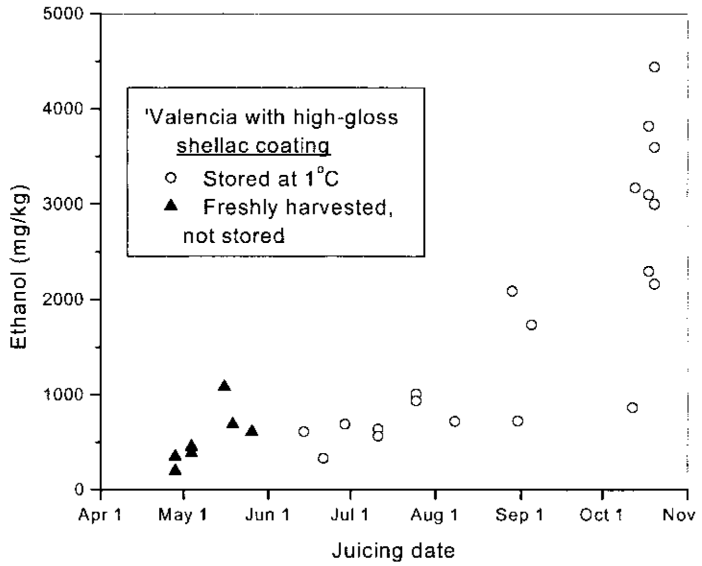

Fig. 2. Ethanol content of 'Valencia' oranges with high-gloss shellac coating stored at 1 °C as a function of date of squeezing for juice.

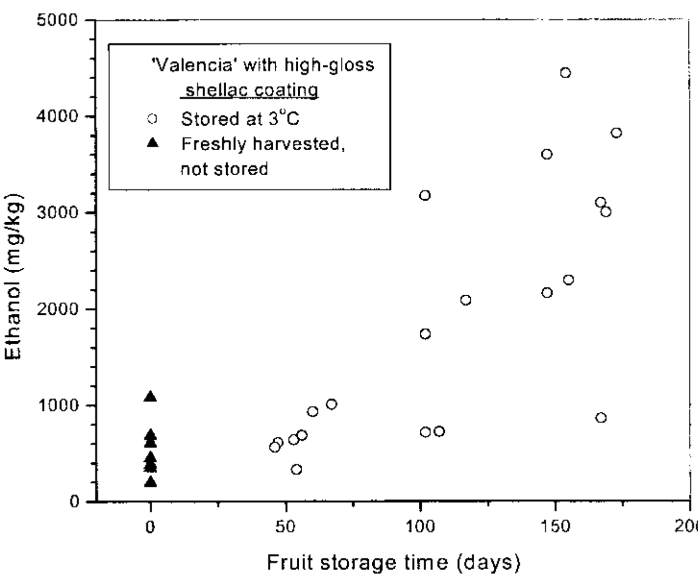

Fig. 1. Ethanol content of 'Valencia' oranges with high-gloss shellac coating as a function of time in storage at 1 °C.

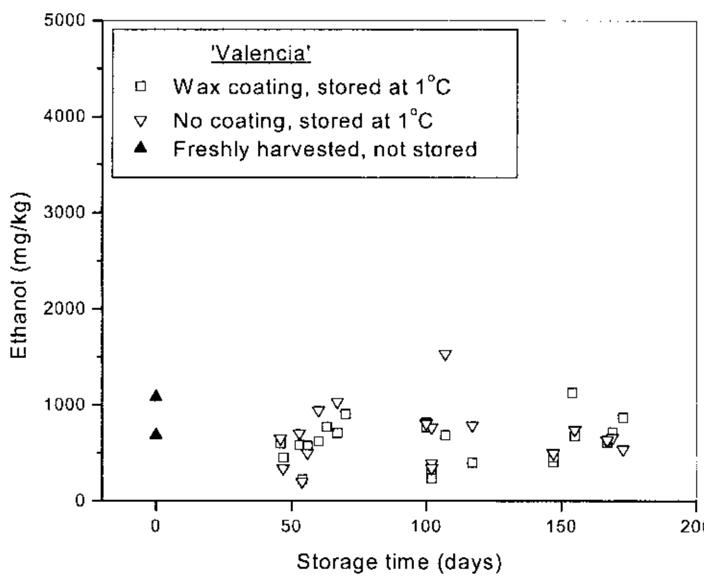

Fig. 3. Ethanol content of 'Valencia' oranges with wax coating or no coating as a function of time in storage at 1 °C.

Table 4. Rates of increase in ethanol content during cold storage.

	'Valencia' oranges		'Marsh' grapefruit	
Coating	Rate (mg_kg^{-1}/week)	R^2 (adjusted)[a]	Rate (mg_kg^{-1}/week)	R^2 (adjusted)[a]
None	5 ± 6	-0.01 NS	36 ± 5	0.61 ***
Wax	6 ± 5	0.01 NS	30 ± 4	0.61 ***
High-gloss shellac	108 ±18	0.59 ***	79 ± 13	0.47 ***

[a]NS not significant, *** $p < 0.001$.

'Marsh' grapefruit ethanol contents followed a similar pattern during storage, but with smaller increases for the high-gloss shellac coating (Figs. 4-6, Tables 4-6). There was a low but discernible increase in ethanol of the grapefruit with wax and no coatings, with the wax coating had slightly lower ethanol than fruit with no coating [Ethanol (no coating - wax) = (7 ± 1) mg·kg^{-1}/week]. The difference in rate of ethanol increase (high-gloss - no coating) was 48 ± 5 mg·kg^{-1}/week. Ethanol contents of grapefruit stored at 3 °C were not significantly different from those stored at 5 °C. The mean ethanol content of juice from freshly harvested 'Marsh' grapefruit (not stored, harvested April 28-May 26) was 90 ± 11 mg·kg^{-1} (Table 5).

It is generally well known that the flavor of fresh fruit decreases as ethanol content increases, and the same applies to citrus juices (Ahmad and Khan, 1987; Cohen 1990a,b; Hagenmaier, 2002; Ke and Kader, 1990). For the high-gloss shellac

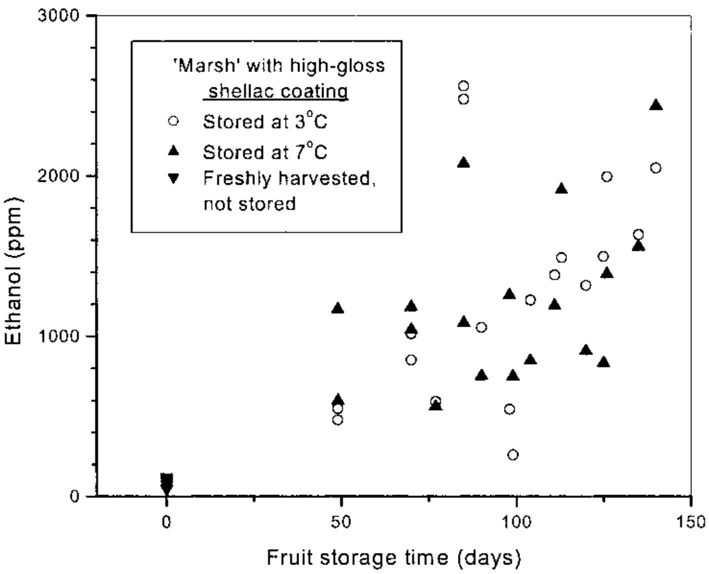

Fig. 4. Ethanol content of 'Marsh' grapefruit with high-gloss shellac coating as a function of time in storage at 3 ° or 7 °C.

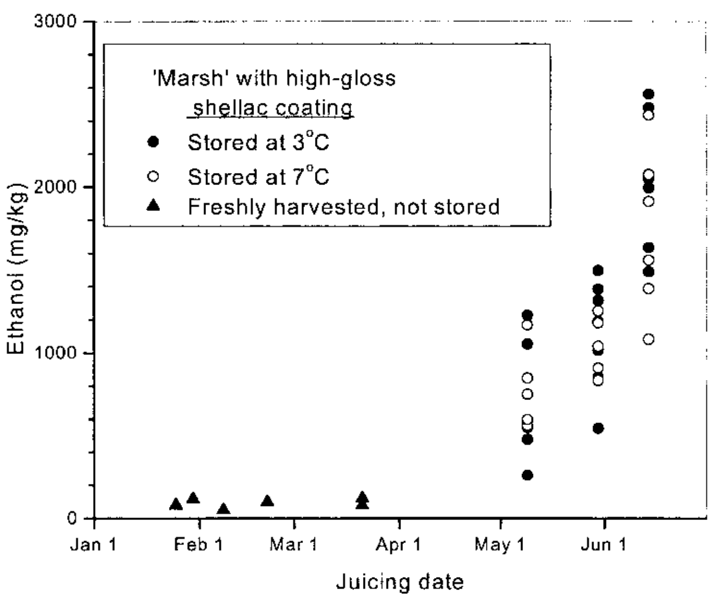

Fig. 5. Ethanol content of 'Marsh' grapefruit with high-gloss shellac coating stored at 3 ° or 7 °C as a function of date of squeezing for juice.

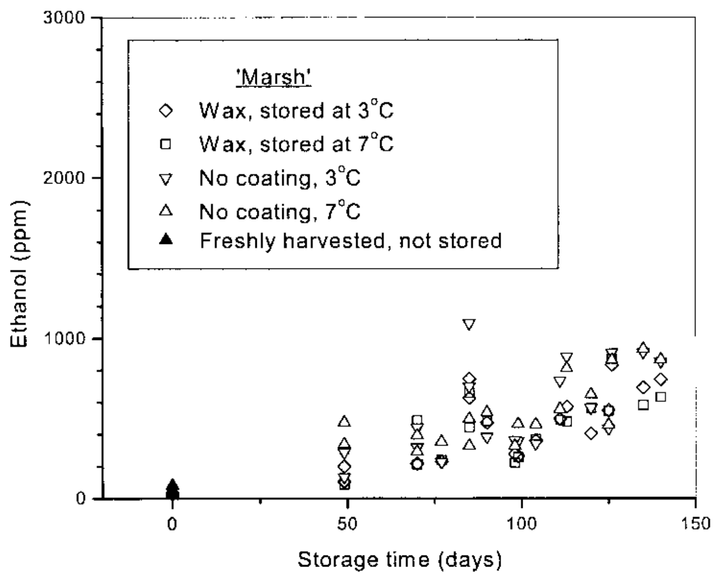

Fig. 6. Ethanol content of 'Marsh' grapefruit with wax coating or no coating as a function of time in storage at 1 °C.

Table 5. 'Valencia' Flavor panel results: A = high gloss coating, B = wax coating and U = uncoated.

		Hedonic score[a]		
Harvest I.D.	Fruit storage time (days)	A	B	U
V1	47	11.1	11.9	8.9
V2	54	10.8	11.7	8.2
V3	54	11.0	9.7	8.8
V4	117	9.8	10.6	9.1
V5	107	10.3	8.4	10.6
V9	102	8.0	9.6	8.0
	mean scores:	10.2[b]	10.3[b]	8.9[b]

[a]0-15 range, dislike and like extremely, respectively.
[b]Mean values in the same column not with the same letter are significantly different (Tukey, $p < 0.05$).

Table 6. Flavor attributes of 'Marsh' grapefruit juiced on June 14 after 85 - 140 d storage at 3 ° or 7 °C.

	Flavor quality[a]		Off flavor[b]	
	3 °C	7 °C	3 °C	7 °C
High-gloss shellac	2.5 b[c]	2.3 b	3.0 b	3.0 b
Wax	2.9 a	2.2 b	2.5 a	3.1 b
No coating	2.3 b	2.3 b	3.0 b	3.0 b

[a]Rated on 1-5 scale, 1 = poor, 5 = excellent.
[b]Rated on 1-5 scale, 1 = weak, 5 = strong.
[c]Mean values for flavor quality or off-flavor not with the same letter are significantly different (Tukey, $p < 0.05$).

coating about half the 'Marsh' and 'Valencia' samples had ethanol >1000 mg/kg^{-1}, with 14% of the 'Marsh' and 45% of the 'Valencia' samples having >2000 mg·kg^{-1} ethanol (Figs. 1,2,4,5). Only one sample of wax-coated fruit had ethanol >1000 ppm, suggesting these fruit have superior internal quality.

Electronic Nose measurements. The Nordic electronic nose responses for the juice of 'Marsh' grapefruit stored 85-140 d and juiced on June 14 showed that the fruit with the high-gloss shellac coatings (treatment A) had somewhat different response from the fruit with wax coating or no coating (Fig. 7). This difference in response was most likely caused by elevated levels of ethanol and other flavor volatiles. Unfortunately, the grapefruit with wax coating stored at 3 °C, which was the treatment with best flavor (Table 6), was not separated from the other samples by multivariate analysis (Fig. 7). These results suggest somewhat limited usefulness for the electronic nose to distinguish between fruit of differing internal quality. The ethanol data seem about as useful as the electronic nose signal, and these are much easier to measure and can be directly related to a chemical property.

Flavor panel results. The panel was unable to detect a significant difference in flavor of stored 'Valencia' oranges (Table 4). This is difficult to understand in light of the large differences in ethanol content. The 'Marsh' grapefruit with the wax coating stored at 3 °C (Table 6) had better flavor quality and less off-flavor than all other treatments.

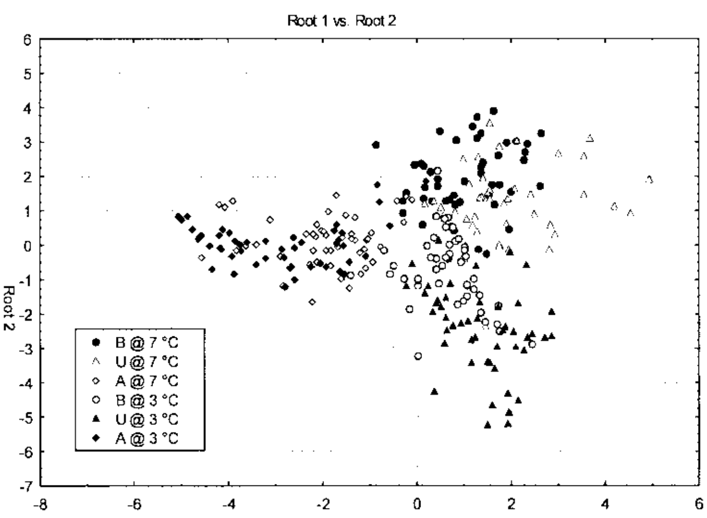

Fig. 7. Discriminate analysis of electronic nose measurements for 'Marsh' grapefruit with three coating treatments after 85 to 160 d storage at 3 ° or 7 °C. B = wax coating, A = high-gloss shellac, U = no coating.

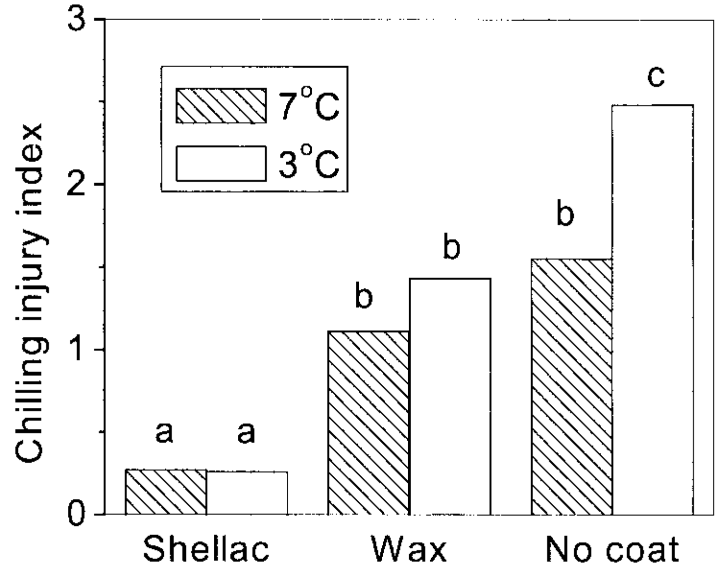

Fig. 8. Chilling injury of 'Marsh' grapefruit.

Chilling injury. Chilling injury was very severe for non-coated fruit stored at 3 °C, moderate to quite low for fruit with the high-gloss shellac coating and intermediate for other treatments (Fig. 8). This indicates that for grapefruit the best coating might have a coating permeance between that of the shellac and the wax (Table 2). This could be a mixture of wax and shellac or wax and resin. Schirra (1992) found more chilling injury and ethanol at 4 °C than at 8 °C for Stare Ruby' grapefruit. Chilling injury was quite severe for non-coated fruit at both temperatures but especially at 3 °C.

Mean brix-acid ratios for the grapefruit with shellac, wax or no coating, when juiced June 14 were 8.9, 8.9, and 8.6 at 3 °C and 8.8, 9.4 and 9.0 at 7 °C, respectively (mean SD was 1.50). The brix- acid ratios were not significantly different for any of these treatments and showed no correlation with storage time, storage temperature, flavor, chilling injury or ethanol content.

Conclusion

'Valencia' oranges and 'Marsh' grapefruit, coated with a high-gloss shellac coating, developed rather high ethanol content, suggesting reduced internal quality, during cold storage despite the fact that internal O_2 was roughly 10%. For the same fruit with wax coatings or no coatings, the ethanol content was considerably lower. Grapefruit appearance and flavor was best with the wax coating and 3 °C storage, whereas chilling injury was least with the high-gloss shellac coating. The electronic nose signal was different for grapefruit with the high-gloss coating, but did not separate out the fruit with best flavor (wax coating, 3 °C).

Literature Cited

Ahmad, M. and I. Khan. 1987. Effect of waxing and cellophane lining on chemical quality indices of citrus fruit. Plant Foods Human Nutr. 37:47-57.

Baldwin, E. A., M. Nisperos-Carriedo, P. E. Shaw, and J. K. Burns. 1995. Effect of coatings and prolonged storage conditions on fresh orange flavor volatiles, degrees brix and ascorbic acid levels. J. Agric. Food Chem. 43:1321-1331.

Cohen, E, Y. Shalom, and I. Rosenberger. 1990a. Postharvest ethanol buildup and off-flavor in 'Murcott' tangerine fruits. J. Amer. Soc. Hort. Sci. 115:775-778.

Cohen, E., S. Ben-Yehoshua, I. Rosenberger, Y. Shalom, and B. Shapiro. 1990b. Quality of lemons sealed in high-density polyethylene film during long-term storage at different temperatures with intermittent warming. J. Hort. Science. 56:603-610.

Cuquerella-Cayuela, J., J. M. Martinez-Jarega, and M. Jimenez-Cuesta. 1983. Frigoconservacion de citricos. Hoja-Tecnica,-Instituto-Nacional de Investigaciones Agrarias 45:5-20.

Hagenmaier, R. and R. A. Baker. 1994. Internal gases, ethanol content and gloss of citrus fruit coated with polyethylene wax, carnauba wax, shellac or resin at different application levels. Proc. Fla. State Hort. Soc., 107:261-265.

Hagenmaier, R. 2000. Evaluation of a polyethylene-candelilla coating for 'Valencia' oranges. Postharvest Biol. Technol. 19:147-154.

Hagenmaier, R. 2002. The flavor of Mandarin hybrids with different coatings. Postharvest Biol. Technol. 24:79-87.

Jimenez-Cuesta, M., J. M. Martinez-Jarega, and J. Cuquerella. 1983. Refrigeration in the Service of Man, XVI Congress of Refrigeration, 3:251-257.

Ke, D. and A. A. Kader. 1990. Tolerance of 'Valencia' oranges to controlled atmospheres as determined by physiological responses and quality attributes. J. Am. Soc. Hort. Sci. 115:779-783.

Schirra, M. 1992. Behaviour of 'Star Ruby' grapefruits under chilling and onchilling storage temperature. Postharvest Biol. Technol. 2:317-327.