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Gas Exchange, Ripening Behaviour and Postharvest Quality of Coated Pears

A thesis presented in partial fulfilment
of the requirements

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*To my parents,
Iraci and João Wellington,
and my brother Alessandro,
for so much love,
support and encouragement*

Abstract

Pear cultivars ‘Bartlett’, ‘Beurre Bosc’, ‘Doyenne du Comice’, and ‘Packham’s Triumph’ were treated with different levels of deposits of a carnauba based wax on the skin and assessed for gas exchange, ripening behaviour and postharvest quality. The response to coating treatments was strongly dependent on cultivar, ripening stage and environmental temperature. ‘Bartlett’, ‘Comice’ and ‘Packham’s’, with non-lignified skin, had substantial reductions in skin permeance (P'_j) with small increases in coating deposit. Magnitudes of reduction in P'_j to different gases were observed in the order: $P'_{O_2} > P'_{CO_2} \gg P'_{H_2O}$. The skin of ‘Bosc’, with lignified cells, had high P'_{H_2O} and low P'_{CO_2} , and increasing the amount of coating deposited on the skin resulted in small reductions of P'_{H_2O} and a gradual reduction of P'_{O_2} and P'_{CO_2} . ‘Bartlett’ and ‘Bosc’ had a high risk of developing internal disorders caused by excessive internal accumulation of CO_2 at low temperatures when treated with substantial coating deposits, as a result of high respiration rate (‘Bartlett’) or low P'_{CO_2} of coated skin (‘Bosc’). These cultivars were also less tolerant to hypoxia (expressed in terms of internal lower O_2 limit, LOL^i) created by high coating concentrations, and their level of tolerance reduced with increasing ripeness. ‘Comice’ and ‘Packham’s’ were highly tolerant of hypoxia [the fruit did not ferment despite of an internal O_2 partial pressure ($p_{O_2}^i$) \cong 0 kPa]. Respiration rates, softening and colour change followed a Michaelis-Menten model when plotted against $p_{O_2}^i$, while internal CO_2 partial pressure ($p_{CO_2}^i$) had virtually no explanatory power for these variables during shelf life. Variable cover of skin pores in cultivars having high P'_j might result in variable P'_{O_2} and, consequently, variable $p_{O_2}^i$. This could increase the naturally high ripening variability of pears treated with a given coating concentration. Softening had a lower Michaelis-Menten constant for $p_{O_2}^i$ than skin colour. Therefore, coated pears with intermediary $p_{O_2}^i$ might have variable postharvest quality mainly in terms of colour change, and the fruit may still soften while being unable to change in colour. For ‘Comice’, higher levels of coating deposit resulted in more substantial modification of internal atmosphere during cold storage,

slightly increasing ripening delay. These treatments reduced wastage by diminishing the incidence of senescent breakdown and senescent scald after long term storage and by reducing skin friction discolouration during shelf life. Increasing the amount of coating deposit improved skin gloss and reduced senescent breakdown of 'Bartlett', 'Comice' and 'Packham's' during shelf life. The results show that optimisation of surface coatings should take into account differences between cultivars, ripening stage when the fruit is coated and storage temperature to avoid the risk of fermentation and physiological disorders. Even though there are some quality problems due to uneven ripening, wax coatings represent a technology with high potential for the pear industry, improving the finish of the skin, reducing water loss, delaying ripening and reducing the incidence of senescence related disorders.

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List of Symbols and Abbreviations

A	=	surface area (m^2)
\AA	=	Ångstrom
AAT	=	alcohol acyltransferase
ACC	=	1-aminocyclopropane-1-carboxylic acid
ACC-O	=	ACC oxidase
ACC-S	=	ACC synthase
Acet	=	acetaldehyde
ACP	=	anaerobic compensation point
ACP^e	=	external anaerobic compensation point
ACP^i	=	internal anaerobic compensation point
ADP	=	adenosine diphosphate
ADH	=	alcohol dehydrogenase
ANOVA	=	analysis of variance
ATP	=	adenosine triphosphate
ATP-PFK	=	ATP-phosphofructokinase
c^i_{EtOH}	=	internal ethanol concentration ($\text{mol}\cdot\text{m}^{-3}$)
CA	=	controlled atmosphere
CCA	=	canonical correlation analysis
CDA	=	canonical discriminant analysis
CDF_n	=	canonical discriminant function number n
C_2H_4	=	ethylene
cm	=	centimetre
CMC	=	carboxymethylcellulose
CO_2	=	carbon dioxide
D_j	=	diffusion coefficient for gas j ($\text{m}^2\cdot\text{s}^{-1}$)
df/dt	=	derivative of fruit firmness for time
dh/dt	=	derivative of fruit hue angle for time
DHAP	=	dihydroxyacetone phosphate

<i>DL</i>	=	change in lightness of the skin after FD
DNA	=	deoxyribonucleic acid
DRC	=	parallel discriminant ratio coefficient, defined as the product of SCC and <i>r</i> .
DS	=	degree of substitution, or number of substituted hydroxyl groups per monomeric cellulose unit
dy/dt	=	derivative of fruit ripening process <i>y</i> for time
E_p	=	activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)
EDTA	=	ethylene-diaminetetraacetic acid
<i>EP</i>	=	extinction point
Eq.	=	equation
EtAc	=	ethyl acetate
ETC	=	electron-transport system
EtOH	=	ethanol
<i>f</i>	=	'Kiwifirm' fruit firmness (arbitrary units)
F1,6-P ₂	=	fructose 1,6-biphosphate
F2,6-P ₂	=	fructose 2,6-biphosphate
F6P	=	fructose 6-phosphate
FD	=	friction discolouration
Fig(s).	=	figure(s)
<i>FT</i>	=	fermentation threshold
<i>FT</i> ⁱ	=	internal fermentation threshold
<i>FT</i> _{EtOH} ⁱ	=	internal fermentation threshold based on ethanol accumulation
<i>FT</i> _{RQ} ⁱ	=	internal fermentation threshold based on respiratory quotient
g	=	gram
GAP	=	3-phosphoglyceraldehyde
Glu	=	glucose
G6P	=	glucose 6-phosphate
h	=	hour
<i>h</i> ^o	=	fruit skin hue angle

H ₂ O	=	water
HPC	=	hydroxypropylcellulose
HPMC	=	hydroxypropyl methylcellulose
kg	=	kilogram
K_m	=	Michaelis-Menten constant
kPa	=	kilopascal
l	=	liter
Lac	=	lactate
LDH	=	lactate dehydrogenase
<i>LOL</i>	=	lower oxygen limit
<i>LOL^e</i>	=	external lower oxygen limit
<i>LOLⁱ</i>	=	internal lower oxygen limit
<i>M</i>	=	mass (kg)
m	=	metre
MA	=	modified atmosphere
MC	=	methylcellulose
mg	=	milligram
min	=	minute
mm	=	millimetre
mN	=	millinewton
mol	=	mole
mRNA	=	messenger ribonucleic acid
μm	=	micrometre
μM	=	micromolar
N	=	newton
N ₂	=	nitrogen
NAD ⁺	=	adenine dinucleotide (oxidised form)
NADH	=	adenine dinucleotide (reduced form)
nm	=	nanometre
nmol	=	nanomole

O_2	=	oxygen
OAA	=	oxaloacetate
OPP	=	<i>o</i> -phenylphenol
P	=	probability or level of significance of a statistical test
$P_{C_2H_4}$	=	permeability to ethylene ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
$P'_{C_2H_4}$	=	permeance to ethylene ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
P_{CO_2}	=	permeability to carbon dioxide ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
P'_{CO_2}	=	permeance to carbon dioxide ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
P_{H_2O}	=	permeability to water ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
P'_{H_2O}	=	permeance to water ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
P_i	=	inorganic orthophosphate
P_j	=	permeability to gas j ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
p_j	=	partial pressure of gas j (Pa)
P'_j	=	permeance to gas j ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
$P'_{j,k}$	=	permeance of coating film k to gas j ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
$P'_{j,skin}$	=	permeance of the commodity skin to gas j ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
$P'_{j,total}$	=	total permeance to gas j of a commodity coated with a tightly adhering film ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
P_{O_2}	=	permeability to oxygen ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
P'_{O_2}	=	permeance to oxygen ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$)
$P'_{O_2,T}$	=	permeance to oxygen at temperature T ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$);
$p_{CO_2}^e$	=	external partial pressure of carbon dioxide (Pa)
p_j^e	=	partial pressure of gas j in the external atmosphere (Pa)
$p_{O_2}^e$	=	external partial pressure of oxygen (Pa)
$p_{CO_2}^i$	=	internal partial pressure of carbon dioxide (Pa)
p_j^i	=	partial pressure of gas j in the internal atmosphere (Pa)
$p_{O_2}^i$	=	internal partial pressure of oxygen (Pa)
Pa	=	pascal
PCK	=	pyruvate carboxykinase
PDC	=	pyruvate decarboxylase

PDH	=	pyruvate dehydrogenase
PEP	=	phosphoenolpyruvate
PEPC	=	phosphoenolpyruvate carboxylase
PEP-CK	=	phosphoenolpyruvate carboxykinase
pH	=	measure of a solution concentration of hydrogen ions
PK	=	pyruvate kinase
pmol	=	picomole
PP _i	=	inorganic pyrophosphate
PPi-PFK	=	pyrophosphate phosphofructokinase
ppm	=	part per million
PPO	=	polyphenol oxidase
PYR	=	pyruvate
Δp_{H_2O}	=	water vapour pressure difference between the fruit and air stream (Pa)
Δp_j	=	difference in partial pressures of gas <i>j</i> between the internal and the external atmospheres (Pa)
Q_{10}	=	temperature coefficient ($=$ [rate of O ₂ uptake at $(T+10^\circ\text{C})$] / [rate of O ₂ uptake at T])
<i>r</i>	=	canonical correlation, or “pooled within-group canonical structure” (correlation between “within-group standardized canonical discriminant functions” and original variables)
®	=	registered brand
R^2	=	coefficient of determination (%), or proportion of variation in <i>y</i> values that is explained by <i>x</i>
r_{CO_2}	=	specific rate of transfer of carbon dioxide between internal and external atmospheres ($\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)
$r_{\text{CO}_2(\text{ox})}$	=	specific rate of oxidative CO ₂ production ($\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)
$r_{\text{CO}_2(\text{fer})}$	=	specific rate of fermentative CO ₂ production ($\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)
$r_{\text{CO}_2(\text{tot})}$	=	specific rate of total CO ₂ production ($\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)

$r_{\text{H}_2\text{O}}$	=	specific rate of transfer of water between the fruit and external atmosphere ($\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)
r_j	=	specific rate of transfer of gas j between internal and external atmospheres ($\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)
r'_j	=	rate of transfer of gas j between internal and external atmospheres ($\text{mol}\cdot\text{s}^{-1}$)
$r'_{j,k}$	=	rate of transfer of gas j through the coating film k ($\text{mol}\cdot\text{s}^{-1}$)
r_{O_2}	=	specific rate of transfer of oxygen between internal and external atmospheres ($\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)
r'_{O_2}	=	rate of transfer of oxygen between internal and external atmospheres ($\text{mol}\cdot\text{s}^{-1}$)
$r'^T_{\text{O}_2}$	=	rate of oxygen uptake for the system at temperature T ($\text{mol}\cdot\text{s}^{-1}$)
RH	=	relative humidity
rpm	=	rotations per minute
RQ	=	respiratory quotient
RQB	=	respiratory quotient breakpoint
s	=	second
S_{CO_2}	=	solubility for carbon dioxide ($\text{mol}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$)
$S_{\text{H}_2\text{O}}$	=	solubility for water ($\text{mol}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$)
S_j	=	solubility for gas j ($\text{mol}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$)
S_{O_2}	=	solubility for oxygen ($\text{mol}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$)
$[S]_{0.5}^{[\text{O}_2]e}$	=	half-saturating substrate concentration with respect to O_2 in the external atmosphere for ACC-O activity
SAM	=	S-adenosylmethionine
SCC	=	standardized canonical coefficient
SD	=	standard deviation
SDH	=	succinate dehydrogenase
SE	=	standard error
T	=	temperature
v	=	volume (m^3)

V_{max}	=	maximum rate constant of Michaelis-Menten model
w	=	weight (kg)
Δx	=	film thickness (m)

1.1 Background for the project

The magnitude of postharvest losses in fresh fruits and vegetables is estimated to range typically between 25-80%, depending upon the commodity and the technological level of postharvest operations (Wills et al., 1981). This reflects a lack of knowledge by postharvest handlers of the biological and environmental factors involved in deterioration or the absence of adequate postharvest technologies required to preserve fresh quality. Considering that, for horticultural products, the main costs from production until transfer to the final consumer are incurred after harvesting, these losses represent a large proportion of total costs along the hort-business, greatly reducing the profitability of the marketing chain.

Extension of the postharvest life of fresh fruits and vegetables is critically dependent upon four factors: (1) reduction in desiccation; (2) reduction in the physiological processes of ripening and senescence and in the incidence of physiological disorders; (3) reduction of physical damage; (4) and reduction in the onset and rate of microbial growth. Unless all four interdependent factors are carefully controlled, optimum extension of postharvest life is not achieved. Understanding of the physiological basis of different storage techniques in preserving quality is of prime importance in extending the postharvest life of horticultural products.

Refrigeration is the primary methodology to maintain quality in harvested fruits and vegetables, but additional benefits can be achieved with modified atmosphere (MA) storage (Kader et al., 1989). With MA techniques, internal atmosphere composition of the product is modified to achieve physiological benefits. Controlled atmosphere (CA) storage is one MA technique in which there is a very precise control of atmosphere composition around the commodity in storage rooms (Kader, 1995). Other approaches to MA involve selectively permeable materials such as packaging films or edible coatings. These techniques provide less accurate control of internal atmosphere

composition (Smith et al., 1987). CA storage has provided extension of storage period and improved the quality of many horticultural commodities (Kader, 1995). However, this technique usually involves high capital and maintenance costs and it may be uneconomic to store small quantities of product or commodities of low economic value (Smith et al., 1987). When the product is removed from the store, it is again subjected to air and ambient temperatures that can result in rapid loss of quality (Smith and Stow, 1984).

MA storage in plastic packages provides a less expensive alternative for small volumes of produce and provides good control of water loss (Ben-Yehoshua, 1985). However, the strong effects of temperature on gas exchange of packed products means there may be either inadequate or excessive modification of the package internal atmosphere during cold storage and shelf life, respectively (Smith et al., 1987). Plastic packages can increase risk of decay as a result of water vapour condensation in the package (Ben-Yehoshua, 1985) and there is increasing world-wide concern about environment contamination with disposable plastic films (Rose, 1992).

Coatings are not as efficient as plastic packages in reducing water loss, and are similarly temperature dependent in terms of their effects on internal atmosphere modification (Banks et al., 1993a). In a coated commodity, the coating adheres tightly to the edges of the pores so that there is no opportunity for mixing of gases between the commodity surface and the coating. On the other hand, in a commodity sealed in a plastic film, there is an opportunity for exchange of gases in the space between the fruit surface and film. Therefore, the decrease in total permeance to O₂ and CO₂ exchange will be much smaller for a sealed than for a coated commodity, in spite of using films with the same permeability in both techniques (Banks et al., 1993a). The blockage of the pores greatly impairs O₂ and CO₂ exchange, especially in the case of O₂ for which diffusion is restricted to the pores. Therefore, the treatment of a commodity with a coating can result in much more dramatic changes in the internal atmosphere and increase in risk of anaerobiosis than wrapping it in a plastic film (Banks et al., 1993a; Ben-Yehoshua et al., 1985)

The skin permeance of the coated commodity can be optimised by changing the total solids concentration in the coating formulation (Hagenmaier and Baker, 1993). Reducing the coating concentration can result in less extensive blockage of pores in the skin, ameliorating the resulting reduction of skin permeance to gases. With this approach, coatings can be optimised for each commodity and storage environmental temperature. Edible coating films represent an environmentally ideal packaging material as their main ingredients can be produced from renewable resources, in contrast to synthetic films, which are manufactured from a limited supply of fossil fuels. Also, edible coatings can be used to improve the product quality by serving as a carrier of several additives, such as anti-oxidants, biological control agents, growth regulators, colouring compounds (Cuppert, 1994). They can also add extra nutritional value to fruits and vegetables by incorporating rich dietary components (Gennadios et al., 1994) and coatings can also improve the visual appeal by increasing sheen or perceived depth of colour (Hagenmaier and Baker, 1995; Johnston and Banks, 1998). The use of surface coatings provides an opportunity to mimic CA and/or MA (plastic or shrink-wrap) storage, that is labour-intensive and/or expensive, with an environmentally friendly, biodegradable edible coating (Baldwin, 1994).

1.2 Research objectives and structure of the thesis

The main objectives of the current work were to investigate the impacts of improving the character of skin cover with a carnauba-based coating, on the postharvest physiology and quality of four pear cultivars (Fig. 1.1) with very contrasting skin permeance, respiration rate and storage potential: ‘Bartlett’ (with high respiration rate, high skin permeance and short storage potential), ‘Beurre Bosc’ (with low respiration rate, high skin permeance and medium storage potential), ‘Doyenne du Comice’ (with low respiration rate, low skin permeance and long storage potential)

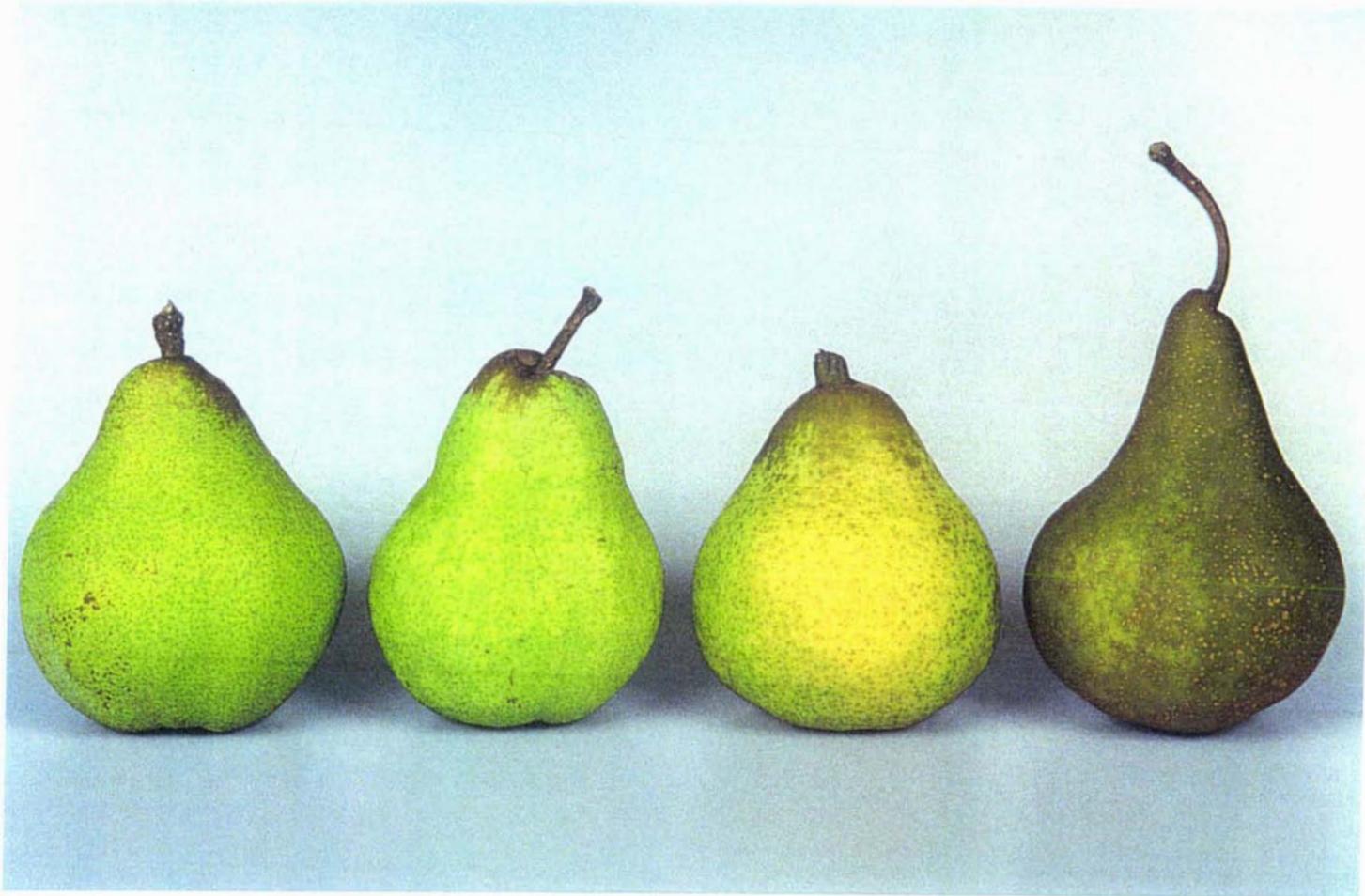


Figure 1.1 Pear (*Pyrus communis* L.) cultivars (left to right) 'Doyenne du Comice', 'Packham's Triumph', 'Bartlett' and 'Beurre Bosc'.

and 'Packham's Triumph' (low respiration rate, very low skin permeance and very long storage potential).

The present study was focussed on characterising:

- the changes in permeance to water vapour, O₂ and CO₂ with variation in coating deposits on the skin, achieved by treating the fruit with coating formulations having different total solids composition;
- the relationship between the changes in permeance to gases and internal atmosphere modification of the fruit;
- ripening behaviour and postharvest quality in relation to skin permeance, internal atmosphere gas composition, storage temperature and ripening stage when the fruit were coated.

In Chapter 2 a review of relevant literature is presented. The first part of the literature review focuses on describing how the physico-chemical properties of coating films affect their barrier properties to water vapour and gases. The second part reviews the main factors affecting gas exchange and modification of coated commodity internal atmosphere, including surface coating barrier properties, mode of application, environmental factors (temperature and RH) and commodity's physiology and nature of the skin. In the third part, physiological and biochemical effects of modified atmospheres on respiration and ethylene metabolism are reviewed. The last part covers the published literature describing the effects of surface coatings on postharvest physiology and quality of coated commodities.

Chapters 3 to 6 are written in the format of papers for publication in the journal *Postharvest Biology and Technology* and are the focus of the main research goals outlined above.

Chapter 3 investigates the effects of different concentrations of a commercial wax coating on ripening behaviour, skin gloss, sensory attributes and physiological disorders of pears coated at different ripening stages. Chapter 4 evaluates the relationships between character of skin cover and changes in permeance to water

vapour, O₂ and CO₂. Chapter 5 investigates the relationship between modification of internal atmosphere and changes in respiration rate, softening and skin colour change of coated pears. This chapter is mainly devoted to characterising the ripening behaviour and the lower internal O₂ limit (*LOLⁱ*, the internal O₂ partial pressure at which accumulation of the products of anaerobic respiration resulting in off-flavours and degradation of the tissue are likely; Banks et al., 1993b) of coated fruit. The impact of ripening stage when the fruit was coated on *LOLⁱ* is also investigated. The importance of such an approach for the optimisation of modified internal atmospheres, particularly with respect to their effects on postharvest quality of coated commodities is outlined. Chapter 6 investigates the potential of surface coatings for reducing friction discolouration on pears, as well as the effects of ripening stage, water status and fruit temperature on pear susceptibility to such skin damage.

Chapters 3 to 5 explore the application of multivariate analysis techniques to improve data interpretation of postharvest research with surface coatings. Canonical discriminant analysis was used in Chapters 3 and 4 to identify differences among coating treatments and to improve the understanding of the relationships among the attributes measured within those coating treatments. Canonical correlation analysis was used in Chapter 6 to identify which gas (O₂ or CO₂) internal partial pressure was more strongly related to ripening behaviour of coated pears.

Chapter 7 is a general discussion drawing together the main benefits and drawbacks of surface coatings for pears. A conceptual model is presented and discussed, focussed on physical and physiological basis for the beneficial effects of surface coatings in preserving postharvest quality of pears and on physiological and environmental factors affecting the response to coating treatments. The implication of the study for the optimisation of surface coatings on pears, including other CA/MA storage techniques, and potential areas for extending the research are discussed.

In appendices are included copies of papers presented at three international postharvest conferences with results of this study.

1.3 References

- Baldwin, E.A., 1994. Edible coatings for fresh fruits and vegetables: past, present, and future. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 25-64.
- Banks, N. H., Dadzie, B. K. and Cleland, D. J., 1993a. Reducing gas exchange of fruits with surface coatings. *Postharvest Biology and Technology*, 3: 269-284.
- Banks, N. H., Cleland, D. J., Yearsley, C.W., and Kingsley, A.M., 1993b. Internal atmosphere composition – a key concept in responses of fruits and vegetables to modified atmospheres. *Proceedings of the Australasian Postharvest Conference*. The University of Queensland, Gatton College, Lawes, Queensland, Australia. pp. 137-143.
- Ben-Yehoshua, S., 1985. Individual seal-packaging of fruit and vegetables in plastic film - a new postharvest technique. *HortScience*, 20: 32-37.
- Ben-Yehoshua, S., Burg, S. P. and Young, R., 1985. Resistance of citrus fruit to mass transport of water vapor and other gases. *Plant Physiology*, 79: 1048-1053.
- Cuppett, S. L., 1994. Edible coatings as carriers of food additives, fungicides and natural antagonists. In: J.M. Krochta, E.A. Baldwin, and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 121-137.
- Gennadios, A., T. H. McHugh, C. L. Weller, and J. M. Krochta., 1994. Edible coatings and films based on proteins. In: J.M. Krochta, E.A. Baldwin, and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 201-277.
- Hagenmaier, R.D. and Baker, R.A., 1993. Reduction in gas exchange of citrus fruit by wax coatings. *Journal of Agricultural and Food Chemistry*, 41: 283-287.
- Hagenmaier, R.D. and Baker, R.A., 1995. Layered coatings to control weight loss and preserve gloss of citrus fruit. *HortScience*, 30: 296-298.
- Johnston, J.W. and Banks, N.H., 1998. Selection of a surface coating and optimisation of its concentration for use on 'Hass' avocado fruit. *New Zealand Journal of Crop and Horticultural Science* (submitted) .
- Kader, A. A., Zagory, D. and Kerbel, E. L., 1989. Modified atmosphere packaging of fruits and vegetables. *Critical Reviews in Food Science and Nutrition*, 28: 1-30.
- Kader, A. A., 1995. Regulation of fruit physiology by controlled/modified atmospheres. *Acta Horticulturae*, 398: 59-70.
- Rose, P. 1992. Never mind the food, the packaging tastes great. *Food Manufacture International*, 9: 27, 29-30.
- Smith, S. M. and Stow, J. R., 1984. The potential of a sucrose ester coating material for improving the storage and shelf-life qualities of Cox's Orange Pippin apples. *Annals of Applied Biology*, 104: 383-391.
- Smith, S., Geeson, J. and Stow, J., 1987. Production of modified atmospheres in deciduous fruits by the use of films and coatings. *HortScience*, 22: 772-776.
- Wills, R.H., Lee, T.H., Graham, D., McGlasson, W.B.; Hall, E.G., 1981. *Postharvest, an Introduction to the Physiology and Handling of Fruit and Vegetables*. Westport, CN, USA; AVI Publishing Co. Inc., pp. 1-2.

2.1 Introduction

In recent years, great attention has been paid to improving the use of surface coatings to maintain quality of harvested fresh produce and, at the same time, protect the environment by reducing the volume of disposable non-biodegradable packaging materials (Rose, 1992). The use of edible coatings is not new; the Chinese were coating fruits and vegetables with wax in the twelfth and thirteenth centuries (Hardenburg, 1967).

Surface coatings have been used extensively on bulky organs to modify the internal atmosphere and delay ripening (Baldwin, 1994; Banks, 1984a; Banks et al., 1993a and 1997b; Smith et al., 1987), reduce water loss (Hagenmaier and Baker, 1993a and 1994a), and improve the finish of the skin (Hagenmaier and Baker, 1994b and 1995; Johnston and Banks, 1998; Mellenthin et al., 1982). The latter attribute has been considered by the fruit industry as the main benefit from a marketing point of view, without much consideration about the physiological impacts of coatings on other aspects of fruit quality. Coatings may have no effect in delaying ripening at low temperature, when the modification of internal atmosphere is low (Banks, 1984c; Smith and Stow, 1984). At high temperatures, when respiration is high and a substantial decrease of O₂ (and increase of CO₂) occurs, inhibition of ripening can be excessive and the tissue may ferment (Banks et al., 1997a and 1997b; Davis and Hofmann, 1973; Hagenmaier and Baker, 1993a and 1994b; Magness and Diehl, 1924; Smock, 1935; Trout et al., 1953). The degree of reduction in water loss and modification of internal atmosphere is also greatly affected by the permeance of the coating film itself (Hagenmaier and Baker, 1993a and 1993c; 1994a and 1994b; 1995; 1996) and the character of cover of commodity skin by the surface coating (Banks et al., 1993a; 1997b; Hagenmaier and Baker, 1993a; 1994a and 1994b). Coated fruits and vegetables may also manifest many physiological disorders during refrigeration or

shelf life (Edward and Blennerhassett, 1990; Farooqui and Hall, 1973; Hitz and Haut, 1938; Kerbel et al., 1989; Lau and Meheriuk, 1994; Lau and Yastremsky, 1991; McGuire and Hallman, 1995; Smith and Stow, 1984; Smock, 1935; Trout et al., 1953; Van Zyl et al., 1987). As these effects are not necessarily known and understood by people in the marketing chain, or by manufacturers of edible coatings, use of coatings may be far from optimal and can, in such cases, impair rather than enhance product quality.

The majority of published papers dealing with surface coatings do not provide full descriptive information about the main components and their concentrations in the commercial formulations, because the manufacturers keep such information confidential. This makes the interpretation of results published by various authors quite difficult, limiting the potential to improve coating formulations for different products and storage conditions.

Most of the literature about surface coatings has been largely empirical, describing the quality changes occurring from the application of a particular coating treatment, without providing information about the degree of change in permeance to gases and how this is related to the extent of internal atmosphere modification in coated commodities. Several authors have published values of permeance to gases and water vapour of coating films (Avena-Bustillos and Krochta, 1993; Donhowe and Fennema, 1993; Elson et al., 1985; Gennadios et al., 1993; Gontard et al., 1993, 1996; Hagenmaier and Shaw, 1990, 1991a, 1991b, 1992; Hagenmaier and Baker, 1994a and 1996; Kamper and Fennema, 1984a and 1984b; Kester and Fennema, 1989a, 1989b and 1989e; Koelsch, 1994; Mannheim and Soffer, 1996; Martín-Polo et al., 1992; McHugh and Krochta, 1994b; Rico-Peña and Torres, 1990; Wong et al., 1992), with some published information for coated commodities (Avena-Bustillos et al., 1994 and 1997; Banks 1984a; Banks et al., 1997a and 1997b; Ben-Yehoshua et al., 1985; Hagenmaier and Baker, 1993a; Johnston and Banks, 1998; Paull and Chen, 1989). Permeance values of commodities treated with surface coatings can be very different from the permeance of the coating films themselves. Coatings mainly exert their

effects on skin permeance to gases by blocking a greater or lesser proportion of the pores on the product surface (Banks et al., 1993a, 1997b; Hagenmaier and Baker, 1993a). On this basis, it might be expected that fruit with different skin characteristics may present very different responses to a certain coating by exhibiting distinct types of interaction with the surface coating.

The published information about barrier properties of coating films has been obtained using several different techniques in a variety of environmental conditions (temperature, RH and gas partial pressures; McHugh and Krochta, 1994a). In most cases, these conditions are very distinct from the real situation encountered by the surface coating during the storage of a coated product. This, coupled with the variety of terms used to characterise the barrier properties of films (such as transmission rate, permeability, permeability coefficient, permeance and resistance) and the multitude of units used to express each term (Donhowe and Fennema, 1994), makes it difficult for the end users of data to compare results from different studies. Conversions made from alternative systems of units is time consuming and must rely on assumptions that may not be true (Banks et al., 1995).

This literature review outlines the main factors to be considered for a better understanding of the physical and physiological issues involved in preserving postharvest quality of coated fresh fruits and vegetables. The most pertinent literature available is presented and discussed, highlighting the most important benefits and risks of coatings, which may have serious impacts on final product quality. The review focuses on fresh fruits and vegetables, not on processed products. Information about application of coatings in processed horticultural products can be obtained in recent publications elsewhere (Baldwin et al., 1995a; Nisperos-Carriedo and Baldwin, 1996; Wong et al., 1994).

2.2 Permeability of coating films and permeance of coated commodities

For coating films, when there are no pores, faults, or membrane punctures, the primary mechanism of gas and water vapour transfer through a coating film is by activated diffusion; i.e., the permeant dissolves in the film matrix at the high concentration side, diffuses through the film driven by a concentration gradient, and evaporates from the outer surface (Kester and Fennema, 1986). The second step of the process, i.e., diffusion, depends upon size, shape, and polarity of the permeant as well as polymer-chain segmental motion within the film matrix (Kester and Fennema, 1986). Factors affecting segmental motion of the polymer chain include inter-chain attractive forces such as hydrogen bonding and van der Waals' interactions, degree of crosslinking, and amount of crystallinity (Kumins, 1965). The dissolution and evaporation steps are influenced by solubility of the permeant in the film (Pascat, 1985).

Permeability of film k to gas j ($P_{j,k}$, $\text{mol}\cdot\text{s}^{-1}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$) is then defined by the product of the diffusion coefficient (D_j , $\text{m}^2\cdot\text{s}^{-1}$), representing the mobility of permeant molecules j in the film k , and the solubility coefficient (S_j , $\text{mol}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$), representing the permeant j concentration in the film k balanced with the external pressure:

$$P_{j,k} = D_j \cdot S_j \quad [2.1]$$

Permeability of a coating film k at steady state can also be estimated by Fick's First Law of Diffusion (Banks et al., 1995):

$$P_{j,k} = \frac{r'_j \cdot \Delta x}{\Delta p_j \cdot A} \quad [2.2]$$

where: r'_j = rate of transfer of gas j through the coating film k ($\text{mol}\cdot\text{s}^{-1}$); Δx = film k thickness (m); Δp_j = difference in partial pressures of gas j across the film k (Pa); and A = surface area (m^2).

For coated commodities, it may be difficult to separate the gas exchange into the diffusivity and solubility components, as diffusion through the skin involves parallel transfer through pores and cuticle (Banks et al., 1993a). Also, the surface coating on a treated commodity may be heterogeneous or of unknown thickness, so permeance is more useful to estimate its gas exchange properties (Banks et al., 1995). Permeance of coating film k to gas j ($P'_{j,k}$, $\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$) is related to permeability by:

$$P'_{j,k} = \frac{P_{j,k}}{\Delta x} \quad [2.3]$$

From Banks et al. (1993), the total permeance to gas j ($P'_{j, total}$) of a commodity coated with a tightly adhering film actually comprises the effective permeance of the commodity skin ($P'_{j, skin}$) and the coating barrier k ($P'_{j,k}$) operating in series:

$$\frac{1}{P'_{j, total}} = \frac{1}{P'_{j, skin}} + \frac{1}{P'_{j,k}} \quad [2.4]$$

From equations 2.2, 2.3 and 2.4, the magnitude of difference between internal and external atmosphere composition of the fruit is directly proportional to rate of transfer of gas j and inversely proportional to total permeance of the coated commodity to gas j :

$$\Delta p_j = p_j^i - p_j^e = \frac{r'_j}{P'_{j, total} \cdot A} \quad [2.5]$$

where: p_j^i = partial pressure of gas j in the internal atmosphere (Pa); p_j^e = partial pressure of gas j in the external atmosphere (Pa); and for a commodity $r_j' = r_j \cdot M$, with r_j being the specific rate of transfer of gas j between the commodity internal and external atmospheres ($\text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$) and M the commodity mass (kg).

Eq. 2.5 is only valid if internal atmosphere composition is reasonably uniform within the organ (Cameron and Yang, 1982). This is not always true in commodities with high-density flesh tissue or following flooding of the intercellular spaces due to ripening. Problems caused by heterogeneity of internal atmosphere composition can, in some cases, be minimized by sampling internal gas composition non-destructively from under the skin using the external glass chamber method (Yearsley et al., 1996).

Gases diffuse mainly through pores in the skin, while water moves preferentially by a different pathway, probably through a liquid aqueous phase in the cuticle where water solubility is high. Gases are constrained from using this pathway due to their low solubility in the water and wax components of the cuticle matrix ($S_{\text{H}_2\text{O}} \gg S_{\text{CO}_2} > S_{\text{O}_2}$; Banks et al., 1993a; Foust et al., 1980) and low diffusivity in liquid water (which is 10^4 -fold less than in air; Foust et al., 1980). As a result, improving the blockage of pores in the skin with a surface coating results in $P_{\text{O}_2}' < P_{\text{CO}_2}' \ll P_{\text{H}_2\text{O}}'$ (Ben-Yehoshua et al., 1985). Covering the pores of the skin provides some limited reduction in water loss, but there is still an extensive diffusion of water through the cuticle and the coating film (Banks et al., 1993a; Ben-Yehoshua et al., 1985). However, covering the pores in the skin has a dramatic effect in reducing P_{O_2}' and P_{CO_2}' , especially P_{O_2}' , since O_2 has a lower solubility in the water and wax components of the coating matrix than CO_2 (Banks, 1984a; Banks et al., 1993a; Trout et al., 1953). On citrus fruit, waxing with a coumarone indene resin depressed $P_{\text{H}_2\text{O}}'$, P_{CO_2}' , and P_{O_2}' to about 85%, 40% and 30% of the control values, respectively (Ben-Yehoshua et al., 1985). On bananas coated with TAL Pro-long (1.5% w/v) P_{CO_2}' and P_{O_2}' were depressed to about 64% and 20% of their controls, respectively (Banks, 1984a). This results in coated commodities having more substantial reduction of O_2 than of CO_2 internal concentration (Banks, 1984a; Ben-Yehoshua, 1967; Trout et al., 1953), while water loss is little affected (Banks, 1984a;

Banks et al., 1993a). For ethylene (C_2H_4) $P'_{C_2H_4}$ in coated commodities has been reported to be reduced to levels between those observed for P'_{O_2} and P'_{CO_2} (Banks, 1984a; Ben-Yehoshua et al., 1985).

Mannheim and Soffer (1996) observed a relationship between P_{H_2O} of coating films and weight loss of coated fruit, but not between P_{CO_2} and P_{O_2} of the coating films and concentration of these gases in the fruit. This is in agreement with observations made by Banks et al. (1997). According to these authors, whilst to reduce fruit's water loss, the permeability of the coating film is much more important than pore blockage, the extent of fruit internal atmosphere modification is more strongly determined by the proportion of pores blocked by the coating than by the permeability of the coating film. However, Hagenmaier and Baker (1993a) observed that for both CO_2 and water vapour, the skin permeance of coated fruit is reduced by both the coating's tendency to seal pores in the fruit peel and the barrier properties of coating material itself. Thus, the nature of the commodity skin can affect its interaction with a surface coating and, hence, the permeance of the coated commodity (Claypool and King, 1941). This, in association with the product respiration rate, determines the level of internal atmosphere modification and the resulting effects on quality attributes. Therefore, although information about the effect of film type, formulation, temperature and RH on permeability of edible films is quite useful for film evaluation, information pertaining to permeance to gases of coated fruit would provide a more realistic approach for coating selection. With direct measurement of commodity permeance to gas exchange under controlled environmental conditions (temperature, RH and pressure) it would be possible determine *in loco* if the coating film exhibits the properties required to attain an optimised modified internal atmosphere for a given commodity in a specific storage condition (Hagenmaier and Baker, 1993a).

2.3 Edible coatings used today: physico-chemical characteristics and barrier properties to water vapour and gases

Many different coating formulations have been investigated for their potential benefits in preserving the postharvest quality of fruits and vegetables. These studies have mainly focused on assessing barrier properties of coating films made of components of different chemical nature and composite films made of mixtures of these. The literature concerned with the composition of these coatings and their main physico-chemical properties is discussed below.

2.3.1. Lipids and resins

Lipids and resins are added to coating formulations to reduce gas exchange, but mainly to impart hydrophobicity (to reduce water loss) and gloss (Baldwin, 1994; Baldwin et al., 1997; Hernandez, 1994). Lipid components of coatings include natural waxes such as carnauba wax, candelilla wax, rice bran wax, and beeswax; petroleum-based waxes such as paraffin and polyethylene wax; oils, mineral oil (mixture of paraffinic and naphthenic hydrocarbons) and vegetable oils (corn, soybean, or palm); and acetoglycerides and oleic acid (used as components of coatings to alter their mechanical and permeability properties). Resins are represented by shellac, wood rosin and coumarone indene and these are the main coating components used to impart gloss to the commodity (Hagenmaier and Baker, 1994b and 1995). However, fruit coated with resins have been reported to develop a whitening of the skin due to condensation that develops when they are brought from cold storage to ambient temperature (Hagenmaier and Baker, 1994a). Waxes are less likely to whiten and can also add some sheen to the product (Nisperos and Baldwin, 1996). Other compounds normally added to these coating formulations are plasticizers, emulsifiers, lubricants, binders, de-foaming agents, or formulation aids. Most natural waxes (beeswax, carnauba wax, and candelilla wax) also have emulsifying properties, as they are long-chain alcohols

and esters (Baldwin et al., 1997). The common lipid compounds and additives permitted for use as components in commercial and experimental coatings for food systems have been listed recently by Baldwin et al. (1997) and Hernandez (1994).

The permeability of lipid components of coatings to water vapour and gases depends on chain length, polarity, and degree of saturation and branching of their main components (Baldwin et al., 1997; Donhowe and Fennema, 1993; Hagenmaier and Shaw, 1990; Kamper and Fennema, 1984a and 1984b; Kester and Fennema, 1989a, 1989b, and 1989e). Lipid molecules with long chain length, low polarity, high saturation, and high linearity tend to produce films with a high degree of cohesiveness and rigidity as a result of stronger inter-chain attractive forces such as van der Waals' interactions, and low permeability, as opposed to short chain polar molecules with a high degree of branching and low saturation. Molecules with high linearity and long chain length have a more efficient packing of acyl chains. This, in addition to high saturation levels, tends to reduce the hydrocarbon chain mobility, reducing the diffusion (and solubility) of gases and water vapour molecules through the coating matrix.

Martín-Polo et al. (1992) observed that the proportion of liquid and solid components of a hydrophobic film determines moisture transfer of coatings. For coating films containing different proportions of a solid phase (paraffin wax or n-octacosane) mixed with a liquid phase (paraffin oil or n-hexadecane), a significant increase in $P_{\text{H}_2\text{O}}$ of the coating film was obtained for mixtures containing less than 25% solids. The results suggest that up to 75% liquid lipids may be used in coating formulations to overcome the problem of the rigidity of solid materials like edible waxes and to improve their flexibility and adhesiveness and to improve the character of cover without seriously diminishing their moisture barrier properties.

The excellent barrier properties of lipid crystals to moisture and gases are also dependent on the packing of the lipid crystals and their orientations to the direction of permeant flow. Kester and Fennema (1989a and 1989b) reported a dependence of $P'_{\text{H}_2\text{O}}$ and P'_o of lipids on polymorphic form and the structural morphology of the fatty acid

coating film. Fatty acids of the α -polymorphic form in the solid state, with molecular packing in a hexagonal system, had higher $P'_{\text{H}_2\text{O}}$ and P'_{O_2} than those fatty acids of the more stable β and β' polymorphic forms, packed in a common orthorhombic system. Tristearin (a triacylglycerol) and acetylated monoglyceride have the hexagonal type, while straight chain lipids such as fatty acids (stearic acid), fatty alcohols (stearyl alcohol), and alkanes, have the orthorhombic type. In the orthorhombic form, hydrocarbon chains are aligned with each other and arranged in sheets with strong van der Waals' interaction between laterally adjacent chains. The hydrocarbon chains of the α -polymorphic form are packed in a hexagonal orientation that is molecularly less dense and possesses greater mobility than the orthorhombic lateral packing, resulting in a higher $P'_{\text{H}_2\text{O}}$ and P'_{O_2} . Kester and Fennema (1989c) reported that changing the polymorphic form of lipid films from α to β polymorph substantially decreased P'_{O_2} but not $P'_{\text{H}_2\text{O}}$. These results may indicate that the hydration capacity of the various polymorphs, which may not be significantly different between the polymorphs, is more important for water permeation. Kester and Fennema (1989a and 1989b) suggested that differences in packing density and molecular mobility between the hexagonal and orthorhombic orientations are of relatively minor importance in comparison to the structural morphology of the coating film. According to these authors, it appears that the properly layered morphology with platelets that compactly overlay one another is the predominant factor accounting for the low $P'_{\text{H}_2\text{O}}$ and P'_{O_2} of some lipid films.

Kester and Fennema (1989d) also observed that tempering a stearyl alcohol coating film improved the gas exchange barrier properties of the film, despite no apparent changes in the polymorphic form of the lipid during the tempering period. Tempering at 48°C for 35 days caused P'_{O_2} and $P'_{\text{H}_2\text{O}}$ to decrease 45% and 33%, respectively. According to the authors, likely mechanistic explanations included the healing of crystal imperfections and the development of a more extensive and better-linked arrangement of lipid crystalline platelets.

Resins have polar groups and therefore have higher $P_{\text{H}_2\text{O}}$ and lower P_{O_2} , P_{CO_2} and $P_{\text{C}_2\text{H}_4}$ than waxes (Hagenmaier and Shaw, 1992). Coatings formed on polymer films had

lower $P'_{\text{H}_2\text{O}}$ when made with wax microemulsions rather than with mixtures of wax with shellac and resin (Hagenmaier and Baker, 1994b). Hagenmaier and Shaw (1992) reported that for commercial coatings, P_{O_2} at 50% RH and 30°C ranged from $5.5 \times 10^{-5} \text{ pmol} \cdot \text{s}^{-1} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$ for a shellac-based coating to $2.5 \times 10^{-3} \text{ pmol} \cdot \text{s}^{-1} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$ for a coating made of waxes (natural and synthetic) and fatty acids, with P_{CO_2} two to eight times as high. The $P_{\text{C}_6\text{H}_6}$ was between the values of P_{O_2} and P_{CO_2} for wax-based coatings, but lower than P_{O_2} for shellac and resin-based coatings.

The choice of solvent and neutralizing agent is important in determining the coating film permeability (Hagenmaier and Shaw, 1991a and 1991b). Hagenmaier and Shaw (1991a) observed that shellac coatings made from water-soluble formulations were more permeable to O_2 , CO_2 and water vapour than formulations made with ethanol, especially at RH above 80%. Using shellac solubilized in water with morpholine instead of shellac in ethanol increased P_{O_2} by 200% and P_{CO_2} by 435%, resulting in an increase of $P_{\text{CO}_2}/P_{\text{O}_2}$ from 3.5 to 6.3 at 30°C and 75% RH. At 75% RH shellac solubilized with NaOH was about 17 times as permeable to water as shellac solubilized with morpholine. The authors attributed the high permeability of films made of shellac solubilized in water to the addition of morpholine or NaOH to neutralize the shellac (a weak acid). Hagenmaier and Shaw (1991b) also reported higher P_{O_2} and P_{CO_2} for polyethylene-based coatings containing ammonia or morpholine instead of non-volatile surfactants. According to these authors, ammonia and morpholine keep the polyethylene dissolved and then evaporate as the coating dries. Thus, these have a minimum effect on the permeability of dried coatings. In contrast, non-volatile surfactants (that remain in the coating after drying) are polar and tend to reduce the coating permeability (Ashley, 1985).

Differences in formulation of coating films made with the same basic components can also affect permeability. Shellac varnish was more permeable to O_2 ($5.16 \times 10^{-5} \text{ pmol} \cdot \text{s}^{-1} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$) than bleached shellac ($3.04 \times 10^{-5} \text{ pmol} \cdot \text{s}^{-1} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$) at 28.5°C and 55% RH (Hagenmaier and Shaw, 1991a). High density polyethylene wax had $P_{\text{H}_2\text{O}}$, P_{O_2} , and P_{CO_2} 30-50% of the corresponding values for low density polyethylene waxes

(Hagenmaier and Shaw, 1991b). This is the result of denser polymers having a more crystalline structure and a lower permeability (Ashley, 1985). For wax emulsions, the size of the suspended globules in the emulsion affects the permeability of the film to water vapour and gases (Baldwin et al., 1997). Macroemulsions (turbid and milky in colour, with particle size of 2,000 to 100,000 Å) are thermodynamically less stable than microemulsions (clear in colour and with particle size of 1,000 to 2,000 Å; Hernandez, 1994), with macroemulsions being expected to impart higher permeability and lower gloss to the coated fruit than microemulsions (Baldwin et al., 1997). Therefore, the method of emulsion preparation (affecting particle size in the emulsion) may have a substantial impact on the commodity final quality. However, most research on preparation of wax emulsions, particularly formulations of edible coatings, is proprietary and little information is available (Hernandez, 1994). This makes it very difficult for researchers to compare results published in the literature for coatings having similar formulations but containing different additives and having been prepared by different methods of emulsification. In fact, in some published papers, the only information of this kind is that the commodity was coated with a 'wax-based coating' without specifying the main components in the formulation.

Donhowe and Fennema (1993) reported the values of P_{O_2} and P_{H_2O} for candelilla, carnauba, beeswax and microcrystalline waxes. The x-ray diffraction scans of the four wax films showed that all waxes were partially crystalline with characteristic orthorhombic packing. Candelilla wax had the lowest P_{H_2O} of the waxes tested, reflecting the low concentration of polar compounds and the large concentration of alkanes in its composition. Beeswax had the greatest P_{H_2O} ; this may have been the result of higher concentrations of fatty acids, fatty alcohols and esters in this wax than in the other three. The P_{H_2O} of candelilla wax was somewhat less than that of polypropylene and somewhat greater than that of high-density polyethylene films. Carnauba and candelilla waxes had the lowest P_{O_2} . Values for P_{O_2} of beeswax and microcrystalline wax were about six to nine times greater than those of candelilla and carnauba waxes. The greater P_{O_2} of beeswax and microcrystalline wax is the result of

these waxes containing crystals in both the hexagonal and orthorhombic systems. Candelilla contains crystals only in the orthorhombic system. Carnauba wax has some proportion of crystals in the hexagonal system, but because of its rigid nature, as reflected by its high terminal melting point and lack of low-melting fraction, the P_o , was comparatively low.

Carnauba is presently the most commonly used wax component, while polyethylene wax is permitted for use as a coating component for some fresh produce where, generally, the peel is not normally ingested (such as avocado, citrus, banana, pineapple, melon, mango, pumpkin, papaya, Hernandez, 1994). Consumer trends are leading towards more natural products. As a result, petroleum-based waxes, such as polyethylene and paraffin, and resins (mainly wood rosin and coumarone indene, a petroleum-based product), are becoming increasingly unpopular and restricted in use (Baldwin, 1994; Hernandez, 1994). Only shellac resin has recently been granted the GRAS (“generally recognized as safe”) status by the American authorities (Baldwin, 1994; Hernandez, 1994). Some countries have imposed strong restrictions on the use of waxes. Norway has recently prohibited all imports of waxed fruit, while petroleum waxes, morpholine, and carnauba wax are prohibited in the United Kingdom and petroleum wax is prohibited in Japan (Baldwin, 1994). Probably, the naturally derived waxes, such as beeswax, carnauba wax, and candelilla wax, will be considered more acceptable in the next few years. The same reasoning applies to oils, with mineral oil expected to be replaced by vegetable-based oils. This has also led towards increasing research for alternative coating formulations based on composite edible films made of polysaccharides and proteins in combination with lipids (mainly fatty acids), with all components having the GRAS status. The goal is to combine the desirable properties of good barrier to gases, strength and film forming attributes of the polymer structural matrix with the hydrophobicity and flexibility imparted by the lipid.

2.3.2 Polysaccharides

Polysaccharide-based coatings have been extensively studied for their selective permeabilities to O₂ and CO₂, resulting in modified internal atmosphere composition and delayed ripening in fruits and vegetables. These coating films are very effective barriers to O₂ and CO₂ but not to water (Wong et al., 1992). This property is probably related to the dense structure and high polarity of the film (McHugh and Krochta, 1994a). The inability of these coatings to provide sufficient gloss or prevent moisture loss can be improved by the incorporation of functional food ingredients such as resins and rosins, plasticizers, oils, waxes and emulsifiers (Hagenmaier and Baker, 1996; Hagenmaier and Shaw, 1990; Nisperos-Carriedo, 1994).

This group of coatings is mainly represented by cellulose derivatives, namely methylcellulose (MC), hydroxypropylcellulose (HPC), hydroxypropyl methylcellulose (HPMC), and carboxymethylcellulose (CMC; Nisperos-Carriedo, 1994; Kester and Fennema, 1986). Changing the level of methoxyl, hydroxypropyl and carboxymethyl substitution affects a number of physical and chemical properties such as water retention properties, sensitivity to electrolytes and other solutes, dissolution temperature, gelation properties, and solubility in non-aqueous systems (Nisperos-Carriedo, 1994; Kester and Fennema, 1986). The number of substituted hydroxyl groups per monomeric unit, expressed as degree of substitution (DS), can vary from zero to three, with higher DS resulting in increased solubility, compatibility with other ingredients (e.g. salts) and acid stability of the cellulose derivative (Nisperos-Carriedo, 1994).

The nonionic cellulose esters MC, HPMC, and HPC, are available in powder or granular form in varying molecular weights and DS. They are soluble in cold water but not hot water, and they are also soluble in organic solvents (except for MC with low DS). Solutions of these cellulose coatings are stable at pH 2-11 (Nisperos-Carriedo, 1994). These compounds are good film formers owing to the linear structure of the polymer backbone. They yield tough and flexible, transparent films. Plasticity can be improved by adding polyols such as glycerol, sorbitol, mannitol, sucrose, propylene

glycol, and polyethylene glycol (Koelsch, 1994; Kester and Fennema, 1986). Several formulations have been developed by Nisperos-Carriedo and co-workers, containing different concentrations of MC, HPMC, and HPC, and registered as Nature Seal (Nisperos-Carriedo, 1994).

The anionic cellulose ester CMC is soluble in either hot or cold water, but insoluble in organic solvents. However, the gum dissolves in suitable mixtures of water and water-miscible solvents such as ethanol or acetone. CMC solutions are stable at pH 7-9 (Nisperos-Carriedo, 1994). Lowings and Cutts (1982) proposed coating fruits and vegetables with a semi-permeable film composed of CMC and sucrose fatty acid esters. These coatings reduced O₂ uptake without causing an equivalent increase in CO₂ level in internal atmospheres of fruit and vegetables tissues (Banks, 1984a). Commercial coating formulations based on CMC and sucrose esters have included TAL Pro-long (later called simply Pro-long) and subsequently Semperfresh. These coatings extended the shelf life and preserved important flavour components of some fresh commodities (Banks, 1984a; Bayindirli et al., 1995; Drake et al., 1987; Kerbel et al., 1989; Köksal et al., 1994; Lau and Meheriuk, 1994; Nisperos-Carriedo et al., 1990; Santerre et al., 1989; Smith and Stow, 1984; Sümnü and Bayindirli, 1994, 1995a and 1995b; Van Zyl et al., 1987).

Chitosan (2-amino-2-deoxy- β -D-glucan), another water-soluble polysaccharide coating, is a diacetylated form of chitin derived from a naturally occurring cationic biopolymer. Theoretically, it should be an ideal preservative coating material based on its numerous positive effects. Chitosan can form a semi-permeable coating that can modify the internal atmosphere (El Ghaouth et al., 1992b) and reduce weight loss (El Ghaouth et al., 1991b), thereby delaying ripening and preserving postharvest quality of fruits and vegetables. However, Wong et al. (1992) reported that chitosan film formed a very effective barrier to O₂ and CO₂ but not to water. It can inhibit the growth of several fungi and reduce postharvest decay (Cheah et al., 1997; El Ghaouth et al., 1991a, 1991b, 1992a, 1992b, 1997). Nutri-Save, a chitosan-based commercial coating has been shown to delay ripening and preserve postharvest quality of several pome

fruits (Elson et al., 1985; Lau and Meheriuk, 1994; Lau and Yastremski, 1991; Meheriuk, 1990; Meheriuk and Lau, 1988).

2.3.3 Proteins

Proteins have been less investigated as film formers than lipids and polysaccharides. The use of protein-based coatings on fruits and vegetables has been restricted due to the high P_{H_2O} of such films (Gennadios et al., 1994; Gontard et al., 1993 and 1996; Koelsh, 1994; McHugh and Krochta, 1994a). Protein films are good O_2 and CO_2 barriers at low RH, but not in high humidity environments because of protein film's susceptibility to moisture absorption and swelling (Gontard et al., 1996). However, the development of composite or bilayer coatings, combining proteins with hydrophobic materials, presents many opportunities for coating fresh commodities (Avena-Bustillos and Krochta, 1993; Gennadios et al., 1994; Hagenmaier and Baker, 1996; Koelsch, 1994). Several chemical and physical treatments show some effectiveness in promoting cross-linking, "hardening" the protein film structure and improving film barrier and mechanical properties (Gennadios et al., 1994).

Film formation is facilitated by the development of hydrophobicity and hydrogen and disulphide bonds in the film matrix. Such films are brittle, as a result of extensive intermolecular associations (Gennadios et al., 1994). Addition of plasticizers is necessary to disrupt some of these associations and induce film flexibility (Koelsh, 1994; McHugh and Krochta, 1994b). McHugh and Krochta (1994b) observed improved properties of whey protein films plasticized with glycerol and sorbitol. However, glycerol was more effective than sorbitol as a coating plasticizer in that lower concentrations of the glycerol were required to increase the tensile strength, elongation, and elastic modulus of whey protein films and also the film presented higher P_{O_2} . According to the authors, the smaller size of glycerol enables it to influence film mechanical properties (and possibly gas exchange barrier properties) more readily than sorbitol.

Avena-Bustillos and Krochta (1993) observed that adjusting the pH of edible films made of sodium caseinate to the protein isoelectric point (pH 4.6) reduced P_{H_2O} by 36%. However, Gennadios et al. (1993) observed that film formation was inhibited by poor protein dispersion around the isoelectric pH region of soy protein isolate (pH 4.5) and wheat gluten (pH 7.6) films, resulting in poor water vapour barrier properties.

2.3.4 Composite and bilayer coatings

Several composite and bilayer films have been investigated in a search for improved barrier characteristics. The goal is to combine the desirable properties of different materials to improve permeability characteristics, gloss, strength, flexibility, nutritional value, and general performance of coating formulations.

Plasticizers have been incorporated into edible coatings as a processing aid, to facilitate coating application and to increase its machinability (Koelsch, 1994). The most commonly used plasticizers are polyols (such as sorbitol and glycerol), mono-, di- or oligo-saccharides, lipids and derivatives (Gontard et al., 1993). The plasticizing effect is due to their ability to reduce internal hydrogen bonding while increasing intermolecular spacing (Lieberman and Gilbert, 1973). By decreasing the intermolecular forces along polymer chains (of lipids, proteins or cellulose entities), plasticizers reduce the brittleness of the film but increase its P_{H_2O} (Koelsch, 1994; Gontard et al., 1993), P_{O_2} (McHugh and Krochta, 1994b), and P_{CO_2} (Lieberman and Gilbert, 1973). Plasticizers weaken the intermolecular forces between polymer chains, and therefore increase the diffusion coefficient.

Using more hydrophobic plasticizers, such as lipids, would be less likely to increase P'_{H_2O} of polymeric coating films (Kester and Fennema, 1986). Lipid compounds added to polysaccharide and protein-based coating formulations improve the mechanical properties of the film, by acting as plasticizers and emulsifiers. Commonly used lipids for these purpose are oils, lecithin, fatty acids and derivatives, and waxes (Donhowe and Fennema, 1994; Hernadez, 1994; Kester and Fennema, 1986).

Emulsions formed by adding lipid materials to hydrophilic coatings can sometimes improve their moisture barrier properties. Hagenmaier and Shaw (1990) have shown that the poor water vapour barrier properties of HPMC can be improved by increasing the chain length and the concentration of the fatty acid in the coating. The tensile strength of the polysaccharide film was increased while $P_{\text{H}_2\text{O}}$ was substantially reduced (from $5.88 \text{ pmol}\cdot\text{s}^{-1}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$ to $2 \times 10^{-2} \text{ pmol}\cdot\text{s}^{-1}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$) by increasing the stearic acid composition from 0% to 40% (total solids w/w). However, at high RH's (94-97% RH) the film tended to swell, thus increasing $P_{\text{H}_2\text{O}}$.

Wong et al. (1992) have shown that the uniformity of the distribution of the lipid molecules might be a crucial factor in the determination of the effectiveness of the water barrier of a composite film made of chitosan. The authors observed that a chitosan-laurate film had low $P_{\text{H}_2\text{O}}$, while films containing other fatty acids (including palmitic acid, a fatty acid of longer chain length) or esters were not effective in this respect. The authors postulated that the unique properties of the chitosan-laurate film could suggest the importance of the morphological arrangements of the lipid within the chitosan matrix. Lauric acid was believed to be the only fatty acid incorporated evenly throughout the film. These results further suggest that the uniformity of the distribution of the lipid molecules might be also a crucial factor in the determination of the water barrier effectiveness of the composite surface coatings.

Kamper and Fennema (1984b) studied the improvement of water vapour moisture barrier properties of HPMC film by adding a blend of stearic and palmitic acids to the coating formulation. The film provided considerable protection against moisture transmission at RH up to 90%. Above this humidity the film became progressively hydrated leading to a loss of structural integrity and increased $P'_{\text{H}_2\text{O}}$. The same authors (Kester and Fennema, 1989e) observed that the use of a blend of MC and HPMC (70% MC and 30% HPMC) instead of HPMC alone improved the barrier properties of the polysaccharide-lipid-based coating film, and covering this film with a beeswax layer greatly reduced $P_{\text{H}_2\text{O}}$. According to the authors, MC is less hydrophilic than HPMC. Hence, it improves lipid solubilization, which may cause a greater percentage of the

fatty acids to become entrapped in the bulk of the cellulose ether matrix during film formation, improving the moisture barrier properties. The hydrophobic nature of beeswax and its morphology of tightly packed small crystals greatly improved the moisture barrier of the bilayer film.

Kamper and Fennema (1984a and 1984b) tested composite films for $P'_{\text{H}_2\text{O}}$. Films were prepared by coating lipids (hydrophobic) onto a dried HPMC film (bilayer technique) or by adding the lipids to the film-forming solution containing HPMC (emulsion technique) before the film formation. They were tested at 25°C and with a RH differential of 85%. The $P'_{\text{H}_2\text{O}}$ of the HPMC film was 3.046 $\text{nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$. Lipid layers applied to the surface of the HPMC film, forming a bilayer film, decreased $P'_{\text{H}_2\text{O}}$, with better results achieved with lipids of decreased fluidity (greater saturation). Bilayer films containing solid lipids, such as beeswax, paraffin or hydrogenated palm oil yielded $P'_{\text{H}_2\text{O}}$ of 0.065 $\text{nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$ or less, which was much smaller than that for an 25.4 μm thick low-density polyethylene film (0.114 $\text{nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$ at 37.8°C and RH differential of 90%). Permeance through emulsion films was also highly dependent on the amount of lipid added to the film forming solution and their degree of saturation and chain length. Small increases of stearic acid concentration in the coating film provided large reductions of $P'_{\text{H}_2\text{O}}$, with comparatively smaller additional beneficial effects being achieved at higher lipid concentration levels. Introduction of the one double bond to the fatty acid hydrocarbon chain increased $P'_{\text{H}_2\text{O}}$ from 0.014 $\text{nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$ for stearic acid (C18:0, solid at 25°C) to over 1.206 $\text{nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$ for oleic acid (C18:1, liquid at 25°C). According to the authors, the double bond in the oleic acid hydrocarbon chain presumably changed the packing of the lipid molecules at the air-water (film forming solution) to a more expanded layer with greater molecular mobility. Decreasing the chain length of the saturated fatty acid increased $P'_{\text{H}_2\text{O}}$ of the coating film. The emulsion films of stearic acid (C18:0) and lauric acid (C12:0) had $P'_{\text{H}_2\text{O}}$ values of 0.014 and over 0.060 $\text{nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$, respectively. Fatty acids with shorter chain length have greater mobility and are consequently more permeable to water vapour. When a blend of stearic and palmitic acid was used in both film forming

techniques (bilayer and emulsion techniques), the HPMC film coated with the lipids had P'_{H_2O} of $0.279 \text{ nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$ as compared to P'_{H_2O} value of $0.019 \text{ nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$ for the emulsion film, even though the lipid layer in the emulsion film was about one-tenth as thick as that of the coated film ($90 \text{ g lipid}\cdot\text{m}^{-2}$ film vs. $8 \text{ g lipid}\cdot\text{m}^{-2}$ film; Kamper and Fennema, 1984a). In the emulsion technique the fatty acids were allowed to orient at the air-water (film forming solution) interface before allowing the lipid to solidify at the HPMC matrix, greatly improving the moisture barrier properties of the coating film. The film was also very flexible and quite resistant to mechanical damage.

Hagenmaier and Baker (1996) reported that the addition of protein or polysaccharide components into candelilla wax formulations to improve the gloss also decreased P_{O_2} and increased P_{H_2O} of the film. The results show that the mixing hydrophilic components with waxes may have detrimental effects on permeability of the composite film. Commodities treated with such coatings may be rendered anaerobic and still have high water loss.

Avena-Bustillos and Krochta (1993) evaluated the water vapour barrier properties of edible films made of sodium or calcium caseinate and from emulsions of these proteins with acetylated monoglyceride, beeswax, and stearic acid. Adjustment of pH to protein isoelectric point (pH 4.6), calcium ion crosslinking and combined effects of calcium ascorbate buffer (pH 4.6) reduced P'_{H_2O} of sodium caseinate films by 36%, 42%, and 43%, respectively. Beeswax incorporation into sodium caseinate film was more effective in reducing P'_{H_2O} , followed by stearic acid and acetylated monoglyceride. Calcium caseinate-beeswax emulsion films had P'_{H_2O} as low as 10% of permeance values reported for pure sodium caseinate films.

2.4 Factors affecting water loss, gas exchange and modification of internal atmosphere of coated commodities

Apart from the intrinsic physical barrier properties of coatings to gas exchange, the degree of modification of the internal atmosphere of the fruit is also greatly dependent on character of cover of the skin by the surface coating, fruit physiological status and also on environmental conditions, the latter having an impact on both metabolic activity of the fruit and permeability characteristics of the coating film. ●

The main factors affecting gas exchange, modification of internal atmosphere and postharvest physiology of fruits and vegetables, which are relevant for the optimisation of surface coatings, are discussed below.

2.4.1 Coating formulation

The physical and chemical properties of coating films affect their barrier properties to water vapour and gases (Section 2.3) and may also be important in determining the potential of the coating formulation in blocking pores in the skin, and then reducing the gas exchange of gases and water vapour of coated commodities (Hagenmaier and Baker, 1993a).

Claypool and King (1941) observed that the type of wax used seemed to be more important than the film thickness in reducing water loss. Pears, cherries, apricots and tomatoes lost less water when treated with wax formulations having an higher proportion of low polarity waxes in their composition (high proportion of paraffin to carnauba wax; Claypool, 1939; Claypool and King, 1941).

Hagenmaier and Baker (1993a) have shown that for waxes and resin coatings the chemical nature is far more important than coating thickness for CO₂ exchange, while for water vapour, coating thickness seems as important as type. Grapefruit treated with polyethylene wax and shellac coatings (both with a concentration of 14% w/v) had P'_{co_2} depressed to 26.0% and 6.5% of control values, respectively. For both formulations,

fruit treated with thicker coatings tended to have lower P'_{CO_2} , though these differences were not as large as those observed between coating formulations. Fruit treated with the thinnest shellac coating ($0.9 \text{ g}\cdot\text{m}^{-2}$) had P'_{CO_2} corresponding to 40% of fruit treated with the thickest polyethylene wax ($5.3 \text{ g}\cdot\text{m}^{-2}$). Citrus fruit coated with shellac and resin had higher internal concentrations of CO_2 and ethanol and a poorer flavour than fruit coated with polyethylene and carnauba waxes, as a result of over-restriction of gas exchange and fermentative metabolism on the former group (Hagenmaier and Baker, 1993a and 1994b). Hagenmaier and Baker (1993a) did not estimate P'_{O_2} , but similar and more dramatic effects on restriction to O_2 than to CO_2 may be expected. The authors observed that for $P'_{\text{H}_2\text{O}}$, coating thickness seemed to be as important as type. Increasing the concentration of polyethylene wax and shellac from 5% to 25% (w/v) reduced the weight loss from 40% to 50% and from 30% to 40% of the weight loss of non-coated grapefruit, respectively, at 21°C and 50% RH. The lowest concentration of polyethylene wax (5% w/v) was as effective as the highest concentration of shellac (25% w/v) in reducing weight loss.

Hagenmaier and Baker (1993a) reported that the reduction of P'_{CO_2} and $P'_{\text{H}_2\text{O}}$ in coated citrus fruit was caused more by sealing pores than reducing cuticle permeance. This indicates that changes in the formulation of hydrophobic coatings (waxes) to reduce pore blockage may improve coating performance. For example, wax emulsions that have larger globule size (macroemulsions) might not be so effective in sealing pores, therefore preventing the fruit becoming anaerobic, but the coating may still beneficially suppress water loss. Resin-based coatings may penetrate and block skin pores that wax microemulsions can not, rendering the commodity anaerobic.

Mannheim and Soffer (1996) reported that a mixture of carnauba wax and shellac (Primafresh 30), had the lowest $P'_{\text{H}_2\text{O}}$ and was the best coating in reducing citrus fruit water loss. This coating also did not excessively modify the fruit internal atmosphere (the fruit did not have very low O_2 and high CO_2 internal concentrations), and did not result in excessive ethanol accumulation and off-flavours development. The fruit treated with this coating also had very high scores for appearance. However, coating

films made of carnauba wax emulsion or shellac had very low values of permeability to gases, and fruit treated with them had very low O₂ and high CO₂ and ethanol internal concentrations, and the fruit developed off-flavours. These results contradict other published results which indicate that coatings made of waxes are more permeable to O₂ and CO₂ than coatings containing shellac, and therefore are less likely to induce fruit fermentation. Interpretation of such effects remains difficult whilst commercial secrecy prevents the emulsification method and composition of coating formulations (including both solids and solvents contents) being reported.

Hagenmaier and Baker (1993a) observed that increasing the alcohol content of a shellac formulation increased wettability by reducing coating surface tension. However, coating formulations with different alcohol content applied to the fruit with brushes resulted in fruit having virtually the same respiration, internal CO₂, and weight loss. These authors observed that citrus fruit treated with water-based commercial wax coatings had higher respiration and skin permeance, lower internal CO₂ and weight loss than those treated with shellac dissolved in 10-25% alcohol, despite both formulations having equivalent surface tension values. These results suggest that the surface tension is apparently less important than the chemical formulation (which determines the coating potential in blocking pores in the skin) for performance of the coating applied to fruit surface by brushing. Oranges treated with water-based wax coating had higher weight loss than fruit treated with solvent-based wax, and while multiple coatings of solvent-based wax further reduced weight loss, the same was not observed for water-based wax (Davis and Hofmann, 1973). Trout et al. (1953) observed higher P'_{CO_2} for wax emulsion coatings than for corresponding alcoholic solutions. The results indicate that in water-based wax coatings the continuous aqueous soap phase can facilitate the diffusion of water and gases through wax emulsion coatings.

Wax- and shellac-based coatings were more effective in reducing water loss and delaying ripening than polysaccharide-based coatings in several coated commodities. Cherry fruit coated with wax formulations had lower P'_{H_2O} , lower weight loss and better

firmness retention than fruit coated with Semperfresh (1.0% w/v; Drake et al., 1988). Guavas coated with Nature Seal emulsions (HPC, 2% or 4% w/v) lost more weight during storage than fruit coated with a carnauba wax (5% w/v) while the extent of ripening retardation was not greatly affected by coating type (McGuire and Hallman, 1995). Also, guavas treated with palm oil (20% w/v) had lower weight loss than fruit treated with Semperfresh (0.75% w/v; Mohamed et al., 1994). Nature Seal (1 and 2% w/v) did not significantly reduce O₂ internal concentration to delay ripening of avocados (Bender et al., 1993). Surface coatings made of carnauba wax and/or polyethylene wax mixed with shellac had more positive effects than Semperfresh in reducing weight loss and respiration of pears (Sümnü and Bayindirli, 1994) and apples (Sümnü and Bayindirli, 1995b) and in reducing the weight loss of mandarins (Bayindirli et al., 1995), resulting in an overall better retention of postharvest quality. Baldwin et al. (1995b) reported that citrus fruit coated with a shellac-based coating had lower internal O₂ and higher internal CO₂ than fruit coated with a polysaccharide-based coating when the fruit were stored at 21°C. However, Drake et al. (1987) observed that apples coated with a commercial wax had similar, if not identical, quality attributes in comparison with control apples and that Semperfresh (1.0% w/v) coated apples had the best quality retention. In most instances, apples coated with the Semperfresh + wax showed quality attributes similar to the singular use of Semperfresh. The authors concluded that the benefits of using a mixture of Semperfresh + wax could be derived from enhanced quality attributes coupled with a desirable fruit finish. However, the authors made no reference to the main components and concentration in the wax formulation used, which makes the results of little significance for further discussion.

Protein-based coatings have shown some potential to reduce water loss and delay ripening of coated commodities. Park et al. (1994) reported delayed changes in colour, softening, and weight loss in tomatoes treated with a corn zein coating (about 25µm thick, made of zein, glycerin, and citric acid). Shelf life was increased by six days as evidenced by sensory evaluation. Avena-Bustillos et al. (1994) found that calcium

caseinate and acetylated monoglyceride emulsion films were more effective than Semperfresh in reducing water loss from zucchini. Using response surface methodology, it was concluded that 0.9% calcium caseinate and 1.1% acetylated monoglyceride film would be the most effective for increasing zucchini shelf life by reducing $P'_{\text{H}_2\text{O}}$ to ~ 60% of the control.

Composite coatings have been tested with the addition of hydrophobic components to protein and polysaccharides-based coatings to improve their water vapour barrier properties. However, this may result in surface coatings with limited potential to reduce $P'_{\text{H}_2\text{O}}$ and with very low P'_{O_2} . Hagenmaier and Baker (1996) reported that grapefruit coated with composite formulations made by the addition of protein or polysaccharide components into candelilla wax had lower internal O_2 and faster weight loss than when coated with candelilla wax alone. A protein content in the film above 20-30% (w/w total solids) resulted in increased internal CO_2 of coated grapefruit and a marked elevation of ethanol content, a strong indication that anaerobic respiration had occurred. Baldwin et al. (1997) observed that the addition of soybean oil or carnauba wax to an HPC coating (Nature Seal) had no effect in improving the water barrier property of the polysaccharide on cherries or cucumbers.

2.5.2 Coating deposit

Improving the amount of coating deposited on the skin by increasing the concentration of Semperfresh, substantially delayed fruit ripening and reduced weight loss in pears (Sümnü and Bayindirli, 1994), apples (Sümnü and Bayindirli, 1995b), and apricots (Sümnü and Bayindirli, 1995a) left at ~ 20°C. Meheriuk and Lau (1988) reported a significant effect of coating concentration of Pro-long and Nutri-Save in delaying ripening and reducing physiological disorders of 'Bartlett' and 'd'Anjou' pears. Linear relationships were observed between coating concentration and firmness and colour retention for both cultivars, and for reduction of core breakdown in 'Bartlett', and superficial scald in 'd'Anjou'. Lau and Meheriuk (1994) also observed a

better retention of firmness and acidity in apples with increasing concentrations of Pro-long or Nutri-Save. Improving the character of cover by increasing the concentration of wax in the coating formulation achieved more beneficial effects in reducing weight loss of mangoes (Yuniarti and Suhardi, 1992) and citrus fruit (Hagenmaier and Baker, 1994b) and in reducing weight loss, delaying ripening and reducing the incidence of decay and of some physiological disorders in apples and pears (Farooqi and Hall, 1973; Smock, 1935). In tomatoes, increasing the concentration of chitosan (El Ghaouth et al., 1992b) or corn zein-based (Park et al., 1994) coatings resulted in more substantial delay in ripening, as a result of a larger reduction of internal O₂.

Increasing coating concentration may delay ripening and improve some aspects of quality, but very high concentrations may predispose the commodity to physiological disorders and production of off-flavours. Heavily coated apples may develop off-flavours, skin damage and decay, probably due to excessive restriction of gas exchange, rendering the fruit anaerobic and increasing the wastage after long term storage, especially after exposure to high temperatures (Farooqi and Hall, 1973; Magness and Diehl, 1924). Bananas (Ben-Yehoshua, 1966) and oranges (Ben-Yehoshua, 1967; Cohen et al., 1990) treated with very thick polyethylene wax developed off-flavours.

More beneficial effects of small improvements in coating deposit in delaying ripening and reducing weight loss have been reported for several commodities. In oranges, small increases in thickness of a polyethylene coating had the largest proportional effects in reducing weight loss (Ben-Yehoshua et al., 1970) and O₂ internal concentration (Ben-Yehoshua, 1967; Ben-Yehoshua et al., 1970) and increasing CO₂ internal concentration (Ben-Yehoshua, 1967); smaller additional effects were observed at higher levels of coating thickness. More substantial effects of a polyethylene coating in delaying ripening of bananas were achieved with small increases in coating thickness (Ben-Yehoshua, 1966). Hagenmaier and Baker (1994a) observed that oranges coated with a wax coating (50% oxidized polyethylene wax and 50% petroleum wax) had most of the beneficial effect in reducing weight loss by

treating the fruit with a very thin coating film. They observed more than 50% reduction in weight loss by increasing the amount of coating from 0 to 10 mg·fruit⁻¹ (coating total solids of ~ 0.5 g·m⁻²), with further smaller beneficial effects when increasing the amount of coating. Another 30% reduction in weight loss was achieved by increasing the amount of coating to 100 mg·fruit⁻¹ (coating total solids of ~ 50 g·m⁻²).

Coating avocados with a polyethylene wax did not provide a complete cover of the fruit, with several discontinuities of coating film being observed on the skin (Durand et al., 1984). As a result, coating had relatively little effect on internal CO₂, O₂, and C₂H₄ levels, with a small impact on delaying fruit softening. However, weight loss was reduced substantially by waxing. In pineapples, treating the fruit with increasing concentrations of paraffin-polyethylene-based commercial coating formulation from 0 to 50% (v/v) resulted in a decreased level of chilling injury, fruit shell appearance was retained and shell degreening rate was reduced, but weight loss was not reduced (Rohrbach and Paull, 1982).

Hagenmaier and Baker (1994b) observed that the effect of application rate on water loss and modification of internal atmosphere depended on coating formulation. Weight loss of citrus fruits decreased with increasing application rate of wax-based coatings (polyethylene and carnauba wax) but not for shellac and resin coatings. Oranges and grapefruit coated with shellac and resin had lower internal O₂ than fruit coated with waxes, but increasing the coating deposit on the fruit of different coatings had little effect on internal O₂. This may be the result of a limited improvement of skin pore blockage (the main path for O₂ exchange) by increasing the coating deposit. However, increasing the thickness of shellac and resin coating films substantially increased the internal CO₂, while polyethylene wax and carnauba wax did not have this effect. This increase in internal CO₂ of fruit coated with thicker films of shellac and resin may be the result of a decrease of P'_{CO_2} and/or start of anaerobic respiration. Since wax films have a higher P'_{CO_2} than resin films and the wax coatings did not reduce the internal O₂

content to very low levels, the fruit may still maintain aerobic respiration, avoiding substantial accumulation of CO₂.

2.4.3 Mode of application

Drake and Nelson (1990) investigated the differences in hot (60°C) and cold (0°C) drying techniques after waxing on apples and noted no advantage in fruit quality in relation to drying temperature for 'Delicious' apples. However, they reported that a 60°C wax-drying temperature on 'Golden Delicious' apples resulted in a more uniform colour after shelf life, but fruit had higher internal C₂H₄, higher weight loss and increased firmness possibly due to desiccation. For pears, Drake et al. (1991) observed that the half-cooling time for hot (60°C) and cold (0°C) dried waxed fruit in boxes were identical and equal to 17 h. However, waxed hot dried pears required an additional 21 h to equilibrate to the cold storage temperature (48 h and 69 h for cold and hot dried waxed fruit, respectively). As a result, after prolonged storage, waxed cold dried pears presented better retention of colour and firmness during the cold storage and after a shelf life than waxed hot dried pears. The authors affirmed that the wax dried with cold air as fast as with hot air (Postharvest News and Information, 1993).

Hagenmaier and Baker (1993b) reported that washing citrus fruits with rotary brushes in the pack house could increase shrinkage rates by 50% to 150%. Fruit washed with polypropylene bristles (of medium stiffness) lost 15% more water than fruit washed with polyethylene bristles (of low stiffness). The water loss of oranges washed with a sponge (to cause minimum abrasion) was not significantly different from non-washed fruit. They also observed that waxed fruit obtained from packhouses and cleaned with rotary brushes and waxed had the same shrinkage rates as those of non-washed controls. Ben-Yehoshua (1967) and Ben-Yehoshua et al. (1970) reported similar results, for oranges coated with polyethylene wax in commercial packhouses. These figures show that in a standard commercial handling system, waxing may be

only restoring the loss of skin resistance to water vapour caused by the abrasion during the washing, not providing any additional benefit to reduce water loss in comparison to non-handled fruit. Thus, controlling the washing process, by using less abrasive cleaning methods before waxing, is an important issue to consider in achieving the best benefit of waxing to reduce water loss.

Coating oranges (Ben-Yehoshua, 1967) and avocados (Johnston and Banks, 1998) by dipping resulted in a more substantial reduction of weight loss and a larger reduction of p'_0 , than spraying on the brushes, as done commercially in packhouses. This may be the result of abrasion on the brushes during the washing removing the natural waxes on the cuticle (Hagenmaier and Baker, 1993b; Ben-Yehoshua, 1967, Ben-Yehoshua et al., 1970). Alternatively, it may be that commercial spraying and brushing techniques created a coating that was thinner or less complete than the dipping method (Ben-Yehoshua et al., 1970; Cohen et al., 1990). More variable results were achieved between fruit coated commercially (Johnston and Banks, 1998) than for fruit coated by dipping. This may be due to more variation in the amount of coating received by each fruit and in the volume of coating application and/or speed of fruit flow through the packing line (Ben-Yehoshua et al., 1970). Therefore, the optimisation of coating concentration in the laboratory should be followed by a trial under normal packhouse conditions, for adjustments on volume of coating application and speed of fruit flow through the packing line to achieve improved results.

The mode of coating application can be critical depending of the nature of the product skin, such as the presence of hairs or trichomes. In zucchini, dipping was 20% more effective than brushing in reducing water loss (Avena-Bustillos et al., 1994). This vegetable has trichomes, which can be removed by mechanical abrasion if coated by brushing, leaving wounds through which large amounts of water loss may occur.

2.4.4 Relative humidity

Although most plastic films are not greatly affected by RH, films made from biological materials such as edible surface coatings do change their mechanical and barrier properties in high moisture conditions (Gontard et al., 1994 and 1996). The permeability of coating films to gases and water vapour increases with increases in RH as the result of presence of hydrophilic components in coating formulations that interact strongly with migrating water molecules. As the environmental RH is increased, the equilibrium RH within the film matrix is elevated. This causes a significant increase in the solubility of water in the film due to the strong sigmoidal shape of the sorption isotherms for polar hydrocolloids (Rico-Peña and Torres, 1990). The elevation in sorbed moisture has a plasticizing effect that increases the diffusion constant for water vapour. Since permeability is determined by the diffusion constant and the solubility coefficient (Eq. 2.1), effective $P_{\text{H}_2\text{O}}$ is greatly increased. Similar changes in P_{O_2} and P_{CO_2} of the film may also be expected (mainly for CO_2 , which is more soluble in water), as high moisture content increases the solubility of these gases in the watery film and improves their diffusion by the plasticizing effect of moisture sorption.

Nutri-Save films (a chitosan-based coating) were impermeable to O_2 and CO_2 at RH below 70% (Elson et al., 1985). The P_{O_2} through MC-palmitic acid (Rico-Peña and Torres, 1990), HPMC-stearic acid (Hagenmaier and Shaw, 1990), whey protein (McHugh and Krochta, 1994b), collagen (Lieberman and Gilbert, 1973), wheat gluten (Gontard et al., 1996), and shellac (Hagenmaier and Shaw, 1991a) coating films increased exponentially with increases in RH.

Hagenmaier and Shaw (1991b) observed that $P_{\text{H}_2\text{O}}$ of different formulations of polyethylene wax was greatly dependent on the RH gradient used to assess gas exchange properties of the coating film. Increasing the RH on the coated side of the film increased $P_{\text{H}_2\text{O}}$. The $P_{\text{H}_2\text{O}}$ increased from two to five times when the RH on the coated side of the film was increased from 32% to 75%. For coating films made of lipids and cellulose ethers, $P'_{\text{H}_2\text{O}}$ increased approximately five-fold as the RH on the low

water vapour-pressure side of the film was elevated from 0 to 65%, while the high water vapour-pressure side had an RH of 97% (Kester and Fennema, 1989e). Increasing the RH gradient (with 0% RH in the drier side) or keeping the same RH gradient (32% RH), but exposing the film to higher RH values increased P'_{H_2O} of the composite film (Kamper and Fennema, 1984b). A greater increase in P'_{H_2O} occurred when one side of the coating was exposed to RH higher than 90% (Kamper and Fennema, 1984b). Hagenmaier and Shaw (1992) reported for more polar coating films, such as shellac and resins, a significant increase in P_{H_2O} by changing the RH from 75% to 92% RH, while increasing the RH from 50% to 85% had almost no effect on P_{O_2} .

Gontard et al. (1996) observed that wheat gluten edible coatings substantially increased in P_{O_2} and P_{CO_2} with increases in RH. At RH higher than 50%, P_{O_2} and P_{CO_2} increased exponentially with increases in RH. However, at high RH's, the increment in P_{CO_2} was larger than that observed for P_{O_2} . From 0% to 60% RH, the selectivity of coating films (expressed by the P_{CO_2}/P_{O_2} ratio) was four to six and increased to 28.4 at 94.5% RH. This value corresponds to the ratio of CO₂ and O₂ solubility in water, since the free water of the film becomes the main medium for the transport of these gases through the coating. The selectivity values decreased when lipidic components were added to wheat gluten, as a result of a much higher depression of P_{CO_2} than P_{O_2} . While P_{O_2} (at 25°C and 91% RH) was reduced by 30% (from 0.982×10^{-3} to 0.687×10^{-3} pmol·s⁻¹·m·m⁻²·Pa⁻¹), P_{CO_2} was reduced by 73% (from 24.5×10^{-3} to 6.6×10^{-3} pmol·s⁻¹·m·m⁻²·Pa⁻¹), by adding 30% beeswax to the wheat gluten formulation, with a consequent reduction in selectivity of the coating film from 25 to 9.6. However, P_{CO_2} in any situation was several times higher than temperature

Increasing RH has an exponential effect in increasing coating films permeability. However, the extent of the impact of environmental RH on permeance to water vapour and gases of fruits and vegetables treated with the coating films is not known.

For apples (Lau and Meheriuk, 1994) and pears (Meheriuk and Lau, 1988) coated with Nutri-Save or Pro-long and held at 20°C, exposure to low (~ 42%) or high (~ 85% for apples and ~ 63% for pears) RH had no consistent effect on ripening and fruit

quality. Smith and Stow (1984) did not observe any effect of high or low humidity on quality of apples coated with TAL Pro-long and held at 3.3°C. However, the author did not report the RH values for the different humidity storage conditions.

Green bell pepper fruit treated with cellulose- and protein-based edible coatings and stored at 10°C and 80-85% RH for 20 days did not have suppressed respiration rates or colour changes, due to very small modification of internal gas composition (Lerdthanangkul and Krochta, 1996). The authors suggested that the absence of any effect was a result of the high permeance of fruit coated with hydrophilic coatings to gas exchange at the high RH of the storage environment, as well as the low respiration rates of pepper, especially at the temperature applied. Only the mineral-oil-based coating significantly reduced moisture loss, thus maintaining fruit firmness and prolonging fruit freshness.

Baldwin et al. (1995b) reported a maximal internal CO₂ concentration in shellac coated oranges of approximately 9% after about one week storage at 21°C and 95% RH, which is considerably lower than that reported by Hagenmaier and Baker (1993a) for shellac and resin-coated oranges of the same cultivar ('Valencia') stored for up to one week at 21°C and 50% RH, who observed internal CO₂ as high as 16-18%. This may be the result of higher skin permeance of coated fruit left at higher RH, as observed for coating films (Hagenmaier and Shaw, 1992).

These results seem to indicate that the effect of RH on coating film in intimate contact with the almost water saturated surface of the commodity is not as large as that observed for the assessment made with coating films. It should be expected that at steady-state, the water transfer from the fruit or vegetable to the coating film would sustain a high water activity in the coating film, with a resultant reduction in the effect of external RH of the air on gas exchange properties of the coating film. On this basis, only for highly hydrophilic coatings in a situation of high water vapour deficit between the commodity and the air would substantial changes in permeance be anticipated. This issue deserves further investigation.

2.4.5 Temperature

2.4.5.1 Effects on barrier properties of coating films

Increasing temperature increases film permeability due to its impact on diffusivity and solubility of the permeant gas in the coating material (Kester and Fennema, 1986). The influence of temperature on gas or water vapour transfer across coating films usually conforms to the Arrhenius relationship (Kester and Fennema, 1989a and 1989b). An Arrhenius plot of logarithm of permeability against reciprocal of absolute temperature normally yields a straight line with the slope being proportional to activation energy (E_p) for permeation of permanent gases and water vapour. Gases migrating through polymeric films generally exhibit E_p of 12.55 to 62.76 kJ·mol⁻¹ (Donhowe and Fennema, 1994).

Kester and Fennema (1989a) observed that lipid films having a good character of cover on a polar support (filter paper) had positive E_p for O₂ at 0% RH. However, they reported unusually high E_p (115.06 kJ·mol⁻¹) for acetyl monoglyceride. According to these authors, this can probably be attributed to the relatively low melting point range and heterogeneous composition of the acetoglyceride. As temperature is elevated, the proportion of lipid components in the fluid state increases markedly, causing a rapid increase in P_{O_2} . Beeswax also displayed a relatively strong dependence on temperature (E_p of 62.76 kJ·mol⁻¹), likely due to the heterogeneous composition of the wax. Activation energies for stearyl alcohol and tristearin were 29.29 and 31.38 kJ·mol⁻¹, respectively. Stearic acid had a negative E_p of -71.96 kJ·mol⁻¹. This may be the result of increasing temperature causing crystalline expansion sufficient to close or lessen the size of interplatelet channels of the film, effectively decreasing the O₂ diffusion constant and causing P_{O_2} to decrease with elevation in temperature.

The E_p for water vapour (with 100% RH gradient across the film) of a bilayer film with the first film made of a blend of MC, HPMC and stearic and palmitic acids and covered by a beeswax layer was 59.41 kJ·mol⁻¹ (Kester and Fennema, 1989e).

Hagenmaier and Shaw (1991a) reported an E_p for water vapour of 50.20 kJ·mol⁻¹ for shellac films (cast from propanol, with 100% RH gradient across the film).

Donhowe and Fennema (1993) observed a high dependence on temperature for P_{O_2} (at 0% RH) and P_{H_2O} (with 100% RH gradient across the film) of wax films. They reported higher E_p for O₂ and water vapour for beeswax and microcrystalline wax (48.12 and 51.04 kJ·mol⁻¹ for O₂, respectively, and 28.87 kJ·mol⁻¹ for water vapour for both waxes) than for candelilla and carnauba wax (40.17 and 30.12 kJ·mol⁻¹ for O₂ and 17.15 and 20.92 kJ·mol⁻¹ for water vapour, respectively). According to the authors, the larger E_p values of beeswax and microcrystalline wax are likely attributable to the larger amount of low-melting components of these waxes. As temperature increases, the liquid fraction would increase to a greater degree in these waxes than in candelilla and carnauba waxes, and this, in turn, would favor increased transport of water vapour and gases.

The permeability of shellac films has been shown to be dependent on temperature, with an E_p for O₂ from 53.14 (shellac cast from ethanol) to 64.85 kJ·mol⁻¹ (for water-soluble shellac) at 55% RH (Hagenmaier and Shaw, 1991a). Hagenmaier and Baker (1996) reported an E_p for P_{O_2} of a microemulsion made of candelilla wax with 20% gelatin of 19.66 kJ·mol⁻¹ at 75% RH. Films made with microemulsions of polyethylene wax had an average E_p for O₂ of 19.66 kJ·mol⁻¹ at 50% RH (Hagenmaier and Shaw, 1991b). These RH's are higher than the RH normally used to assess the barrier properties of coating films to O₂ (0% RH; McHugh and Krochta, 1994a). Increasing RH, mainly for coatings made of hydrophilic components, may increase the permeability to gases (Section 2.4.4), resulting in a much smaller E_p as a result of a comparatively less strong effect of temperature on permeability. Therefore, a smaller temperature effect may be expected at these RHs in relation to 0% RH. Films made with microemulsions of waxes may present lower E_p for O₂ in relation to films made with molten waxes or resins due to the more porous nature of films formed from a globular formulation.

Kemper and Fennema (1984b) and Kester and Fennema (1989e) observed a decrease in moisture barrier properties of composite films made from lipids and polysaccharides when temperature was reduced to 4-5°C. According to the authors this may be the result of increased film hydration at lower temperatures, which would favor increased permeability. Alternatively, low temperatures may fracture the film as a result of lipid rigidity coupled with lipid contraction. This may have detrimental effects in the potential of such coatings in reducing water loss of commodities subjected to “shock cooling” by being refrigerated immediately after coating and hot air drying (Hernandez, 1994).

Kester and Fennema (1989b) reported that when the dependence on temperature of $P'_{\text{H}_2\text{O}}$ was examined using a polar support (filter paper), the regression lines of Arrhenius plots for water vapour transport were negative for most of the films, thus yielding negative E_p . The polar filter paper exhibited a negative E_p when in contact with water vapour, thereby decreasing the overall E_p of the composite film. As temperature is increased, the equilibrium amount of sorbed water at a given RH is reduced: the water solubility coefficient decreases as temperature rises. According to these authors, since sorbed water acts as a plasticizer, decline in its content at elevated temperatures tends to lessen the temperature-induced rise in the effective diffusion constant: the overall E_p for water vapour is reduced in magnitude. This shows that when a hydrophilic structural polymer is embedded in a lipid film, the temperature dependence of $P'_{\text{H}_2\text{O}}$ is very strongly influenced by the moisture sorption behaviour of the polar component. For such composite films, besides their high $P'_{\text{H}_2\text{O}}$, raising temperature should exert almost no reduction in the barrier properties of the films to water vapour.

Gontard et al. (1993) investigated the interaction of film water activity and temperature on mechanical and $P'_{\text{H}_2\text{O}}$ of a wheat gluten film. The plasticizing effect of water was highly temperature dependent. At low water activity range, increasing the water content of the film resulted in an increase of mechanical properties of the film at all temperatures tested (characterised mainly by an increase of puncture strength) as a

result of the plasticizing effects of water in the gluten. However, a sharp decrease in puncture strength, elasticity, and an increase in extensibility and P'_{H_2O} were observed at 5°C, 30°C and 50°C for respective water contents of 30%, 15% and 5%. According to these authors this was related to disruptive water-polymer hydrogen bonding and glass-to-rubber transition. The plasticization by water affects the glass transition temperature of amorphous or partially crystallized hydrophilic compounds such as gluten, resulting in a drop in the glass transition temperature. Increasing film water content results in a loss of cohesiveness and elasticity of the gluten protein, since under this condition, water-polymer interactions probably develop in detriment to polymer-polymer bonds, resulting in a rupture of the inter-chain bonds. This increases free volume allowing increased backbone chain segmental mobility, reducing the glass transition temperature, with a resultant decrease of mechanical and water vapour barrier properties of the coating film.

2.4.5.2 Effects on commodity physiology

Temperature also affects the rate of postharvest physiological processes. Increases in respiration associated with temperature are often described as power (Dadzie et al., 1993; Yearsley et al., 1997a) or exponential (Cameron et al., 1994) functions of temperature, though there is some indication that the relationship flattens off towards high temperatures (Banks et al., 1997a; Yearsley et al., 1997a). Yearsley et al. (1997a) reported a Q_{10} ($=$ ([rate of O₂ uptake at $(T+10^\circ\text{C})$] / [rate of O₂ uptake at T]; T = temperature in °C) of 2.0-2.5 for apples across temperatures from 0°C to about 25°C.

Banks et al. (1997a) observed that raising temperature from 0°C to 25°C had a larger effect in increasing respiration rate than in increasing permeance of apples treated with different concentrations of a carnauba/shellac-based coating. While respiration increased c. seven-fold across the range of experimental temperatures, skin permeance to gases only increased by a factor of about two. Therefore, the extent of internal atmosphere modification increased progressively with increases in

temperature, with an increasing proportion of fruit fermenting at high coating concentrations (low skin permeance) and high temperature. These results show that for commodities treated with thick coating films, the increase in O_2 demanded for respiration may not be accompanied by a comparable increase in P'_{O_2} with increasing temperature. This may result in a drop of p'_{O_2} below the internal lower O_2 limit, resulting in fermentation and accumulation of anaerobic volatiles. Since CO_2 has a higher solubility in the water and waxy components of the cuticle and surface coating than O_2 , the former might be expected to undergo a larger increase in permeation through the coated commodity skin with increases in temperature. Therefore, the p'_{CO_2} would not increase to such an extent as p'_{O_2} would be depressed, at least whilst the coated commodity is respiring aerobically. For successful commercial application of a particular coating, the character of cover needs to be tailored to achieve a P'_{O_2} required for the extremes of environmental temperature conditions to which the commodity will be exposed.

2.4.6 Fruit-coating interaction

Cameron and Reid (1982) reported great differences in natural permeance to gas exchange between commodities. As an example, P'_{O_2} of bananas and oranges (cv. 'Navel') were about 9 to 10 times higher than P'_{O_2} of tomatoes and apples. The P'_{H_2O} of bananas was 7, 25, and up to 175 times higher than P'_{H_2O} of tomatoes, oranges and apples, respectively.

Dadzie (1992) found that skin permeance of apples to gas diffusion was largely dependent on cultivar, with the cultivar having the highest value being about three times more permeable than the cultivar having the lowest value. However, he reported variation in skin permeance by a factor of between two and seven for individual fruit of the same cultivar. Similarly variability in P'_{H_2O} has been observed between cultivars and between fruit of the same cultivar (Maguire, 1998). These differences may be due to anatomical differences such as size of intercellular spaces near the fruit surface;

size, number and distribution of functional lenticels on the skin; and nature, thickness and imperfection (cracks) of wax deposits of the cuticle.

These differences in skin permeance between commodities and the variability observed between cultivars of the same commodity and between fruit of the same cultivar, imply that the variable nature and barrier properties of the commodity skin should not be overlooked in the optimisation of surface coatings. This coupled with the differences in respiration rate and surface area can cause large variations in product internal atmosphere composition.

Surface coatings mainly exert their effects on skin permeance to gases by blocking a greater or lesser proportion of the pores on the fruit surface (Banks et al., 1993a; Banks et al., 1997b; Hagenmaier and Baker, 1993a). On this basis, it might be expected that commodities with different skin characteristics might present very distinct types of interaction with a surface coating. For coated commodities held in the same environmental conditions this may result in some fruits having a very small modification of internal atmosphere composition while others become anaerobic. The small modification of fruit internal atmosphere may be the result of an inadequate cover of pores on the skin and/or low respiration rate. Although these differences would be small at low temperatures, a much larger variation between fruits could occur at higher temperatures due to an increase in respiration rate.

Apples of different cultivars varied considerably in their reaction to skin coatings (Banks, 1984c; Meheriuk and Porritt, 1972; Trout et al., 1953). Trout et al. (1953) observed a great variability of the internal atmosphere composition between coated fruit of different cultivars and among coated fruit of the same cultivar. They attributed this to variability in skin permeance and, to a lesser extent, the variability in respiration rate between fruit. Larger modifications of internal atmosphere composition were expected for fruit having naturally low skin permeance and high respiration rate before coating. Claypool and King (1941) observed a greater variability in coating thickness in fruit having a rough skin, such as pears and nectarines, than in fruit with smooth skin, such as tomatoes. In the first group, the presence of large lenticels and cracks on

the skin made the coverage of these discontinuities very difficult, with coatings providing variable results in skin coverage and being less effective in reducing water loss. Apple cultivars having a high proportion of open calyx showed limited benefit from coatings, since highly variable results were achieved by exacerbating natural variability of internal gas composition between fruit (Trout et al., 1953).

The physiological processes of respiration and C_2H_4 production can be described by a Michaelis-Menten model with respect to $p_{O_2}^i$, with little benefit when $p_{O_2}^i$ remains high and progressively greater benefits in suppressing both processes as $p_{O_2}^i$ is depressed more and more (Dadzie et al., 1996; Yearsley et al. 1996). However, because these processes are more strongly suppressed at very low $p_{O_2}^i$, the application of a surface coating thick enough to block the pores on the skin and reduce $p_{O_2}^i$ can result in a great variability in ripening between coated fruit of the same batch, since small differences in $p_{O_2}^i$ at these low levels of O_2 may result in large differences in ripening rates (Banks et al., 1997b). This might result in variable response of individual fruit to similar coating treatments.

2.5 Postharvest physiology and quality of coated fruits and vegetables

2.5.1 Physiological basis for the CA/MA storage of fruits and vegetables

Surface coatings delay ripening by modifying the commodity internal atmosphere, achieving similar beneficial effects of CA/MA storage. Generally, the effect of reduced O_2 and/or elevated CO_2 on reducing respiration rate and processes linked to respiration, as well as C_2H_4 synthesis and action, have been assumed to be the primary reasons for the beneficial effects of CA/MA on fruits and vegetables (Kader, 1989; Kader et al., 1989). The physiological effects of CA/MA storage on respiration and C_2H_4 metabolism are discussed below.

2.5.1.1 Respiration

The most substantial beneficial effects of CA/MA storage are achieved by reducing O₂ concentration, with improved results observed in combination with elevated CO₂ concentrations (Kader et al., 1989).

The response of oxidative CO₂ production [$r_{CO_2(ox)}$] to O₂ concentration comprises a gradual decrease at relatively high O₂, becoming steeper as O₂ approaches 0 kPa (Fig. 2.1; Andrich et al., 1991; Banks et al., 1993a; Cameron et al., 1995; Dadzie et al., 1996; Peppelenbos et al., 1996; Peppelenbos and van't Leven, 1996; Solomos 1982, 1985). Little CA/MA benefit is achieved when O₂ partial pressure remains high because there is very little effect on respiration rate. Progressively greater benefits are obtained as O₂, and consequently respiration, are depressed more and more. However, at very low O₂ partial pressures, there is a risk of inducing anaerobic respiration (Fig. 2.1; Peppelenbos et al., 1996; Peppelenbos and van't Leven, 1996; Yearsley et al., 1996). Under such conditions, the glycolytic pathway replaces the Krebs cycle as the main source of the energy needed by the plant tissues. Pyruvic acid is no longer oxidized but is reduced to lactate and/or decarboxylated to form acetaldehyde, CO₂, and, ultimately, ethanol; this results in development of off-flavours and tissue breakdown after long term stress (Kader, 1986). The major function of the fermentative metabolism is to utilize NADH and pyruvate when electron transport and oxidative phosphorylation are inhibited so that glycolysis can continue. This allows some production of ATP through substrate phosphorylation, which permits the plant tissue to survive, at least temporarily (Kader, 1995). Ethanol is usually the major product of the pathway in low O₂-stressed fruit (Ke and Kader, 1992; Ke et al., 1991). In some plant tissues, ethanol reacts with acetyl coenzyme A to produce ethyl acetate, catalyzed by the enzyme alcohol acyltransferase (AAT). Ethyl acetate accumulated in CA-treated pears and strawberries, but not in avocados and lettuce (Ke et al., 1993). Some products, such as carrots, lettuce, and avocados, may also divert pyruvate to produce lactate (Ke et al., 1993; Leshuk and Salveit, 1991). Elevated CO₂ levels have

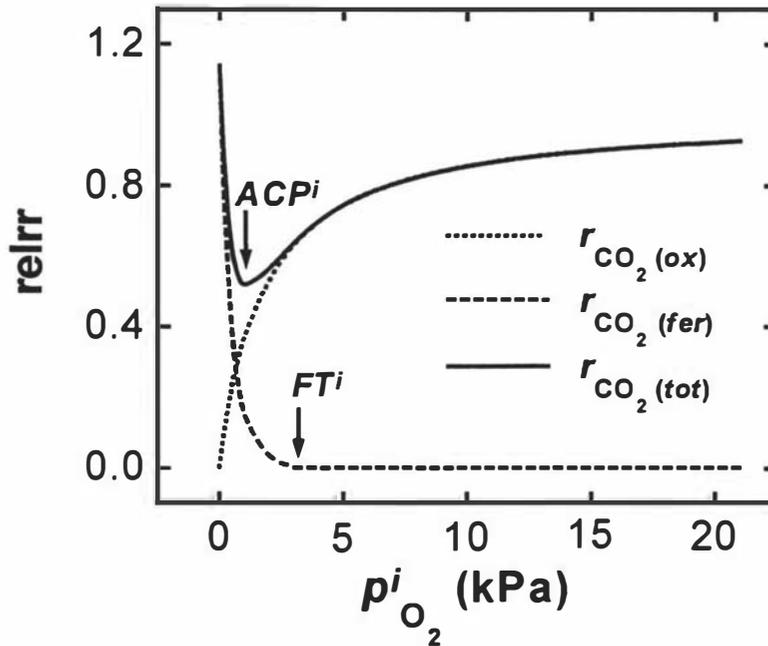


Figure 2.1 Effect of internal partial pressure of O_2 ($p_{O_2}^i$) on relative respiration rate (relrr, expressed as a proportion of respiration rate maximum when O_2 is not limiting) for oxidative [$r_{CO_2(ox)}$], fermentative [$r_{CO_2(fer)}$], and total [$r_{CO_2(tot)}$] CO_2 production. Arrows indicate internal ‘Anaerobic Compensation Point’ (ACP^i) and internal ‘Fermentation Threshold’ (FT^i).

also been reported to induce fermentation (Ke et al., 1990 and 1994), and the combination of low O_2 (0.25%) and high CO_2 (80%) seems to have an additive effect on acetaldehyde and ethanol accumulation in avocados and pears (Ke et al., 1993). The effects of high O_2 and low CO_2 on respiratory biochemistry of plant tissues are represented diagrammatically in Figs. 2.2 and 2.3, respectively.

The biphasic nature of the response of aerobic respiration as a function of O_2 has been attributed to the involvement of at least two enzyme systems (Tucker and Laties, 1985). Suppression of the basal metabolism only occurs at very low O_2 partial pressure

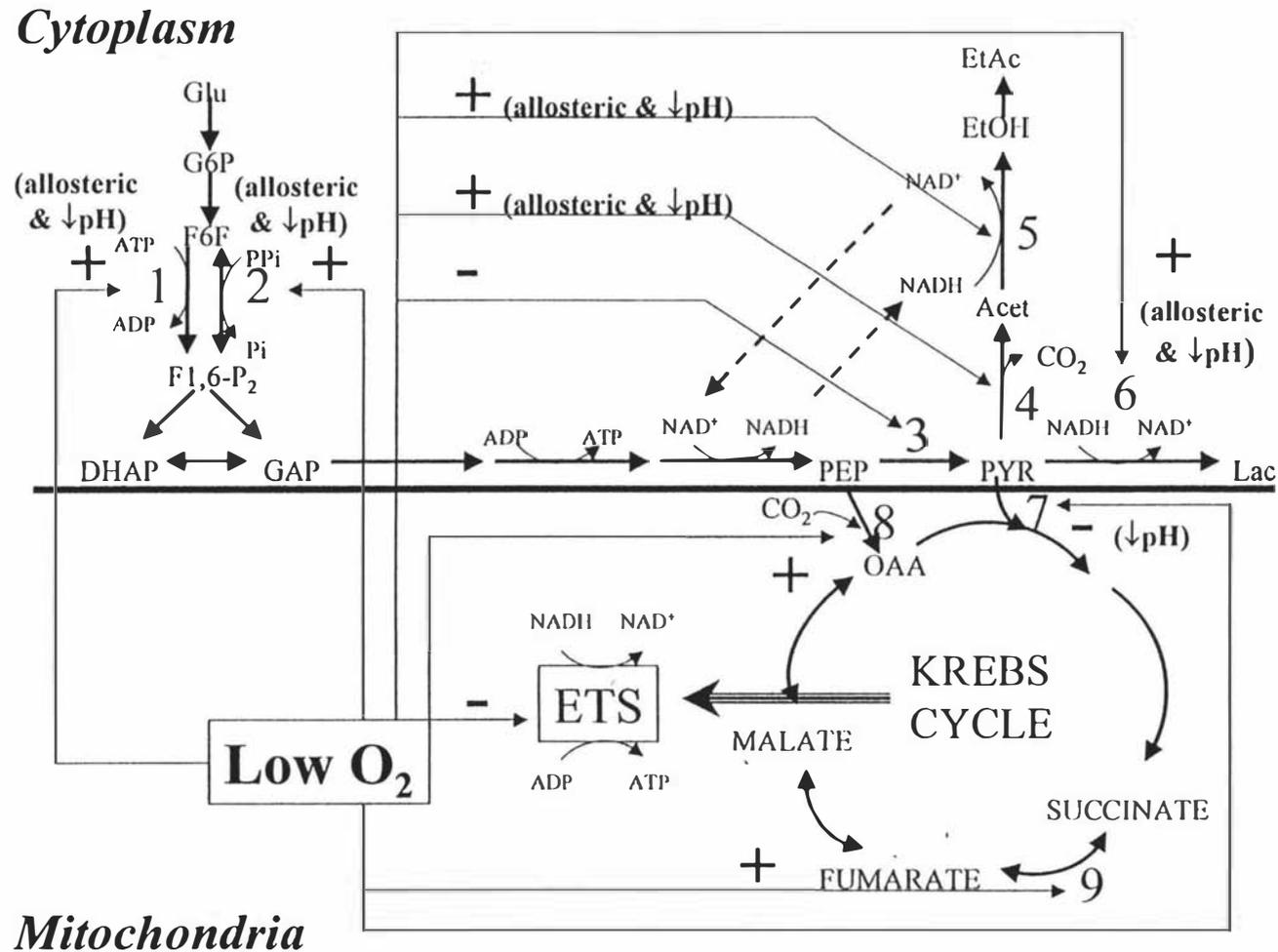


Figure 2.2 Regulation of respiration metabolism by low O_2 . Signs indicate activation (+) or inhibition (-) of biochemical process. Enzymes are represented by: (1) ATP-PFK; (2) PPi-PFK; (3) PK; (4) PDC; (5) ADH; (6) LDH; (7) PDH; (8) PEP-CK; and (9) SDH. ETS = electron-transport system.

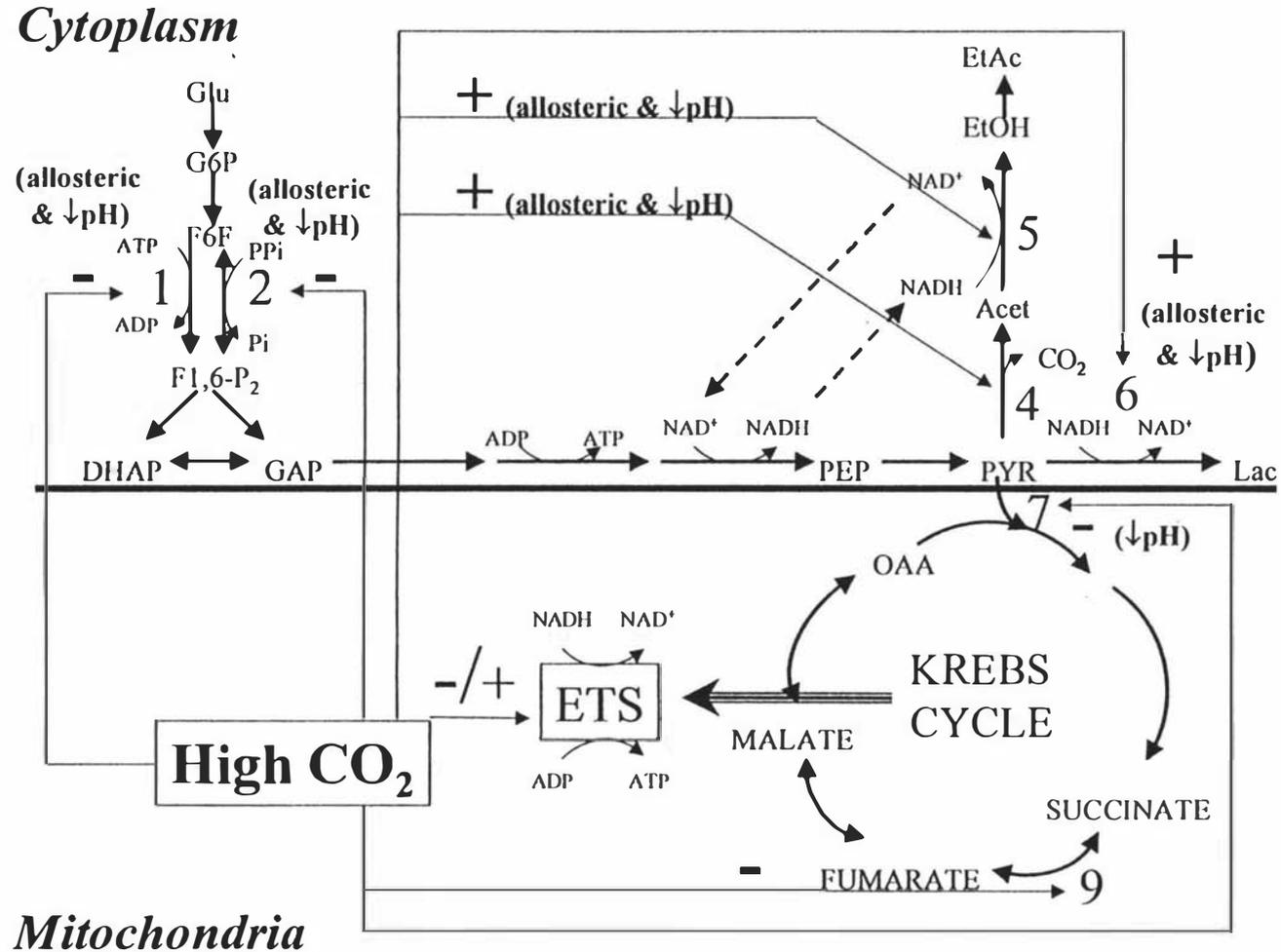


Figure 2.3 Regulation of respiration metabolism by high CO₂. Signs indicate activation (+) or inhibition (-) of biochemical process. Enzymes are represented by: (1) ATP-PFK; (2) PPi-PFK; (3) PDC; (4) ADH; (5) LDH; (6) PDH; and (7) SDH. ETS = electron-transport system.

because it is mediated by cytochrome oxidase which has a Michaelis-Menten constant [K_m] value of about 0.05 μM (equivalent to an O_2 partial pressure < 0.1 kPa; Knee, 1991). Reduction of respiration at higher levels of O_2 occurs by constraining oxidation by alternative oxidases (such as polyphenol oxidase, peroxidase, ascorbic acid oxidase, and glycolic acid oxidase) whose affinity for O_2 may be five to six times lower than that of cytochrome oxidase (Solomos, 1982). The inhibition of these residual oxidases is thought to exert a feedback restraint on the initial steps of glucose oxidation, reducing respiration rate (Solomos, 1994). Knee (1991) also suggested that there might be mechanisms whereby fruit cells sense hypoxic conditions and limit respiration rates so as to minimize the production of anaerobic metabolites. Nanos et al. (1994) reported that cytochrome oxidase activity did not change during hypoxia treatment of pears (0.25% O_2) whereas soluble peroxidase decreased somewhat, which possibly reflects the differing K_m 's for O_2 . At elevated CO_2 levels, electron transport through the cytochrome pathway is reduced (negative effect of CO_2 on electron-transport system [ETS], Fig. 2.3; Bendall et al., 1958) while cyanide-resistant respiration may be transiently induced (positive effect of CO_2 on ETS, Fig. 2.3; Palet et al., 1991).

Several enzymes along the glycolysis pathway have been studied recently for their involvement in regulating tissue response to CA/MA storage. ATP-phosphofructokinase (ATP-PFK) and PPI-phosphofructokinase (PPI-PFK) have been shown to play an important function in response to low O_2 and/or high CO_2 (Hess et al., 1993; Kerbel et al., 1988 and 1990; Nanos et al., 1994). PPI-PFK is a reversible enzyme activated by PP_i and fructose 2,6-bisphosphate ($\text{F}_2,6\text{-P}_2$) in the glycolytic direction (Huber, 1986). The activity of ATP-PFK has been shown to be affected by the levels of ATP, ADP, and several other intermediates of the respiratory metabolism, as well as by pH (Turner and Turner, 1980).

Low O_2 increased $\text{F}_2,6\text{-P}$ in carrot shreds and activated PPI-PFK towards glycolysis (Fig. 2.2), while ATP-PFK was not affected (Kato-Noguchi and Watada, 1996). Since under hypoxic conditions the tissue may also have a higher PP_i and a lower ATP

supply than when O_2 is not limiting, this may activate only PPI-PFK but not ATP-PFK towards glycolysis, as an energy saving mechanism.

Nanos et al. (1994) reported that pear fruit treated with 0.25% O_2 had slightly increased ATP-PFK, PPI-PFK, and succinate dehydrogenase (SDH) activities and decreased pyruvate kinase (PK) activity (Fig. 2.2). Also, the exposure of suspension-cultured pear fruit cells to 0.25% O_2 resulted in an accentuated rise in phosphoenolpyruvate carboxykinase (PEP-CK) activity and a dramatic rise in SDH activity upon transfer to air (Fig. 2.2). According to the authors, the enzymatic activity analysis supports the hypothesis that the rise in succinate levels observed in hypoxic fruit tissues is the result of a partial reductive Krebs cycle, wherein phosphoenolpyruvate (PEP) is carboxylated to produce oxaloacetate (OAA) and, via malate and fumarate, results in succinate accumulation (Fig. 2.2). The increase in ATP-PFK and PPI-PFK activities and decrease in PK activity also supports the hypothesis. High CO_2 reduced SDH activity (Fig. 2.3) and caused succinate accumulation in lettuce (Ke et al., 1993). Frenkel and Patterson (1973) reported that in pears increasing the CO_2 concentration in the storage atmosphere (from 0% up to 20% CO_2 , at $0^\circ C$) decreased the activity of SDH (Fig. 2.3). Therefore, low O_2 and/or high CO_2 can cause an accumulation of succinate, that has been correlated with CO_2 -induced core breakdown in hypoxic apples (Hulme, 1956).

Kerbel et al. (1988, 1990) reported that pears (intact fruit or suspension-cultured cells) treated with 10% CO_2 over four to six days at $20^\circ C$ presented lower O_2 uptake and C_2H_4 evolution rates and reduced activities of ATP-PFK and PPI-PFK (Fig. 2.3). Concurrently, the levels of fructose 1,6-bisphosphate (F1,6-P₂) decreased and the levels of fructose 6-phosphate (F6P) and F2,6-P₂ increased. None of the other glycolytic enzymes showed any change in activity with enhanced CO_2 levels. The authors suggested that an inhibitory effect of CO_2 at the site of action of ATP-PFK and PPI-PFK may account for the reduction in O_2 uptake. This inhibition may be the result of a suppressive effect of enhanced CO_2 on the activity of existing ATP-PFK and PPI-PFK enzymes and/or synthesis of them. Suppression of protein synthesis is supported

by a decrease in total extractable protein in CA treated fruit. ATP-PFK activity is also pH dependent (Hess et al., 1993). Since high levels of CO₂ can decrease cytoplasmic pH (Chavez-Franco, 1991), this may reduce ATP-PFK activity (Fig. 2.3) resulting in lower O₂ consumption rates. However, Ke et al. (1990) reported that pears exposed to 80% CO₂ showed an increase in ATP-PFK and PPi-PFK activities (Fig. 2.3) and an accumulation of acetaldehyde and ethanol. Therefore, the activation or inhibition of the enzymes activities might depend on the level of CO₂ stress to the tissue.

Pears treated with low O₂ (0.25% O₂, Ke et al., 1994; Nanos et al., 1992) and/or high CO₂ (0.25% O₂ + 80% CO₂ or 80% CO₂, Ke et al., 1994) for one to four days at 20°C had increased pyruvate decarboxylase (PDC) and alcohol dehydrogenase (ADH) activities (Figs. 2.2 and 2.3), which resulted in a higher accumulation of acetaldehyde and ethanol. The increase in ADH activity was largely due to the enhancement of one or two new ADH isozymes.

Fermentative metabolism can be regulated by two mechanisms: molecular control (also called 'coarse control') of the levels of ATP-PFK, PPi-PFK, PDC, ADH, and LDH and metabolic control (also called 'fine control') of the actual function of these enzymes in the plant tissue under O₂ and/or CO₂ stresses (Ke et al., 1993). Ke et al. (1994) pointed out that, although low O₂ and high CO₂ generally increased PDC and ADH activities in pears, the changes in the extractable activities of these two fermentation enzymes did not always correlate with the concentration of their corresponding products. Roberts et al. (1989) found that ethanol production rate was correlated with ADH activity when the enzyme level was very low; but at high levels, ethanol accumulation was independent of ADH activity. With limited enzyme levels, the induction of a fermentative enzyme through molecular control (transcription/translation) is essential for the accumulation of fermentation products. Low O₂ (0.25%) increased the PDC and ADH activities in pears, lettuce, avocados, and strawberries, which has been found to be largely due to *de novo* synthesis of the enzymes (Fig. 2.2; Ke et al., 1993). If the enzyme level is already very high even under air control, like the ADH activity in avocado fruit, then it may not be critical to

induce more enzyme biosynthesis (Ke et al., 1995). Therefore, metabolic control of the actual functions of the fermentative enzymes by changes in pH and concentrations of substrates, cofactors, and/or inhibitors may be more important in regulating fermentative metabolism (Ke et al., 1994 and 1995).

The cytoplasmic pH of pears exposed to 0.25% O₂ decreased from 7.4 to 7.0 (Nanos and Kader, 1993), and the exposure to elevated CO₂ atmospheres caused the cytoplasmic pH to drop to 6.6 (Chavez-Franco, 1991). The optimum pH for PDC and ADH for pears was 6.0 (Ke et al., 1994). The decrease in cytoplasmic pH by low O₂ or high CO₂ would significantly activate PDC and ADH (Figs. 2.2 and 2.3).

The optimum pH for PDC, LDH and ADH of avocado fruit was 6.0-6.5, 6.5 and 7.0, respectively (Ke et al., 1995). A decrease in cytoplasmic pH from 6.9 (in air) to 6.7 by 0.25% O₂ or to 6.3 by 80% CO₂ (Hess et al., 1993) would activate PDC (Figs. 2.2 and 2.3), with a small effect on LDH activity and an inhibitory effect on ADH. However, because the ADH activity was ten times higher than PDC activity in avocados, a partial inhibition of ADH by a decrease in pH would not limit the conversion of acetaldehyde into ethanol (Ke et al., 1995). PDH had an optimum pH of 8.0, and a decrease in pH by low O₂ and/or high CO₂ would inhibit its activity (Figs. 2.2 and 2.3), and therefore the pyruvate flux through the Krebs cycle, favoring the anaerobic pathway (Ke et al., 1995).

In lettuce, PDC had an optimum pH of 5.5 while LDH and ADH had optimum pH values around 6.7 and 7.5, respectively (Ke et al., 1993). A decrease in cytoplasmic pH from 6.7 to 6.3 by CA treatments (Siriphanic and Kader, 1986) would activate PDC (Figs. 2.2 and 2.3) while slightly inhibiting LDH and ADH. Despite some lactic acid accumulation under stress, the cytoplasmic pH would favor PDC action and ethanol accumulation.

Hess et al. (1993) reported that avocado fruit discs kept in air, 0.25% O₂, 20% O₂ + 80% CO₂ or 0.25% O₂ + 80% CO₂ (for 2 days at 20°C) had cytoplasmic pH values of 6.9, 6.7, 6.3, and 6.3, respectively. When ATP-PFK and PPi-PFK activities were assayed at the optimum pH for these enzymes of 8.0, no difference in enzyme activity

was observed in comparison to the control fruit left in air. However, when assayed at pH equivalent to the cytoplasmic levels for fruit in CA treatments, ATP-PFK activity was reduced by 9% and 23% at pH 6.7 and 6.3 respectively, while PPi-PFK did not show any activity at these pH values.

Another factor affecting the fermentative activity of fruit treated with low O₂ or high CO₂ could be the changes in substrate concentrations. The activities of several enzymes of the respiratory pathway, such as ATP-PFK, PPi-PFK, PDC, ADH, and LDH, have been shown to be allosterically modulated (Huber, 1986; Hubner and Shellenberger, 1978; Turner and Turner, 1980). PPi-PFK is activated by PP_i and F_{2,6}-P₂ in the glycolytic direction (Huber, 1986). The activity of ATP-PFK has been shown to be affected by the levels of ATP, ADP, and several other intermediates of the respiratory metabolism (Turner and Turner, 1980). Ke et al. (1995) reported that PDC, LDH and ADH activities are increased by increased concentrations of their substrates (pyruvic acid for PDC and LDH, and acetaldehyde for ADH) and by high NADH:NAD ratio. Under anaerobiosis, PDC may be activated through combination to its substrate (pyruvate). Pyruvate tends to accumulate in the cytoplasm under low O₂ or high CO₂, as a result of inhibition of PDH (under conditions of low cytoplasmic pH created by these CA conditions) and reduced activity of the oxidative phosphorylation and the Krebs cycle in the mitochondria. Such an increase in pyruvate concentration by stress atmospheres (and reduced cytoplasmic pH) would activate PDC (Figs. 2.2 and 2.3), heading the metabolic reactions towards fermentation. The accumulation of acetaldehyde and NADH and depletion of NAD could also stimulate the activity of ADH (Figs. 2.2 and 2.3). LDH activity is also increased by increased concentrations of F6P and by decreased ATP levels. Nanos and Kader (1993) reported that pear fruit tissue treated with 0.25% O₂ had higher cytoplasmic P_i (relative to the vacuolar P_i) and lower ATP/ADP ratio, indicating lower energy charge. The authors pointed out that the above changes could alter the *in vivo* activity of a number of respiratory enzymes in fruit subjected to hypoxic treatment.

Some of the published literature about effects of CA/MA storage on *in vitro* enzymatic activity has been done in conditions of pH, substrates and cofactors which may not reflect the conditions *in vivo* for the enzyme activity. The *in vitro* activity assay can indicate that the enzyme is present (the molecular control - transcription and/or translation - is not limiting the enzyme levels), but it may not be active (the enzyme may be under metabolic control of its activity) under the current physical-chemical conditions of the tissue *in vivo*. Therefore, care must be taken when interpreting the published information about CA/MA effects on postharvest biochemistry and physiology of fruits and vegetables.

From the published literature, a model is proposed for the mode of action of low O₂ and high CO₂ in regulating respiratory metabolism (Figs. 2.2 and 2.3). Low O₂ and/or high CO₂ may reduce NADH flux through the ETS (Figs. 2.2 and 2.3), resulting in reduced NAD and ATP levels, while NADH increases (Ke et al., 1995; Nanos and Kader, 1993). At the onset of anaerobiosis, cytosolic pH is higher than neutral and PDC, which has an acidic pH optimum, is not active (Davies, 1980; Ke et al., 1995). In products which accumulate lactic acid (e.g. avocados), the increase in NADH and decrease in NAD and ATP drive the reactions towards the lactic fermentation pathway (Figs. 2.2 and 2.3), resulting in a fall in cytosolic pH as lactic acid accumulates (Davies, 1980). In commodities that do not produce lactic acid, pyruvic acid accumulates instead, also reducing cytoplasmic pH. Following a cytoplasmic pH decrease (from pyruvic or lactic acid accumulation), pyruvate dehydrogenase (PDH) activity is partially reduced (Figs. 2.2 and 2.3) and pyruvic acid flux through the Krebs cycle is reduced (Ke et al., 1995). Further falls in pH progressively inhibits LDH (for commodities that transiently accumulate lactic acid) and activates PDC (Figs. 2.2 and 2.3; Ke et al., 1995). Under stress conditions, new ADH isozymes can also be induced (Ke et al., 1994 and 1995; Nanos et al., 1992). PDC activity, enhanced by the decrease in pH and increase in pyruvic acid concentration, leads to the production of acetaldehyde; the increase in acetaldehyde and NADH and decrease in NAD drive the

reaction resulting in ethanol accumulation (Figs. 2.2 and 2.3; Ke et al., 1994 and 1995).

A decrease in cytosolic pH in response to low O₂ and /or high CO₂ has been reported for several commodities (Hess et al., 1993; Nanos and Kader, 1993; Siriphanich and Kader, 1986). Apart from the accumulation of acids, the drop in cytoplasm pH may also reflect a reduced energy charge of cells under conditions of low O₂ and/or high CO₂, resulting in a low activity of the pump system that maintains pH and other ion gradients across the tonoplast and plasmalemma (Chervin et al., 1996).

2.5.1.2 Ethylene

Tissue exposure to low concentrations of O₂ and/or high concentration of CO₂ suppresses C₂H₄ biosynthesis and action of climacteric fruits. The way by which such atmospheres reduce C₂H₄ biosynthesis and action (and hence the rate of ripening and senescence) is, like respiratory effects, of prime importance in understanding the overall mode of action of CA/MA storage in preserving the postharvest quality of climacteric products.

Reducing O₂ levels decreases C₂H₄ biosynthesis by fresh fruits and vegetables and reduces their sensitivity to C₂H₄ (Kader, 1986). Under anoxic conditions, conversion of ACC to C₂H₄ can be completely inhibited because O₂ is a co-substrate in the oxidation of 1-aminocyclopropane-1-carboxylic acid (ACC) to C₂H₄ by ACC oxydase (ACC-O; Yang, 1985; Fig. 2.4).

Elevated CO₂ levels can enhance, reduce or have no effect on C₂H₄ biosynthesis in fruit tissue, depending upon the tissue and amount of CO₂ present (Kader, 1986). The increase in C₂H₄ production by some commodities during and/or following exposure to high CO₂ may be the result of physiological injury. In general, non-stressful CO₂-enriched atmospheres have been reported to reduce C₂H₄ biosynthesis in numerous climacteric fruits (Chavez-Franco and Kader, 1993; Gorny and Kader, 1996a and

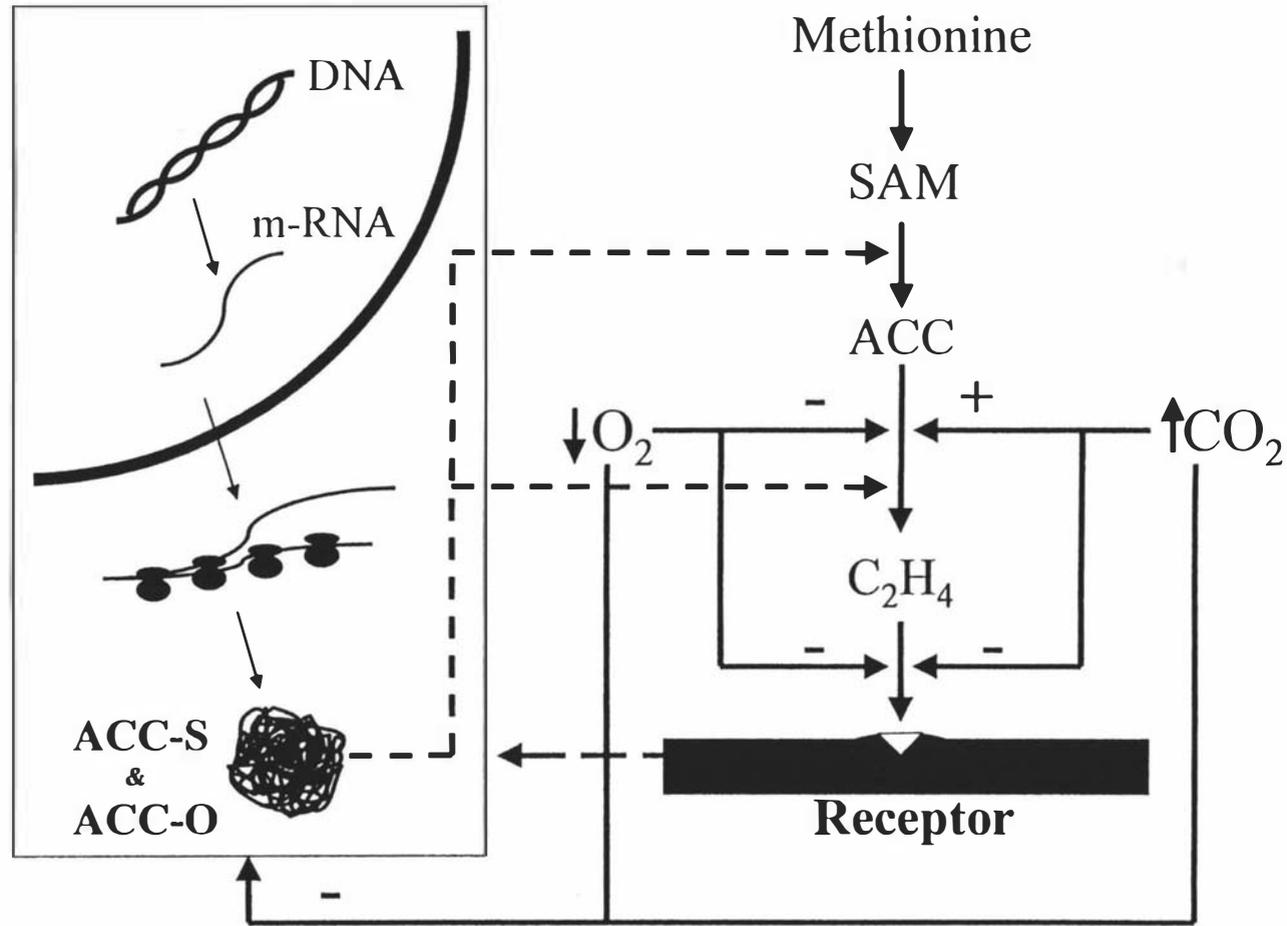


Figure 2.4 Regulation of C_2H_4 biosynthesis and action by low O_2 and high CO_2 . Signs indicate activation (+) or inhibition (-) of biochemical process (ACC-S and ACC-O are ACC synthase and ACC oxidase, respectively).

1996b; Kerbel et al., 1988; Kubo et al., 1990; Li et al., 1983).

Reduced O₂ and/or elevated CO₂ concentrations may inhibit C₂H₄ biosynthesis by impeding the binding of C₂H₄ to the receptor (Fig. 2.4; Burg and Burg, 1967) blocking System II upregulation of C₂H₄ biosynthesis (Gorny and Kader, 1996a). The combination of low O₂ and elevated CO₂ can have a synergistic effect in suppressing C₂H₄ biosynthesis (Gorny and Kader, 1996a).

The activity of the enzymes involved in C₂H₄ biosynthesis, ACC synthase (ACC-S) and ACC-O can also be affected by reduced O₂ and/or elevated CO₂ concentrations (Gorny and Kader, 1996a, 1996b; Poneleit and Dilley, 1993; Yip et al., 1988). Gorny and Kader (1996b) reported that autocatalytic (System II) C₂H₄ biosynthesis in climacteric apples was inhibited by short-term exposure (four days at 20°C) to reduced O₂ (0.25%) or elevated CO₂ (20%). The authors observed that while low O₂ reduced the activity of ACC-S and ACC-O, elevated CO₂ reduced ACC-S activity and increased the ACC-O activity (Fig. 2.4). Also, low O₂ or high CO₂ reduced ACC-S activity by affecting the abundance of the ACC-S protein, but not via direct inhibition of ACC-S catalytic competency, and these treatments did not affect ACC-O protein abundance, but its activity (Fig. 2.4). The same authors (Gorny and Kader, 1996a) reported that the non-autocatalytic (System I) C₂H₄ biosynthesis in pre-climacteric apples was reduced by low O₂ and/or high CO₂ (2% O₂, 5% CO₂ and 2% O₂ + 5% CO₂) during long-term cold storage (for up to four months at 0°C). This was achieved mainly by delaying and suppressing expression of ACC-S at the transcriptional level (Fig. 2.4) and, to a lesser extent, by reducing the abundance of active ACC-O (by affecting the post-transcriptional and post-translational processing of ACC-O). These results show that low O₂ and/or high CO₂ reduce C₂H₄ biosynthesis by delaying and suppressing expression of ACC-S at the transcriptional level and by reducing the abundance of active ACC-O protein, and low O₂ by reducing ACC-O catalytic ability to convert ACC to C₂H₄ (Fig. 2.4).

The half-saturating substrate concentration with respect to O₂ in the external atmosphere ($[S]_{0.5}^{O_2}$, equivalent to the K_m) for apple ACC-O *in vitro* was 0.4% O₂ (Kuai

and Dilley, 1992). *In vivo* estimates of $[S]_{0.5}^{[O_2]}$ depend on the commodity, having been estimated as 1.7-2.2% O₂ in bananas (Banks, 1985a; Elyatem et al., 1994) and 1.2-1.3% O₂ in apples (Banks et al., 1985; Bufler and Streif, 1986). For intact apples, Dadzie et al. (1996) reported that the relationship between rate of C₂H₄ production and internal partial pressure of O₂ ($p_{O_2}^i$) was reasonably described by a Michaelis-Menten type hyperbolic curve, with small changes in $p_{O_2}^i$ having a much greater effect on C₂H₄ production at low $p_{O_2}^i$. The K_m was estimated as ~ 1.8 kPa O₂, with a substantial inhibition of C₂H₄ production by reducing $p_{O_2}^i$ below ~ 6 kPa.

2.5.2 Postharvest physiology of coated commodities

2.5.2.1 Coating effects on ripening of fruits and vegetables

Surface coatings have been reported to reduce respiration rate (Banks, 1984a; 1985b; Bayindirli et al., 1995; Ben-Yehoshua, 1966; Blake, 1966; Díaz-Sobac et al., 1996; Drake et al., 1987; El Ghaouth et al., 1991a, 1991b and 1992b; Elson et al., 1985; Farooqui and Hall, 1973; Kerbel et al., 1989; Miszczak, 1994; Smock, 1935; Sümnü and Bayindirli, 1994 and 1995a), and C₂H₄ evolution (Banks, 1984a and 1985b; Bauchot et al., 1995b; Drake et al., 1987; El Ghaouth et al., 1992b; Elson et al., 1985; Farooqui and Hall, 1973; Kerbel et al., 1989; Meheriuk and Porritt, 1972; Miszczak, 1994) of several commodities held at ambient temperatures. Higher suppression of respiration rate (Ben-Yehoshua, 1966; Blake, 1966; Elson et al., 1985; Farooqui and Hall, 1973; Kerbel et al., 1989; Smock, 1935; Sümnü and Bayindirli, 1994), C₂H₄ evolution (Elson et al., 1985; Farooqui and Hall, 1973; Kerbel et al., 1989) and ripening (Banks, 1984c; Ben-Yehoshua, 1966; Castrillo and Bermudez, 1992; Elson et al., 1985; Farooqi and Hall, 1973; Kerbel et al., 1989; Lau and Meheriuk, 1994; Magness and Diehl, 1924; Meheriuk and Lau, 1988; Smith and Stow, 1984; Sümnü and Bayindirli, 1995b) were observed by increasing the concentration of total solids in the coating formulation, and with coating formulations having low permeance to gases and providing better character of cover of pores in the skin.

However, commodities treated with very high concentrations of wax (Ben-Yehoshua, 1966; Cohen et al., 1990; Edward and Blennerhassett, 1990 and 1994; Magness and Diehl, 1924; Trout et al., 1953; Smock, 1935), polysaccharide (Van Zyl et al., 1987) or protein-based (Park et al., 1994) surface coatings may cause excessive over-restriction to gas exchange through the skin, resulting in anaerobiosis and development of off-flavours when exposed to high environmental temperatures.

Coatings are reported to have limited effects in delaying ripening of coated commodities during cold storage (Banks, 1984c; Drake and Nelson, 1990; Elson et al., 1985; Kerbel et al., 1989; Köksal et al., 1994; Lau and Meheriuk, 1994; Magness and Diehl, 1924; Meheriuk and Lau, 1988; Miszczak, 1994; Santerre et al., 1989; Smith and Stow, 1984; Trout et al., 1953), with more substantial results being achieved during shelf life (Banks, 1984a, 1984c and 1985b; Bayindirli et al., 1995; Castrillo and Bermudez, 1992; Dhalla and Hanson, 1988; Díaz-Sobac et al., 1996; Drake and Nelson, 1990; El Ghaouth et al., 1991a, 1991b and 1992b; Elson et al., 1985; Erbil and Muftugil, 1986; Kerbel et al., 1989; Lau and Meheriuk, 1994; Magness and Diehl, 1924; Meheriuk, 1990; Meheriuk and Lau, 1988; Sümnü and Bayindirli, 1994, 1995a and 1995b; Yuniarti and Suhardi, 1992). Less significant differences in ripening between coated and non-coated fruit were observed for fruit treated in a more advanced maturity/ripening stage (Banks, 1985b; Drake and Nelson, 1990; Kerbel et al., 1989; Sümnü and Bayindirli, 1995b) and with polysaccharide instead of lipid- and resins-based coatings (Drake et al., 1987 and 1988; Sümnü and Bayindirli, 1994). The delay in ripening was largely dependent on commodity (Elson et al., 1985; Köksal et al., 1994; Van Zyl et al., 1987) and cultivar of the same commodity (Drake and Nelson, 1990; Elson et al., 1985; Lau and Meheriuk, 1994; Magness and Diehl, 1924; Meheriuk and Porritt, 1972; Trout et al., 1953).

Coatings have been reported to have variable results in delaying softening. This may reflect differences in water loss between coated and non-coated commodities. Trout et al. (1953) observed that sensory tests often indicated that coated apples were crisper and juicier than non-coated fruits, but this difference was frequently not

reflected in penetrometer values, with non-coated fruits being firmer than coated ones. According to the authors, this was probably due to the greater water loss from non-coated than from coated fruits. In general, wilting was found to toughen the flesh and cause higher penetrometer readings that did not then truly reflect the stage of ripening. Therefore, caution should be taken when interpreting results presented in the literature about the effect of coatings in delaying softening, mainly after exposing the commodity to conditions causing excessive water loss (such as long term storage at low temperature or short period shelf-life under very dry conditions). Methods other than penetrometer readings to assess flesh texture should be explored.

The variable results in delaying ripening (in terms of change in firmness, skin colour, soluble solids and acidity) between commodities and between cultivars of the same commodity treated with the same coating formulation may be the result of differences in initial quality (maturity/ripening stage), respiration and ripening rates, and character of skin cover by the surface coating. Commodities (such as pears, plums, nectarines, strawberries) or cultivars of the same commodity that have high respiration and ripening rates might be expected to have larger modification of internal atmosphere when coated, leading to more substantial reduction in respiration, C_2H_4 biosynthesis and action and, therefore, potential to achieve a greater relative delay in ripening. Those commodities or cultivars of the same commodity having better character of cover by the surface coating (resulting in low skin permeance to gases) and high respiration rates, when exposed to higher temperatures would similarly be expected to have larger modification of internal atmosphere and more substantial effect in delaying ripening.

Coatings have been reported to have a more substantial effect in delaying change in skin colour than in firmness (Köksal et al., 1994; McGuire and Hallman, 1995; Smith and Stow, 1984). Guavas treated with HPC (2% or 4% w/v) or a carnauba wax (5% w/v) fail to develop a full colour during shelf life (McGuire and Hallman, 1995). Coated pears treated with a very thick coating layer may remain green while still being able to soften (Smock, 1935). For pears (Farooqi and Hall, 1973; Meheriuk and Lau,

1988; Sümnü and Bayindirli, 1994; Van Zyl et al., 1987) and bananas (Blake, 1966; Ben-Yehoshua, 1966), coatings can cause uneven colour change characterised by skin blotchiness, with yellow areas interspersed with green tissue. This seems to indicate differences in responses to internal atmosphere modification between physiological ripening processes in some coated commodities.

Coatings have been reported to improve retention of vitamin C in apples (Sümnü and Bayindirli, 1995b), pears (Sümnü and Bayindirli, 1994) apricots (Sümnü and Bayindirli, 1995a), peaches (Erbil and Muftugil, 1986), mangoes (Dhalla and Hanson, 1988), limes (Paredes-López et al., 1974) and mandarins (Bayindirli et al., 1995) during shelf life. The decrease in ascorbic acid loss by means of coatings may be due to the low P'_{O_2} of coated fruit, reducing the internal O_2 and retarding ascorbic acid oxidation (Sümnü and Bayindirli, 1995a and 1995b).

2.5.2.2 Mode of action of surface coatings in delaying ripening

Research with surface coatings to preserve postharvest quality by modifying the commodity internal atmosphere began in 1920s (Magness and Diehl, 1924). About the same time Kidd and West started their pioneering work on controlled atmosphere storage of apples and pears. The initial work focused on inhibitory effects of reduced concentrations of O_2 and elevated concentrations of CO_2 on ripening, representing the start point for all subsequent research on the physiological and biochemical basis of CA/MA storage of fruits and vegetables. The effects of low O_2 and high CO_2 in suppressing the main metabolic processes related to ripening are well known (Section 2.2). However, it is not clear if the main mechanism by which coatings achieve their effects is by reducing O_2 , by increasing CO_2 , or both (Ben-Yehoshua, 1966 and 1967).

Magness and Diehl (1924) first reported that coating apples with paraffin wax or oil reduced skin permeance to gases, resulting in a marked increase in CO_2 and a decrease of O_2 within the tissue. The authors observed for apples stored at $0^\circ C$ an abundance of O_2 ($p'_{O_2} > 10$ kPa, except for heavily oiled fruit, which had $\cong 3$ kPa O_2),

and a large increase of internal partial pressure of CO₂ ($p'_{\text{CO}_2} > 10$ kPa, against about 2 kPa for the controls) in coated fruit. As a result of substantial accumulation of internal CO₂, the authors suggested that elevated p'_{CO_2} , instead of low p'_{O_2} , was responsible for the observed effects of coatings in suppressing respiration rate and delaying ripening at 0°C. Kerbel et al. (1989) and Lau and Yastremsky (1991) also observed substantially higher p'_{CO_2} in coated apples (4 to 6 kPa against 1 to 2 kPa for the controls) immediately after removal from storage at 0°C (with fruit treated with higher concentrations of coatings having higher p'_{CO_2}), while the p'_{O_2} was no less than 15-16 kPa. Larger reductions of respiration rate of apples are achieved by reducing p'_{O_2} below 4-5 kPa (Dadzie et al., 1996; Yearsley et al. 1996). These values are much lower than the p'_{O_2} reported above for coated apples, and indicates that during low temperature storage, coatings may slightly suppress respiration and delay ripening mainly by increasing p'_{CO_2} .

Gas solubilities in liquids are highly dependent on temperature. The solubility in water of CO₂ is more than 25 times higher than that of O₂ at 20°C, and this difference increases at lower temperature values since by decreasing temperature there is a higher increase of CO₂ than O₂ solubility (Foust et al., 1980). This implies that for the same p'_{O_2} and p'_{CO_2} in the intercellular gas phase, there would be much higher concentrations of CO₂ dissolved in the cell sap of fruit stored at low temperature, than of O₂. The increased p'_{CO_2} in the intercellular space at low temperature observed for coated fruit combined with the greater solubility of CO₂ in the cell sap in such conditions would result in a much higher increase of CO₂ concentration in the liquid phase. This supports the notion that the increase of CO₂ concentration in the liquid phase may make a major contribution to delay in ripening of coated fruit at low temperatures.

Since the early work done by Magness and Diehl (1924), some authors have still focussed on increase of p'_{CO_2} in coated commodities held at ambient temperatures as the main way by which coatings delay ripening (Drake et al., 1987; Drake and Nelson, 1990; Meheriuk and Porritt, 1972; Miszczak, 1994; Smith and Stow, 1984; Smith et

al., 1987; Smock, 1935). Although an effect of high CO₂ seems likely at low temperatures, this does not appear to be the case at high temperatures.

Smith and Stow (1984) reported that 'Cox's Orange Pippin' apples treated at harvest with Pro-long (1.25% w/v) had a significant retention of skin colour but not of firmness after 4-5 months in cold storage. More substantial retention of firmness and skin colour was achieved for fruit treated with higher coating concentrations (from 1% up to 4% w/v) and held at higher temperatures (from 3.5°C up to 18°C), as a result of greater modification of fruit internal atmosphere. These authors also reported a larger modification of internal concentration of CO₂ than of O₂ at higher temperatures, suggesting that coatings delay ripening mainly by increasing CO₂ instead of depressing O₂. However, Banks (1984c), working with the same cultivar and similar concentrations of Pro-long (from 1% up to 3% w/v), reported much larger reductions of internal O₂ concentrations than those reported by Smith and Stow (1984) for fruit held at similar temperatures. Smith et al. (1987) also observed that for fruit held at 18°C, when apples were exposed to CA conditions to create an $p_{CO_2}^i$ similar to those achieved by coating (8.5 kPa CO₂ for fruit coated with 3% Pro-long and 7.9 kPa CO₂ for CA stored fruit), there was a larger inhibition of colour change in coated fruit than in CA stored fruit, while firmness was little affected by both treatments in comparison to the controls. In this study the authors did not assess $p_{O_2}^i$, which might have explained the differences in fruit skin colour between treatments. Instead, the authors suggested that coatings might have interfered with colour change by a mechanism other than by modifying fruit internal atmosphere. They suggested that the coating may have penetrated through the skin and directly interfered with the degradation process of chlorophyll in the chloroplasts. However, Bhardwaj et al. (1984) did not observe a migration of a similar coating formulation (TAL Pro-long containing [¹⁴C]-labeled sucrose esters of fatty acids in its composition) to the pulp of coated bananas, apples and pears. When the coating (TAL Pro-long 1.5% w/v) was labeled with aurothioglucose, the presence of gold in stomata aperture on areas of coated skin of banana fruit was demonstrated using energy dispersive X-ray analysis (Banks, 1984b).

Therefore, the mode of action of coatings in retarding ripening seems unlikely to be dependent upon migration into the pulpy tissue, as suspected by others (Smith and Stow, 1984; Smith et al., 1987). Instead, the major effect of coating on permeance seems to be caused by blockage of pores on the skin, physically impeding gaseous diffusion, modifying the commodity internal atmosphere (Section 2.2; Banks, 1984a and 1984b; Banks et al., 1993a and 1997b; Ben-Yehoshua et al., 1985; Hagenmaier and Baker, 1993a).

Magness and Diehl (1924) reported that for coated apples held at temperatures of 18°C and 26.5°C there was a greater reduction of p'_{O_2} (from about 14 kPa to 2 kPa) than increase of p'_{CO_2} (from about 9 to 14 kPa). Similar results have been reported for coated apples by others (Banks, 1984c, Banks et al., 1997b; Kerbel et al., 1989; Magness and Diehl, 1924; Trout et al., 1953). A larger modification of p'_{O_2} than of p'_{CO_2} has also been reported for coated bananas (Banks, 1984a, 1985b; Ben-Yehoshua, 1966), oranges (Ben-Yehoshua, 1967; Hagenmaier and Baker, 1993c, 1994b, 1995; Nisperos-Carriedo et al., 1990), grapefruit (Hagenmaier and Baker, 1994a and 1994b; Hagenmaier and Baker, 1996), and tomatoes (El Ghaouth et al., 1992b) held at ambient temperatures. The relationship between p'_{CO_2} and p'_{O_2} can be seen in Fig. 2.5 for a coated commodity held at ambient temperatures. Improving the character of cover of the commodity by a coating, results in a larger reduction of p'_{O_2} than an increase of p'_{CO_2} when the level of O_2 is not limiting for aerobic respiration (Banks et al., 1997a and 1997b). The larger modification of p'_{O_2} than of p'_{CO_2} at high temperatures under normal aerobic metabolism is the result of increased respiration rate coupled with the selective permeability to these gases of coating films (Section 2.2). However, when p'_{O_2} is reduced below the lower O_2 limit and the commodity starts fermenting, the differential effect of coating on permeance to the two gases will be offset by the increase in RQ , with a burst of p'_{CO_2} (Fig. 2.5).

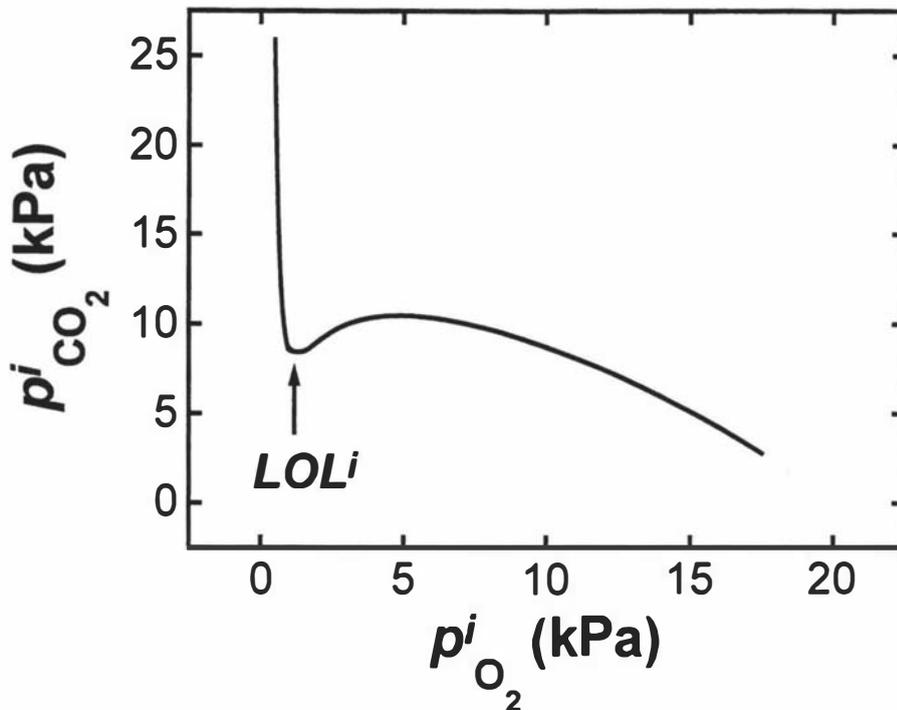


Figure 2.5 Plot of internal partial pressure of CO_2 ($p^i_{CO_2}$) versus internal partial pressure of O_2 ($p^i_{O_2}$) to identify the internal lower oxygen limit (LOL^i) of coated fruit (modified from Banks et al., 1997b).

Surface coatings may also delay ripening by inhibiting C_2H_4 biosynthesis and action. Coatings have been reported to have increased (Baldwin et al., 1995b; Bauchot et al., 1995b; Drake and Nelson, 1990; Lau and Yastremski, 1991) or reduced (Banks, 1984a; Drake et al., 1987) the internal concentration of C_2H_4 in coated commodities. Immediately after removal from cold storage, apples coated with Nutri-Save (Lau and Yastremski, 1991) and Semperfresh (Bauchot et al., 1995b; Kerbel et al., 1989) had higher internal C_2H_4 , with the concentration increasing in proportion to the total solids concentration in the coating formulation (Kerbel et al., 1989; Lau and Yastremski, 1991). However, control fruit tended to reach higher concentrations of internal C_2H_4

than Semperfresh-coated fruit during ripening at 20°C (Kerbel et al., 1989). The contrasting published results for internal concentration of C₂H₄ probably reflect natural variability in C₂H₄ production rates between commodities or cultivars of the same commodity; differences of coating treatments in modifying fruit internal atmosphere (which is dependent on temperature and respiration rate of the commodity); character of cover of the coating film which is related to coating-commodity interaction (determined by the nature of the skin and blockage of the pores by the coating); and differences in $P'_{C_2H_4}$ (which is also affected by temperature and RH) between coating formulations having different chemical composition and total solids concentration.

The results seem to show that coatings can inhibit non-autocatalytic (System I) C₂H₄ biosynthesis during cold storage to an extent that depends on how much the commodity-coating interaction modifies the internal atmosphere. For those coated commodities that have suppressed non-autocatalytic (System I) C₂H₄ production during cold storage as a result of substantial modification of internal atmosphere (mainly accumulation of CO₂), accumulation of C₂H₄ may be suppressed. If the modification of internal atmosphere is not large enough during the storage at low temperature to inhibit System I C₂H₄ biosynthesis, some ripening may occur during this period driven by C₂H₄, but this process may be drastically reduced once the commodity is transferred to ambient temperatures. Under these conditions, the internal atmosphere modification (mainly the reduction of O₂) might suppress System I and System II C₂H₄ production, as well as C₂H₄ action, in spite of some internal accumulation of the hormone. This accumulation may be the result of a burst of C₂H₄ production after exposure at high temperatures (when the tissue is not in a steady state as a result of gradual modification of internal composition of O₂ and CO₂) of a commodity that has already achieved System I C₂H₄ biosynthesis during cold storage. This may also be expected as a result of reduced $P_{C_2H_4}$ of the coating films (Hagenmaier and Shaw, 1992). Ben-Yehoshua et al. (1985) reported a 50% reduction of $P'_{C_2H_4}$ for oranges coated with a coumarone indene resin and Banks (1984a and 1985b) reported an 80% reduction in $P'_{C_2H_4}$ for bananas coated with TAL Pro-long (1.5% w/v).

The published literature indicates that by increasing temperature there is a change from a discrete effect of high $p_{\text{CO}_2}^i$ to a more dramatic effect of $p_{\text{O}_2}^i$ in delaying ripening. Since the reduction of $p_{\text{O}_2}^i$ has a stronger effect in reducing respiration, C_2H_4 biosynthesis and action and delaying ripening, we can expect a more substantial effect of coatings in preserving the commodity quality at higher temperatures. However, this is set against the background of much more rapid ripening at high temperatures.

2.5.2.3 Optimisation of surface coatings in relation to commodity internal atmosphere composition

The majority of literature concerning optimisation of CA/MA storage has focused on the effects of low O_2 concentration, since a smaller and less consistent effect of high CO_2 has been reported on respiratory metabolism of fruits and vegetables in comparison to that observed for low O_2 (Boersig et al., 1988; Dadzie et al., 1996; Yearsley et al., 1996). This seems to be the case for coated commodities exposed to ambient temperatures.

Increasing CO_2 composition can reduce respiration rate, depending on the crop and partial pressure of CO_2 . An inhibition of oxidative CO_2 production by increased CO_2 concentrations has been reported for asparagus, broccoli, mungbean sprouts and cut chicory, but not for apples (Peppelenbos et al., 1996; Peppelenbos and van't Leven, 1996). Evidence that elevated CO_2 has no or little effect in reducing respiration rate has been reported for bananas (Young et al., 1962) and mushrooms (Peppelenbos et al., 1993). Joles et al. (1994) reported that partial pressures of $\text{CO}_2 < 17$ kPa did not affect O_2 uptake for raspberries, and Beaudry (1993) that partial pressures of $\text{CO}_2 > 20$ kPa resulted in only a small reduction in O_2 uptake of blueberries.

Apples exposed to 5 kPa CO_2 for four days (Peppelenbos et al., 1996; Peppelenbos and van't Leven, 1996) or to 8 kPa CO_2 for up to seven days (Yearsley et al., 1997b) at $\sim 20^\circ\text{C}$ did not undergo a suppression in aerobic respiration. However, by modelling data from the literature (data from Fidler and North, 1967) on the respiratory effects of

O₂ and CO₂ of apples stored in CA for 50-200 days, Peppelenbos et al. (1996a) identified a clear effect of CO₂ on O₂ consumption. This seems to show that long-term stress of high CO₂ at low temperature (and also low O₂), may provide different effects on respiratory metabolism than short-term stress at ambient temperature. This should be carefully considered when designing experiments to optimise CA/MA storage. Since the main goal of these techniques is to extend the storage period at low temperatures, the long exposure to the imposed atmospheric conditions may have a stronger influence on metabolic processes than short time exposure. More work on the effects of low O₂/high CO₂ for the optimisation of CA/MA storage conditions should be done after long term exposure at low temperature to different concentrations of these gases. Yearsley et al. (1997b) did not observe an effect of external CO₂ levels between 0 and 8 kPa, on the internal lower O₂ limit in apples at 20°C. However, the authors reported an increase in the internal lower O₂ limit at 0°C, when the external CO₂ level was increased from 0 to 8 kPa, that they attributed to a higher solubility of CO₂ at the lower temperature. These results seem to indicate a lower tolerance of the produce to high levels of CO₂ during low temperature CA storage, affecting the internal lower O₂ limit and commodity quality, especially after long term exposure to these atmospheres. This reinforces the notion that high p'_{CO_2} may have a substantial effect on postharvest physiology of coated commodities exposed to long term storage at low temperatures.

Oxygen has a stronger effect on respiration and much effort has been made to characterise this relationship for the optimisation of CA/MA storage. The relationship between oxidative CO₂ production and either p'_{O_2} (Fig. 2.1) or external partial pressure of O₂ ($p_{\text{O}_2}^e$) of fruits and vegetables has been modelled using the Michaelis-Menten equation (Andrich et al., 1991; Banks et al., 1993a; Cameron et al., 1995; Dadzie et al., 1996; Peppelenbos et al., 1996; Peppelenbos and van't Leven, 1996; Solomos, 1982 and 1985). However, when partial pressure of O₂ drops to very low levels, anaerobic respiration may be induced, which leads to additional CO₂ production (Fig. 2.1). Therefore, modelling the total respiration rate ($r_{\text{CO}_2(\text{tot})}$) of a product needs a distinction

between CO₂ produced by oxidative metabolism ($r_{\text{CO}_2(\text{ox})}$, which is equal to respiratory O₂ consumption - r_{O_2} - when O₂ is non-limiting and the respiratory quotient [RQ] is ~1) and by fermentative metabolism ($r_{\text{CO}_2(\text{fer})}$, Fig. 2.1):

$$r_{\text{CO}_2(\text{tot})} = r_{\text{CO}_2(\text{ox})} + r_{\text{CO}_2(\text{fer})} \quad [2.6]$$

Andrich et al. (1994), Beaudry et al. (1993) and Yearsley et al. (1996) used exponential functions to describe $r_{\text{CO}_2(\text{fer})}$, while Banks et al. (1993) and Peppelenbos et al. (1993), despite using different functions, modelled $r_{\text{CO}_2(\text{fer})}$ regarding O₂ as an inhibitor of fermentative CO₂ production.

One approach to optimise CA/MA storage of fruits and vegetables has been focused in identifying the lower O₂ limit (*LOL*), the O₂ level at which accumulation of products of anaerobic respiration resulting in off-flavours and degradation of the tissue are likely (Banks et al., 1993b). Several authors have used different approaches to identify the *LOL*. Blackman (1928) used the term ‘Extinction Point’ (*EP*), defined as the threshold O₂ concentration at which all anaerobic respiration was just extinguished. Thomas and Fidler (1933) defined the *EP* as the lowest O₂ concentration at which ethanol production ceased. However, because ethanol is a normal constituent of several fruits held in aerobic conditions (Ke et al., 1994; Nanos et al., 1992), defining the *EP* on the basis of ethanol accumulation is of low practical value. Boersig et al. (1988), studying the aerobic-anaerobic transition zone in pears, proposed an alternative concept, the ‘Anaerobic Compensation Point’ (*ACP*). They defined the (*ACP*) as the O₂ concentration at which CO₂ production was minimal (minimal point of total respiration curve of Fig. 2.1). However, anaerobic respiration starts at a partial pressure of O₂ higher than that corresponding to the *ACP* (represented by the increase of $r_{\text{CO}_2(\text{fer})}$ in Fig. 2.1). Beaudry (1993) defined the concept of ‘Respiratory Quotient Breakdown’ (*RQB*), as the O₂ partial pressure at which the steady-state *RQ* begins to increase as O₂ decreases.

All of the above-published work dealing with the identification of the *LOL* has been based on $p_{O_2}^e$ instead of $p_{O_2}^i$. Studies with $p_{O_2}^e$ are simpler to undertake and more readily applicable to empirical design of packages. However, fruit tissue responds more directly to the cell sap O_2 concentration, that can be assumed to be close to the equilibrium with the $p_{O_2}^i$ in the internal atmosphere (Banks et al., 1993b; Dadzie et al., 1996). This is certainly highly relevant when considering the determination of *LOL* of coated fruits and vegetables, when the main interest is in characterising modification of the internal atmosphere, which is dictated by the permeance and respiration rate of the coated product. This led Yearsley et al. (1996) to propose the use of *LOL* based on $p_{O_2}^i$ (LOL^i) instead of $p_{O_2}^e$ (LOL^e), for optimisation of CA/MA storage. For estimation of LOL^i they proposed the internal *ACP* (ACP^i) and the internal 'Fermentation Threshold' (FT^i). ACP^i was estimated by plotting internal partial pressure of CO_2 ($p_{CO_2}^i$) versus $p_{O_2}^i$. When plotting $p_{CO_2}^i$ versus $p_{O_2}^i$, the increase in $p_{CO_2}^i$ when $p_{O_2}^i$ approaches 0 kPa is related to rates of fermentation. The FT^i was described in terms of plots of RQ (FT_{RQ}^i) and internal ethanol concentration (FT_{EtOH}^i) versus $p_{O_2}^i$ (Fig. 2.6). Beaudry (1993) arbitrarily selected a 20% deviation of RQ from the asymptote of the fitted curve to estimate the LOL^i , while the analogous deviation used by Yearsley et al. (1996) was 10%. For coated fruit, Banks et al. (1997b) have proposed plots of $p_{CO_2}^i$ versus $p_{O_2}^i$ to identify the LOL^i (Fig. 2.5), equivalent to ACP^i described by Yearsley et al. (1996). Increasing the amount of coating deposited on the fruit surface depresses $p_{O_2}^i$ and increases $p_{CO_2}^i$. As the $p_{O_2}^i$ decreases, the respiration rate is suppressed and the negative slope of this relationship decreases and becomes positive at a certain $p_{O_2}^i$ level. With further decreases in $p_{O_2}^i$ there is a rapid increase in $p_{CO_2}^i$, indicating the transition to fermentation. The LOL^i corresponds to this point of minimum $p_{CO_2}^i$, before its rapid increase after further reduction of $p_{O_2}^i$ (Fig. 2.5). This approach, in addition to FT_{RQ}^i and FT_{EtOH}^i , can be explored in identifying the safe internal O_2 concentration to optimise the use of surface coatings for fresh fruits and vegetables.

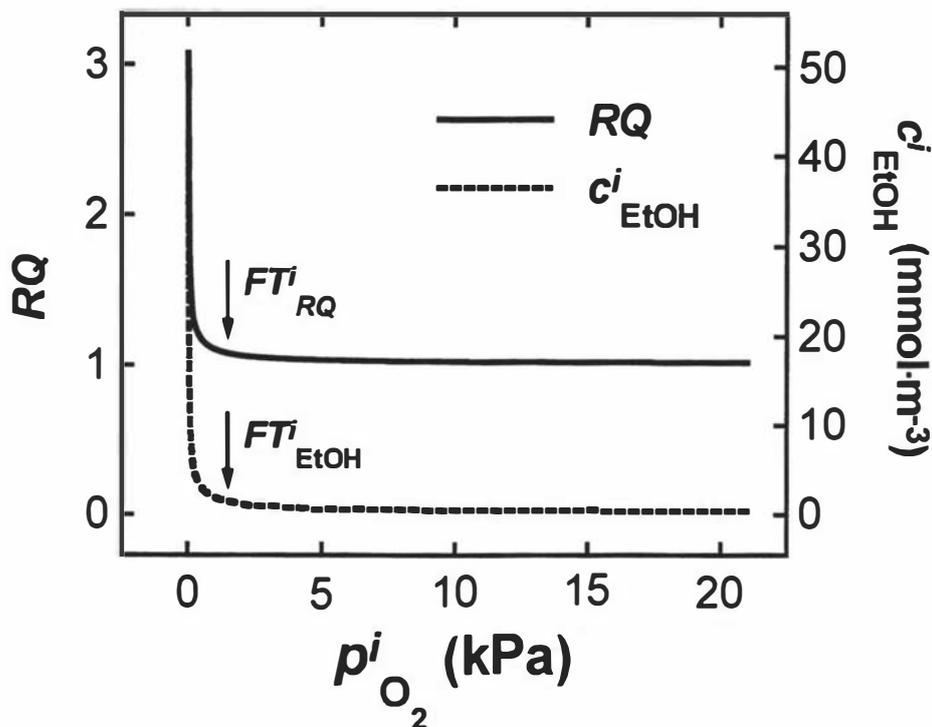


Figure 2.6 Plots of respiratory quotient (RQ) and internal ethanol concentration (c^i_{EtOH}) versus internal partial pressure of O_2 ($p^i_{O_2}$) to identify the internal ‘Fermentation Threshold’ (FT^i) of fruits and vegetables (modified from Yearsley et al., 1996).

The assessment of $r_{CO_2(tot)}$ alone does not necessarily reveal if the coating treatment has a beneficial effect in preserving the commodity quality. As observed by Magness and Diehl (1924), treating different apple cultivars with paraffin wax or oil coatings, resulted in a reduced respiration rate of fruit held at 0°C, 18°C, or at 26.5°C. However, while at 0°C the RQ was $\cong 1$, indicating the predominance of aerobic respiration, at 18°C the O_2 within the tissue was highly depleted, and some fermentation apparently occurred in coated fruit, for the RQ was > 1 , and at 26.5°C the RQ was $\gg 1$, indicating marked levels of fermentation activity. In non-coated fruit the RQ at all temperatures was $\cong 1$, indicating the absence of significant fermentation. As coatings reduce

commodity P'_{CO_2} and P'_{O_2} , they might reduce CO_2 evolution or O_2 consumption rates. However, plots of $r_{\text{CO}_2(\text{tot})}$ versus p'_{O_2} might aid in identify the LOL^i of coated commodities, corresponding to the ACP^i (Fig. 2.1) described by Boersig et al. (1988). Since the relationship between $r_{\text{CO}_2(\text{ox})}$ versus p'_{O_2} is described by a Michaelis-Menten relationship, this approach also permits the identification of the K_m for different commodities. This can be used to characterise the potential benefit of reducing p'_{O_2} (in CA/MA storage, including surface coatings) in suppressing $r_{\text{CO}_2(\text{ox})}$ (Fig. 2.1).

The LOL depends on commodity (Ke and Kader, 1992), cultivar (Yearsley et al. 1996), physiological age (Boersig et al., 1988; Ke et al., 1993; Nanos et al., 1992), temperature (Ke et al., 1990 and 1993; Yearsley et al. 1997b), and duration of exposure (Boersig et al., 1988; Ke et al., 1993). Therefore, all these aspects have to be considered for the optimisation of surface coating for fruits and vegetables.

LOL^i (as opposed to LOL^e) seems to be temperature insensitive for temperatures $\leq 28^\circ\text{C}$ (Yearsley et al., 1997a). Its estimation for different commodities, cultivars, and ripening stages should provide great advances for optimisation of surface coating in the near future. The composition and character of cover of a coating can be tailored to achieve a level of p'_{O_2} near and above the LOL^i , for a certain environmental condition of temperature and RH, to achieve the best results in delaying ripening without the detrimental effects of fermentation.

The optimisation of surface coatings should also consider the assessment of sensory attributes and incidence of physiological disorders after long-term storage in cold storage and also after a shelf life period. Short term exposure of the commodity to low O_2 and/or high CO_2 only indicates fruit tolerance to MA treatments of the same duration. Longer studies are required to ensure the best retention of product quality over long term commercial storage.

2.5.3 Postharvest quality of coated commodities

2.5.3.1 Skin finish

Coatings improved skin finish of apples, with no apparent difference among apples waxed with shellac-, carnauba- or resin-based coatings after long term cold storage (Drake and Nelson, 1990). Glenn et al. (1990) reported that fruit finish in apples coated with a wax was highly dependent of the extent of fruit cracking on the skin. Polishing the fruit before waxing revealed a reticulate pattern of cracks that deeply penetrated the cuticle. More cracking occurred near the calyx end than at the pedicel end of the fruit, and cracking tended to be more severe on surface exposed to the sun. However, waxing the fruit did not always completely fill in the cracks and other irregularities on these regions of the skin, resulting in lower light reflectance and poor finish of coated fruit.

Hagenmaier and Baker (1994b) reported higher gloss on the skin of oranges and grapefruits treated with shellac and resin than with polyethylene and carnauba waxes, while fruit treated with the latter waxes had higher gloss than non-coated fruit. However, fruit treated with shellac and resin underwent a larger decrease in gloss during a two week shelf life period than fruit coated with polyethylene and carnauba waxes, resulting in no significant difference between coating treatments at the end of the shelf life period. Hagenmaier and Baker (1995) observed that the use of bilayer films on citrus fruit could achieve both benefits of reducing water loss and improving the gloss. This approach involved applying two coatings, the first coating being a moisture-barrier wax (petroleum wax) and the second a polyethylene wax or a mixture of shellac and resin. Fruit gloss decreased more rapidly during one week at 20°C with a single glossy coating than with the same coating applied as a second layer over a wax-based first coating. These results reflect differences in water loss of fruit treated with different coatings. Because shellac and resin coated fruit lost more water than polyethylene and carnauba wax coated fruit, the wrinkling of their skin resulted in lower gloss after long shelf life period. The application of a first layer with low

permeance to water can reduce shrivel and maintain the shine imparted by the glossy coating layer.

Hagenmaier and Baker (1996) observed that the gloss of candelilla wax coating films was improved by addition of gelatine and to a lesser extent by adding HPMC. The gloss of candelilla coating film was also affected by thickness and drying temperature; increasing the thickness and the drying temperature increased the gloss. The gloss of candelilla and candelilla plus carnauba wax, but not of a candelilla plus beeswax formulation, was increased by adding gelatine or soy isolate (25% protein).

Coating bananas with a polyethylene-wax emulsion improved the appearance of the skin by imparting gloss and preventing shrinkage and darkening (Ben-Yehoshua, 1966). A carnauba-paraffin mixture improved the finish of the skin in cherries and nectarines (Claypool, 1939). In mandarins a carnauba-based wax improved gloss (Farooqi et al., 1988) while in papaya only some wax-based coatings improved gloss of the skin (Paull and Chen, 1989). Chitosan-coated carrots had a glossier appearance than untreated roots (Cheah et al., 1997). Increasing the concentration of total solids in polyethylene and carnauba waxes improved the gloss of coated avocados (Johnston and Banks, 1998).

Mellenthin et al. (1982) observed that in-line application of a composite coating consisting of water-soluble polysaccharides, natural wax and emulsifiers (Fresh-Cote) on pears at the waxing location of the packing line reduced peel discolouration of 'Bartlett' but not 'd'Anjou' pears due to brush friction. Fruit were also subjected to a return flow belt for five minutes to simulate the sorting sequence during packing. The coating substantially reduced the susceptibility of both pear cultivars to peel discolouration due to belt friction.

2.5.3.2 Disorders

Apples harvested early in the season and coated with wax (Hitz and Haut, 1938) or Semperfresh (Kerbel et al., 1989) had increased incidence of scald. In contrast,

Bauchot et al. (1995a) and Bauchot and John (1996) did not report an effect of Semperfresh on scald incidence in apples. The coating did not appear to have any effect in modifying the volatility of α -farnesene or representing a physical barrier to trap it in the fruit. In apples, Pro-long had no effect on scald incidence (Miszczak, 1994) and Nutri-Save reduced the incidence of scald and core flush (Elson et al., 1985). Farooqi and Hall (1973) reported that increasing the concentration of a carnauba-based coating on apples provided a better control of skin disorders (Jonathan spot and soft scald on 'Jonathan' and superficial scald and senescent blotch on 'Granny Smith') and flesh disorders (internal breakdown in 'Granny Smith'). Smock (1935) reported 20% less scald in waxed apples. Pro-long and Nutri-Save reduced the incidence of scald in apples, and reduced the incidence of core flush in some cultivars but increased it in others (Lau and Meheriuk, 1994). However, increasing the concentration of Nutri-Save, but not Pro-long, exacerbated the incidence of skin purpling in all cultivars. Lau and Yastremski (1991) also observed that apples treated with high concentrations of Nutri-Save developed substantial levels of skin damage. Since skin injury seems to be a symptom of low O₂ injury, Lau and Meheriuk, (1994) suggested that these differences reflect a higher permeance to gases of fruit coated with Pro-long than with Nutri-Save. Fruit treated with Nutri-Save may have accumulated anaerobic volatiles after long term storage.

Apples treated with Semperfresh did not develop any internal disorders after long term storage (Santerre et al., 1989). Pro-long increased core flush and low temperature breakdown incidence in 'Cox's Orange Pippin' stored at temperature below 3.5°C, both disorders exacerbated by increased internal CO₂ levels at close to chilling temperatures (Smith and Stow, 1984). The coating did not induce any internal physiological disorder or cause accumulation of alcohol if applied after cold storage. Waxing significantly reduced core flush incidence in 'McIntosh', while breakdown was not affected in a number of cultivars (Meheriuk and Porritt, 1972).

Meheriuk and Lau (1988) reported that the incidence of core breakdown and senescent scald in 'Bartlett' pears and superficial scald in 'd'Anjou' pears were lower

in fruit coated with Pro-long or Nutri-Save. Semperfresh delayed ripening and reduced incidence of senescent breakdown (Van Zyl and Wagner, 1986; Van Zyl et al., 1987) and senescent scald (Köksal et al., 1994) in 'Bartlett' pears. This pear cultivar treated with wax (Claypool, 1939) or mineral oil (Reyneke and Stubbings, 1940) had lower incidence of senescent scald. The coatings, however, adversely affected normal pear ripening. Coated fruit tended to ripen unevenly, lose the ripening capacity and develop a blotchy appearance of green interspersed with yellow when held at ripening temperatures (Claypool, 1939; Elson et al., 1985; Farooqi and Hall, 1973; Meheriuk and Lau, 1988; Smock, 1935; Sünnü and Bayindirli, 1994; Van Zyl et al., 1987).

Blake (1966) observed blotchiness of bananas treated with paraffin coating. Coating bananas with a polyethylene-wax emulsion increased the irregularity in duration of skin degreening, that was overcome by treating the fruit with C_2H_4 (Ben-Yehoshua, 1966).

Immersing grapefruit in vegetable oils and vegetable oil-water emulsions prior to storage at 3°C markedly delayed and reduced symptoms of chilling injury (Aljuburi and Huff, 1984). Chilling injury (rind breakdown, or pitting) of grapefruit was also reduced substantially by treatment with emulsions of polyethylene before storage (Davis and Harding, 1960). Wild (1991) reported an increase in the postharvest incidence of peteca rind pitting in lemons by brushing and waxing.

Mangoes coated with a composite coating made of CMC and sorbitan fatty acid ester presented lower rates of electrolyte leakage than non-coated fruit (Díaz-Sobac et al., 1996). The coated fruit did not show the incidence of dark spots or discolouration on the skin or in the pulp 24 days after shelf life, although these symptoms occurred in the control fruit after six days of shelf life. After 24 days of shelf life, the coating was removed by washing, and the fruit reached full ripeness three to four days later. Therefore, by delaying the loss of cell integrity, coatings reduced undesirable reactions leading to tissue browning without impairing the ability of mango fruit to ripen.

HPC (2% or 4% w/v) and carnauba wax (5% w/v) coatings negatively affected fruit quality of guavas by increasing the incidence of blackening of the peel after their removal from cold storage to ripening temperature (McGuire and Hallman, 1995). McGuire (1997) reported that 17% of guavas treated with a carnauba wax (5% w/v) coating failed to ripen. The fruit remained green and had a lower acidity and soluble solids concentration.

Edwards and Blennerhassett (1994) reported that a polyethylene wax (Citrusseal) reduced chilling injury in 'Honeydew' melons stored at 3°C for up to four weeks. According to these authors, the decrease in chilling injury achieved by waxing the fruit was most likely due to the reduction of water loss. Semperfresh significantly increased the severity of brown speckle on the rind in 'Honeydew' melons (Edward and Blennerhassett, 1990).

Sriyook et al. (1994) reported that coating materials were effective in preventing durian fruit dehiscence. The coatings reduced weight loss and modified internal atmosphere composition. According to the authors, since C_2H_4 seems to be the main factor influencing durian fruit dehiscence, coatings can prevent the problem by reducing C_2H_4 production and action via its effects in reducing water loss and modifying fruit internal atmosphere.

Waxing fresh pineapple with a paraffin-polyethylene coating diluted to 20% of the commercial formulation (v/v) before storage at 8°C for up to four weeks reduced the incidence and severity of internal browning caused by chilling injury to 15 and 31%, respectively, of the non-waxed control (Rohrbach and Paull, 1982). Further increases in coating concentration up to 50% (v/v) had comparatively small beneficial effect in decreasing the injury. Waxing did not reduce crown leaf chilling injury symptoms.

Semperfresh had no effect on the incidence of internal breakdown in plums and increased the wooliness in nectarines, with some cultivars of nectarine having an unacceptable taint on the skin (Van Zyl et al., 1987).

Nature Seal (York, 1994) and chitosan (Zhang and Qhantick, 1997) significantly reduced pericarp browning in litchi fruit but the treatment effects were not substantial

enough to make these formulations attractive commercially. The undesirable enzymatic browning reactions in mushroom slices were prevented by the application of a polysaccharide edible coating, with the coating anti-browning property being further improved by the incorporation of 1% ascorbic acid (food approved anti-oxidant) and a chelator (0.2% calcium disodium EDTA; Nisperos-Carriedo et al., 1991). Drake et al. (1988) reported that surface pitting and stem discolouration in cherry fruit, two physiological disorders associated with high rates of water loss, were not substantially reduced by wax coatings, especially when the fruit were stored at higher temperatures. Under these conditions wax coatings did not provide enough water loss control of cherry fruit to reduce the incidence of the disorders. However, Lidster (1981) reported that sweet cherries treated with emulsified coatings to decrease weight loss presented reduced incidence of discoloured stems and surface pitting in storage. According to the author, these treatments may reduce the disorders by the inhibition of net volume loss (mainly water loss) from mechanically damaged fruits. Because coating the fruit with a vegetable oil emulsion did not reduce weight loss but reduced the incidence of surface pitting, this may indicate that factors other than weight loss may be involved with the inhibition of surface pitting. Ben-Yehoshua (1966) reported that coating bananas with a polyethylene-wax emulsion not only delayed but also reduced the darkening of the skin of ripe coated fruit. Non-coated fruit left at 10°C developed chilling injury (darkening of the skin), while coated fruit did not. Coatings appear to have a direct effect in reducing the darkening reaction by reducing the internal O₂ concentration and therefore the activity of polyphenol oxidase (Ben-Yehoshua, 1966; Lidster, 1981).

2.5.3.3 Diseases

In 'Honeydew' melons Semperfresh did not reduce the incidence of fungal breakdown but increased the incidence of *Alternaria* rots (Edward and Blennerhassett, 1990) and waxing with a polyethylene wax (CitruSeal) did not reduce breakdown

caused by bacteria or fungi (*Alternaria* and *Fusarium* spp.; Edwards and Blennerhassett, 1994). Coating bananas with a polyethylene wax-based coating delayed and reduced the incidence of decay, particularly of the cut surfaces of fruit (Ben-Yehoshua, 1966). However, Blake (1966) observed an increase of decay in paraffin coated fruit in periods when the occurrence of anthracnose was high, making the use of coatings viable only for bananas in a good phytosanitary condition. Oranges treated with a shellac-based coating had a lower percentage of postharvest decay than non-coated fruit, but there was no beneficial effect if fruit were treated with a MC-based coating (Potjewijd et al., 1995). HPC (2% or 4% w/v) and carnauba wax (5% w/v) coatings did not affect the incidence of postharvest decay of guavas (McGuire and Hallman, 1995). Baldwin et al. (1997) reported that cucumbers treated with a Nature Seal (1-2% HPC) coating, with or without the addition of carnauba wax microemulsion, had lower incidence of decay than controls. Better decay control was achieved with the composite coating than with Nature Seal alone. In citrus, lower levels of decay were achieved by coating the fruit with a candelilla wax coating and a polyethylene wax emulsion ('Tag'), but not with a resin-based coating (Flavorseal; Lakshminarayana et al., 1974). In a considerable number of tests, Claypool (1939) reported that waxing reduced decay of deciduous fruits. Farooqi and Hall (1973) observed a reduction of postharvest decay in coated apples. These authors observed that increasing coating concentration resulted in a better control of decay, but fruit treated with excessively high concentrations tended have a higher incidence, probably by rendering the fruit anaerobic and therefore more prone to pathogenic infection. Waxing cucumbers also seemed to induce anaerobiosis and increased incidence of decay (Risse et al., 1987).

Chitosan, besides its effects in delaying ripening and senescence (El Ghaouth et al., 1992b) has been shown to be effective against decay by inhibiting fungal activity (El Ghaouth et al., 1991a, 1992a, 1997). Tomatoes coated with chitosan (1% and 2% w/v) had lower incidence of decay, mainly caused by *Botrytis cinerea* (El Ghaouth et al., 1992b). Coating cucumber and bell pepper with chitosan (1.0% and 1.5% w/v) reduced

fungus infection caused by *Botrytis cinerea* and by species of *Erwinia* and *Alternaria* (El Ghaouth et al., 1992b). Strawberries coated with chitosan were less affected by postharvest decay compared to the controls. There was no significant difference between chitosan- and fungicide-treated berries up to 21 days storage at 13°C. Thereafter, fungicide-treated berries decayed at a higher rate than chitosan-coated berries (El Ghaouth et al., 1991a). The mechanism by which chitosan reduced the decay appear to be related to its fungistatic property rather than to its ability to induce defence enzymes (such as chitinase, chitosanase, or beta-1,3-glucanase) in the tissue (El Ghaouth et al., 1992a). In peppers, chitosan restricted the proliferation of *Botrytis cinerea* and markedly reduced the maceration of the host cell wall components, pectin and cellulose. This seems to result from the ability of chitosan to cause severe cellular damage to *Botrytis cinerea* and to interfere with its capability to secrete polygalacturonase (El Ghaouth et al., 1997). Cheah et al. (1997) reported that chitosan (2 and 4% w/v) significantly reduced the growth of *Sclerotinia sclerotiorum in vitro* and significantly reduced the incidence of rot (from 88 to c. 28%) and also the lesion size (from 26 to c. 12 mm) of carrots inoculated with the pathogen and left for five days at 22°C. Microscope studies revealed that fungal mycelium exposed to chitosan appeared to be deformed and dead, whereas untreated mycelium was normal in appearance. Apples coated with Nutri-Save (a chitosan-based coating) had a lower incidence of decay (Elson et al., 1985). However, in litchi, the application of chitosan coating only partially inhibited decay of fruit during storage, with best control being achieved with fungicide (thiabendazole) treatment (Zhang and Qhantick, 1997).

Fungicides mixed with wax coating material can provide good control of postharvest decay. Fresh market tomatoes treated with a fungicidal wax containing 2.5% *o*-phenylphenol (OPP) in a commercial packhouse had lower incidence of decay than fruit treated with plain wax, and almost no chemical residue of OPP could be detected on fruit treated with the fungicidal wax mixture (Hall, 1989). In oranges, Brown (1984) observed that the control of stem end rot with fungicides incorporated in wax coating required doubling the fungicide concentration used for application in

water. However, the total amount of fungicide required to treat a certain quantity of fruit is not doubled because less wax than water is lost from the brushes during application. The author observed less control of green mould (caused by *Penicillium digitatum*) developed from infections through minute punctures with wax treatment. This may have been the result of non-availability of the fungicide at the infection site because of encapsulation by the wax (Tugwell, 1973), variable wax coverage (Norman et al., 1972), and higher viscosity of wax than water, which may impede depositing of fungicides in certain infection courts (Brown, 1984).

Incorporation of bio-control organisms into the coatings to restore surface populations of beneficial micro-organisms can provide an opportunity for biological control of postharvest decay pathogens (McGuire and Baldwin, 1994; Potjewijd et al., 1995). One bio-control candidate, the yeast *Candida oleophila* Montrocher, has been shown to prolong the storage life of grapefruits, but its growth on the fruit is dependent upon the coating composition. McGuire and Baldwin (1994) observed that films based upon polysaccharides can support very high populations of this species. In a liquid shellac coating, the added yeast were quickly killed and the few survivors did not multiply, with its population remaining low relative to that of fruit coated with cellulose. Apparently, shellac and wax coatings can be toxic to the yeast, due to the addition of alcohols and bases such as KOH, NH₄OH, and morpholine that are used to dissolve the primary constituent.

Potjewijd et al. (1995) observed that varying the cellulose component of polysaccharide coating formulations affected the survival of two yeast bio-control agents, *Candida guilliermondii* strain US7 and *Debaryomyces* sp strain 230. Using MC as the main film-former gave a higher recovery of the yeast after an incubation period (at 26°C) for both strains as opposed to using CMC or HPC. The authors suggested that MC might be a better source of nutrients and less toxic to the antagonists than CMC and HPC. Significant control of decay on oranges was demonstrated by yeast antagonists incorporated in a MC-based coating for the first two

to four weeks of storage (at 16°C and 90% RH), with *Candida guilliermondii* strain US7 providing more promising results than *Debaryomyces* sp strain 230.

Use of a strain of *Bacillus subtilis* (designated B-3) as a biological control agent has been reviewed by Pusey (1989), with emphasis on the postharvest application to stone fruit for control of brown rot caused by *Monilinia fructicola*. Brown rot control by B-3 was demonstrated on peaches, nectarines, apricots, plums, and cherries. Application of the antagonist was shown to be compatible with commercial fruit waxes (water-based, and mineral oil- and paraffin-based waxes) commonly applied to harvested stone fruit. In packing line trials, B-3 applied with a water-based wax was as efficient as the benomyl in controlling brown rot. Antifungal activity of B-3 was shown to be retained during low-temperature storage of fruit. B-3 had little or no effect against *Rhizopus* rot, another important postharvest disease of stone fruit. The addition of dichloran (the fungicide commonly used for *Rhizopus* control) to B-3 formulation was required for the control of brown rot and *Rhizopus* rot. *In vivo* activity of B-3 against fungi was also shown for apple rots caused by *M. fructicola*, *Botrytis cinerea*, and *Glomerella cingulata*, and for grey mould of grapes caused by *B. cinerea*.

Coating can reduce decay by delaying ripening and water loss. Both these processes lead to senescence, making the commodity more prone to pathogenic infection as a result of loss of cellular integrity and tissue natural defence mechanisms. Besides these physiological effects, coatings can also form a physical barrier against pathogenic infection, reducing incidence of postharvest diseases. There are many cases where coating may actually increase decay, such as when the spore load on the fruit from the field is high or the sanitary conditions of the shed are poor (Blake, 1966). Therefore, the sanitation of the fruit before coating is very important. A widely adopted packhouse practice is to wash the fruit with disinfectant solution (e.g. sodium hypochlorite and sodium *o*-phenylphenate) before spraying with the coating. The discontinuance of the coating bath in favour of the line spray method has also largely eliminated decay resulting from contamination of the waxing solution by decayed fruits (Claypool, 1939). There are cases when coating may be so restrictive to gas

exchange, that it may induce physiological disorders on the skin, possibly by inducing fermentation and accumulation of toxic metabolites. This situation may lead to cellular death of commodity tissue and increase the incidence of decay (Farooqi and Hall, 1973; Risse et al., 1987). This issue is vital in assessing the potential of a certain coating formulation in preserving the product quality.

2.5.3.4 Insects

Recently, coatings have been shown to have the potential for postharvest disinfestation. Coating grapefruit infested with fruit fly larvae provided a significant insect control, with better results being achieved by a combination of coating plus hot-air treatment (Hallman et al., 1994) or coating plus insecticide (Hallman and Foos, 1996). Coating plus insecticide provided a better insect control than insecticide or coating alone, and the combined treatments may also reduce the insecticide residue in the fruit (Hallman and Foos, 1996). Coating formulations providing a better character of cover (having resin or a high concentration of MC or HPC, in association with shellac in its formulation) were more effective in controlling fruit fly (Hallman et al., 1994 and 1995; Hallman and Foos, 1996), but they resulted in fruit with higher content of methanol and ethanol at 20°C, possibly reflecting the occurrence of fermentation in the fruit (Hallman et al., 1994). No larvae emerged from coated grapefruit treated with hot air (48°C for 60 minutes), whereas 24% survived treatment of non-coated fruit (Hallman et al., 1994). However, the combination of wax and hot air treatment (46°C for 35 minutes), for disinfestation of guavas increased the percentage of fruit that failed to ripen properly (McGuire, 1997). Coatings also provided a significant control of fruit fly larvae in mangoes, carambolas (Hallman et al., 1994) and guavas (Hallman et al., 1995). Coatings providing a good character of cover increased the insect mortality and also delayed larvae emergence (Hallman et al., 1995). Coating of cold-stored mangoes and carambolas did not increase fruit fly mortality (Hallman et al., 1994). Oxygen uptake by the fruit is reduced at lower temperatures, resulting in a

small modification of fruit internal atmosphere. The insect also requires less O_2 at these lower temperatures. Therefore, coating may not prove effective for disinfestation during cold storage, but can be very effective in combination with short exposure to hot treatment.

The killing of immature fruit fly inside coated fruit seems to be a combined effect of reduced p'_{O_2} and increased p'_{CO_2} (Hallman et al., 1994 and 1995; Hallman and Foos, 1996). Hallman et al. (1994) have also suggested that internal accumulation of certain volatiles, such as methanol or ethanol, may have contributed to reduced emergence of Caribbean fruit fly from coated grapefruit. In addition, delayed ripening of coated fruit (McGuire and Hallman, 1995) might result in a less favorable environment (firmer tissue, less sugar) for larval development, resulting in a delay in larvae emergence (Hallman et al., 1995).

Fruit coatings can also be used for disinfestation of surface pests. Hallman (1994) reported that in South America, coatings are used to desinfest limes and cherimoyas of a surface mite, *Brevipalpus chilensis* Baker. According to the author, coatings probably kill a surface pest by adhering it to the fruit surface and plugging its respiratory and alimentary openings.

This represents a new technology with a high potential for postharvest disinfestation of pests, which may permit a substantial reduction of chemical residues of products currently being used for this purpose. By exposing coated fruit to higher temperatures for a given period of time, it is possible to achieve efficient insect control without causing severe stress that would impair fruit quality. The goal is to select a coating formulation which will permit a substantial modification of fruit internal atmosphere during exposure to short periods at high temperature, and will provide a fruit skin permeance high enough to permit recovery from disinfestation temperatures during subsequent exposure to ambient temperatures. More research will be required to characterise the relationships between coating treatments, internal atmosphere of the fruit at different temperatures and times of exposure, insect mortality and postharvest quality of the product. This will provide a more mechanistic approach for setting a

combination of temperature and exposure time to provide enough modification of internal atmosphere to kill the insect but without impairing fruit final quality.

2.5.3.5 Flavour

The benefit of coatings in preserving and improving the desirable flavour, instead of inducing the development of fermentative flavours, should be thoroughly studied to evaluate the performance of different postharvest coating treatments.

Commodities treated with coating formulations that provide high reductions in skin permeance to gases might accumulate anaerobic volatiles and develop off-flavours after long term cold storage (Magness and Diehl, 1924; Trout et al., 1953) or exposure to high temperatures (Cohen et al., 1990; Dhalla and Hanson, 1988; Hagenmaier and Baker, 1993a, 1994a and 1994b; Mannheim and Soffer, 1996). However, if excessive accumulation of anaerobic volatiles is avoided, coatings can improve the quality of coated fruit destined for fresh market or for juice processing (Baldwin et al., 1995b; Lakshminarayana et al., 1974; Nisperos-Carriedo et al., 1990).

Nisperos-Carriedo et al. (1990) have shown that the use of edible coatings in oranges generally increased the levels of the volatile components acetaldehyde, ethyl acetate, ethyl butyrate, methyl butyrate, ethanol, and methanol of fruit left at 21°C for up to 12 days. Use of beeswax emulsion and TAL Pro-long (alone or in combination with other coating components) were the most effective coatings in retaining or increasing volatile components. However, the authors did not carry out a sensory analysis of coated fruit to determine if these changes in volatiles were large enough to significantly affect the flavour, but an informal tasting did not detect noticeable off-flavours of treated fruit. Acetaldehyde, ethyl acetate, and ethyl and methyl butyrate are known to be important in improving flavour of orange juice (Ahmed et al., 1978). Therefore, coatings can retain volatile flavour components in oranges during storage that may improve the quality of fruit destined for fresh market or for juice processing.

2.6 References

- Ahmed, E. M., Dennison, R. A. and Shaw, P. E., 1978. Effect of selected oil and essence volatile components on flavor quality of pumpout orange juice. *Journal of Agricultural and Food Chemistry*, 26: 368-372.
- Aljuburi, H. J. and Huff, A., 1984. Reduction in chilling injury to stored grapefruit (*Citrus paradisi* Macf.) by vegetable oils. *Scientia Horticulturae*, 24: 53-58.
- Andrich, G., Fiorentini, R., Tuci, A., Zinnai, A. and Sommovigo, G., 1991. A tentative model to describe the respiration of stored apples. *Journal of the American Society for Horticultural Science* 116: 478-481.
- Andrich, G., Zinnai, A., Balzini, S., Silvestri, S. and Fiorentini, R., 1994. The kinetics effect of PCO_2 on the respiration rate of Golden Delicious apples. *Acta Horticulturae*, 368: 374-381.
- Ashley, R. J., 1985. Permeability and plastics packaging. In: J. Comyn (Editor), *Polymer Permeability*. Elsevier Applied Science Publishing, New York, pp. 269-308.
- Avena-Bustillos, R. J. and Krochta, J. M., 1993. Water vapour permeability of caseinate-based edible films as affected by pH, calcium crosslinking and lipid content. *Journal of Food Science*, 58: 904-907.
- Avena-Bustillos, R. J., Krochta, J. M., Saltveit, M. E., Rojas-Villegas, R. J. and Saucedo-Pérez, J. A., 1994. Optimization of edible coating formulations on zucchini to reduce water loss. *Journal of Food Engineering*, 21: 197-214.
- Avena-Bustillos, R. J., Krochta, J. M. and Saltveit, M. E., 1997. Water vapor resistance of Red Delicious apples and celery sticks coated with edible caseinate-acetylated monoglyceride films. *Journal of Food Science*, 62: 351-354.
- Baldwin, E.A., 1994. Edible coatings for fresh fruits and vegetables: past, present, and future. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Lancaster, Basel, Technomic Publishing Company, Inc., pp. 25-64.
- Baldwin, E. A., Nisperos-Carriedo, M. O. and Baker, R. A., 1995a. Edible coatings for lightly processed fruits and vegetables. *HortScience*, 30: 35-40.
- Baldwin, E. A., Nisperos-Carriedo, M., Shaw, P. E. and Burns, J. K., 1995b. Effect of coatings and prolonged storage conditions on fresh orange flavor volatiles, degrees Brix, and ascorbic acid levels. *Journal of Agricultural and Food Chemistry*, 43: 1321-1331.
- Baldwin, E. A., Nisperos, M. O., Hagenmaier, R. D. and Baker, R. A., 1997. Use of lipids in coatings for food products. *FoodTechnology*, 51: 56-62, 64.
- Banks, N.H., 1984a. Some effects of TAL Pro-long coating on ripening bananas. *Journal of Experimental Botany*, 35: 127-137.

- Banks, N.H., 1984b. Studies of the banana fruit surface in relation to the effects of TAL Pro-long coating on gaseous exchange. *Scientia Horticulturae*, 24: 279-286.
- Banks, N. H., 1984c. Internal atmosphere modification in Pro-long coated apples. *Acta Horticulturae*, 157: 105-112.
- Banks, N.H., 1985a. The oxygen affinity of 1-aminocyclopropane-1-carboxylic acid oxidation in slices of banana fruit tissue. In: J.A. Roberts and G.A. Tucker (Editors), *Ethylene and Plant Development*. Butterworths, London, pp. 29-36.
- Banks, N.H., 1985b. Responses of banana fruit to TAL Pro-long coating at different times relative to the initiation of ripening. *Scientia Horticulturae*, 26: 149-157.
- Banks, N.H., Elyatem, S.M. and Hammat, M.T., 1985. The oxygen affinity of ethylene production by slices of apple fruit tissue. *Acta Horticulturae*, 157: 257-260.
- Banks, N. H., Dadzie, B. K. and Cleland, D. J., 1993a. Reducing gas exchange of fruits with surface coatings. *Postharvest Biology and Technology*, 3: 269-284.
- Banks, N. H., Cleland, D. J., Yearsley, C.W., and Kingsley, A.M., 1993b. Internal atmosphere composition – a key concept in responses of fruits and vegetables to modified atmospheres. *Proceedings of the Australasian Postharvest Conference*. The University of Queensland, Gatton College, Lawes, Queensland, Australia. pp. 137-143.
- Banks, N. H., Cleland, D. J., Cameron, A. C., Beaudry, R. M. and Kader, A. A., 1995. Proposal for a rationalized system of units for postharvest research in gas exchange. *HortScience*, 30: 1129-1131.
- Banks, N. H., Cheng, Q., Nicholson, S. E., Kingsley, A. M. and Jeffery, P. B., 1997a. Variation with temperature in effects of surface coatings on gas exchange of apples. Invited presentation to International Congress for Plastics in Agriculture, Tel Aviv, Israel, 9 - 15 March 1997 (in press).
- Banks, N. H., Cutting, J. G. M. and Nicholson, S. E., 1997b. Approaches to optimising surface coatings for fruits. *New Zealand Journal of Crop and Horticultural Science*, 25: 261-272.
- Bauchot, A. D., John, P., Soria, Y. and Recasens, I., 1995a. Sucrose ester-based coatings formulated with food-compatible antioxidants in the prevention of superficial scald in stored apples. *Journal of the American Society for Horticultural Science*, 120: 491-496.
- Bauchot, A. D., John, P., Soria, Y. and Recasens, I., 1995b. Carbon dioxide, oxygen, and ethylene changes in relation to the development of scald in Granny Smith apples after cold storage. *Journal of Agricultural and Food Chemistry*, 43: 3007-3011.
- Bauchot, A. D. and John, P., 1996. Scald development and the levels of α -farnesene and conjugated triene hydroperoxides in apple peel after treatment with sucrose ester-based coatings in combination with food-approved antioxidants. *Postharvest Biology and Technology*, 7: 41-49.
- Bayindirli, L., Sümnü, G. and Kamadan, K., 1995. Effects of Semperfresh and Jonfresh fruit coatings on

- poststorage quality of "Satsuma" mandarins. *Journal of Food Processing and Preservation*, 19: 399-407.
- Beaudry, R. M., 1993. Effect of carbon dioxide partial pressure on blueberry fruit respiration and respiratory quotient. *Postharvest Biology and Technology*, 3: 249-258.
- Beaudry, R. M., Uyguanco, E.R. and Lenington, T.M., 1993. Relationship between headspace and tissue ethanol level of blueberry fruit and carrot roots in sealed LDPE packages. *Proceedings from the Sixth International Controlled Atmosphere Research Conference*, Cornell University, Ithaca, New York. pp. 87-94.
- Ben-Yehoshua, S., 1966. Some effects of plastic skin coating on banana fruit. *Tropical Agriculture*, 43: 219-232.
- Ben-Yehoshua, S., 1967. Some physiological effects of various skin coatings on orange fruit. *Israel Journal of Agricultural Research*, 17: 17-27.
- Ben-Yehoshua, S., Garber, M. J. and Huszar, C. K., 1970. Use of a physiological parameter as means for operational control of application of orange skin-coating in packing plants. *Tropical Agriculture*, 47: 151-155.
- Ben-Yehoshua, S., Burg, S. P. and Young, R., 1985. Resistance of citrus fruit to mass transport of water vapor and other gases. *Plant Physiology*, 79: 1048-1053.
- Bendal, D. S., Ranson, S. L. and Walker, D. A., 1958. Some effects of carbon dioxide-bicarbonate mixtures on the oxidation and reduction of cytochrome C by *Ricinus* mitochondria. *Nature*, 181: 133-134.
- Bender, R. J., Brecht, J. K., Sargent, S. A., Navarro, J. C. and Campbell, C. A., 1993. Ripening initiation and storage performance of avocados treated with an edible-film coating. *Acta Horticulturae*, 343: 184-186.
- Bhardwaj, C. L., Jones, H. F. and Smith, I. H., 1984. A study of the migration of externally applied sucrose esters of fatty acids through the skins of banana, apple and pear fruits. *Journal of the Science of Food and Agriculture*, 35: 322-331.
- Blackman, F. F., 1928. Analytical studies in plant respiration: I. The respiration of senescent ripening apples. *Proceedings of the Royal Society of London, Series B: Biological Sciences*, 103: 412-445.
- Blake, J. R., 1966. Some effects of paraffin wax emulsions on bananas. *Queensland Journal of Agricultural and Animal Sciences*, 23: 49-56.
- Boersig, M. R., Kader, A. A. and Romani, R. J., 1988. Aerobic-anaerobic respiratory transition in pear fruit and cultured pear fruit cells. *Journal of the American Society for Horticultural Science*, 113: 869-873.
- Brown, G. E., 1984. Efficacy of citrus postharvest fungicides applied in water or resin solution water

- wax. *Plant Disease*, 68: 415-418.
- Bufler, G. and Streif, J., 1986. Ethylene biosynthesis of 'Golden Delicious' apples stored in different mixtures of carbon dioxide and oxygen. *Scientia Horticulturae*, 30: 177-185.
- Burg, S. P. and Burg, E. A., 1967. Molecular requirements for the biological activity of ethylene. *Plant Physiology*, 42: 144-152.
- Cameron, A. C. and Reid, M. S., 1982. Diffusion resistance: importance and measurement in controlled atmosphere storage. In: D.G. Richardson and M. Meheriuk (Editors), *Controlled Atmospheres for Storage and Transport of Perishable Agricultural Commodities*. Oregon State University School of Agriculture, Symposium Series 1, pp. 171-180.
- Cameron, A. C. and Yang, S. F., 1982. A simple method for the determination of resistance to gaseous diffusion in plant organs. *Plant Physiology*, 70: 21-23.
- Cameron, A. C., Beaudry, R. M., Banks, N. H. and Yelenich, M., 1994. Modified-atmosphere packaging of blueberry fruit: Modeling respiration and package oxygen concentrations at different temperatures. *Journal of the American Society for Horticultural Science*, 119: 534-539.
- Cameron, A. C., Talasila, P. C. and Joles, D. W., 1995. Predicting film permeability needs for modified-atmosphere packaging of lightly processed fruits and vegetables. *HortScience*, 30: 25-34.
- Castrillo, M. and Bermudez, A., 1992. Post-harvest ripening in wax-coated Bocado mango. *International Journal of Food Science and Technology*, 27: 457-463.
- Chavez-Franco, S. H., 1991. Effects of CO₂ levels on ethylene biosynthesis and action in pear fruit (*Pyrus communis* L.). PhD Dissertation, University of California, Davis, USA.
- Chavez-Franco, S. H. and Kader, A. A., 1993. Effects of CO₂ on ethylene biosynthesis in 'Bartlett' pears. *Postharvest Biology and Technology*, 3: 183-190.
- Cheah, L. H., Page, B.B.C. and Shepherd, R., 1997. Chitosan coating for inhibition of sclerotinia rot of carrots. *New Zealand Journal of Crop and Horticultural Science*, 25: 89-92.
- Chervin, C., Brady, C. J., Patterson, B. D. and Farager, J. D., 1996. Could studies on cell responses to low oxygen levels provide improved options for fruit storage and disinfestation? *Postharvest Biology and Technology*, 7: 289-299.
- Claypool, L. L., 1939. The waxing of deciduous fruits. *Proceedings of the American Society for Horticultural Science*, 37: 443-447.
- Claypool, L. L. and King, J. R., 1941. Fruit waxing in relation to character of cover. *Proceedings of the American Society for Horticultural Science*, 38: 261-265.
- Cohen, E., Shalom, Y. and Rosenberger, I., 1990. Postharvest ethanol buildup and off-flavor in 'Murcott' tangerine fruits. *Journal of the American Society for Horticultural Science*, 115: 775-778.
- Dadzie, B. K., 1992. Gas exchange characteristics and quality of apples. PhD Dissertation, Massey

- University, Palmerston North, New Zealand. 340 pp.
- Dadzie, B. K., Banks, N. H., Cleland, D. J. and Hewett, E. W., 1993. Role of skin resistance to gas diffusion in the response of fruits to modified atmospheres. *Acta Horticulturae*, 343: 129-134.
- Dadzie, B. K., Banks, N. H., Cleland, D. J. and Hewett, E. W., 1996. Changes in respiration and ethylene production of apples in response to internal and external oxygen partial pressures. *Postharvest Biology and Technology*, 9: 297-309.
- Davies, D. D., 1980. Anaerobic metabolism and the production of organic acids. In: P. K. Stumpf and E. E. Conn (Editors), *The Biochemistry of Plants*, Vol. 2, Academic Press, New York. pp. 581-611.
- Davis, P. L. and Harding, P. L., 1960. The reduction of rind breakdown of Marsh grapefruit by polyethylene emulsion treatments. *Proceedings of the American Society for Horticultural Science*, 75: 271-274.
- Davis, P. L. and Hofmann, R. C., 1973. Effects of coatings on weight loss and ethanol buildup in juice of oranges. *Journal of Agricultural and Food Chemistry*, 21: 455-457.
- Dhalla, R. and Hanson, S. W., 1988. Effect of permeable coatings on the storage life of fruits. II. Prolong treatment of mangoes (*Mangifera indica* L. cv. Julie). *International Journal of Food Science and Technology*, 23: 107-112.
- Díaz-Sobac, R., Luna, A. V., Beristain, C. I., de la Cruz, J. and Garcia, H. S., 1996. Emulsion coating to extent postharvest life of mango (*Mangifera indica* cv. Manila). *Journal of Food Processing and Preservation*, 20: 191-202.
- Donhowe, I. G. and Fennema, O., 1993. Water vapor and oxygen permeability of wax films. *Journal of the American Oil Chemists' Society*, 70: 867-873.
- Donhowe, I. G. and Fennema, O., 1994. Edible films and coatings: characteristics, formation, definitions, and testing methods. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Lancaster, Basel, Technomic Publishing Company, Inc., pp. 1-24.
- Drake, S. R., Fellman, J. K. and Nelson, J. W., 1987. Postharvest use of sucrose polyester for extending the shelf-life of stored 'Golden Delicious' apples. *Journal of Food Science*, 52: 1283-1285.
- Drake, S. R., Kupferman, E. M. and Fellman, J. K., 1988. 'Bing' sweet cherry (*Prunus avium* L.) quality as influenced by wax coatings and storage temperature. *Journal of Food Science*, 53: 124-126, 156.
- Drake, S. R. and Nelson, J. W., 1990. Storage quality of waxed and nonwaxed 'Delicious' and 'Golden Delicious' apples. *Journal of Food Quality*, 13: 331-341.
- Drake, S. R., Cavalieri, R. and Kupferman, E. M., 1991. Quality attributes of d'Anjou pears after different wax drying temperatures and refrigerated storage. *Journal of Food Quality*, 14: 455-465.
- Durand, B. J., Orcan, L., Yanko, U., Zauberman, G. and Fuchs, Y., 1984. Effects of waxing on moisture

- loss and ripening of 'Fuerte' avocado fruit. *HortScience*, 19: 421-422.
- Edward, M. E. and Blennerhassett, R. M., 1990. The use of postharvest treatments to extend storage life and control postharvest wastage of honeydew melons (*Cucumis melo* L. var. *inodorus* Naud.) in coolstorage. *Australian Journal of Experimental Agriculture*, 30: 693-697.
- Edwards, M. and Blennerhassett, R., 1994. Evaluation of wax to extend the postharvest storage life of Honeydew melons (*Cucumis melo* L. var. *inodorus* Naud.). *Australian Journal of Experimental Agriculture*, 34: 427-429.
- El Ghaouth, A., Arul, J., Ponnampalam, R. and Boulet, M., 1991a. Chitosan coating effect on storability and quality of fresh strawberries. *Journal of Food Science*, 56: 1618-1620, 1631.
- El Ghaouth, A., Arul, J., Ponnampalam, R. and Boulet, M., 1991b. Use of chitosan coating to reduce water loss and maintain quality of cucumber and bell pepper fruits. *Journal of Food Processing and Preservation*, 15: 359-368.
- El Ghaouth, A., Arul, J., Grenier, J. and Asselin, A., 1992a. Antifungal activity of chitosan on two postharvest pathogens of strawberry fruits. *Phytopathology*, 82: 398-402.
- El Ghaouth, A., Ponnampalam, R., Castaigne, F. and Arul, J., 1992b. Chitosan coating to extend the storage life of tomatoes. *HortScience*, 27: 1016-1018.
- El Ghaouth, A., Arul, J., Wilson, C. and Benhamou, N., 1997. Biochemical and cytochemical aspects of the interactions of chitosan and *Botrytis cinerea* in bell pepper fruit. *Postharvest Biology and Technology*, 12: 183-194.
- Elson, C.M., Hayes, E.R. and Lidster, P.D., 1985. Development of the differentially permeable fruit coating "Nutri-Save" for the modified atmosphere storage of fruit. In: S.M. Blankenship (Editor), *Proceedings from the Fourth National Controlled Atmosphere Research Conference*. Horticultural Report North Carolina State University, Raleigh, pp. 248-262.
- Elyatem, S. M., Banks, N. H. and Cameron, A. C., 1994. Oxygen concentration effects on ethylene production by ripening banana tissue. *Postharvest Biology and Technology*, 4: 343-351.
- Erbil, H. Y. and Muftugil, N., 1986. Lengthening the postharvest life of peaches by coating with hydrophobic emulsions. *Journal of Food Processing and Preservation*, 10: 269-279.
- Farooqi, W. A. and Hall, E. G., 1973. Effect of wax coatings containing diphenylamine on apples and pears during storage and ripening. *Australian Journal of Experimental Agriculture and Animal Husbandry*, 13: 200-204.
- Farooqi, W. A., Ahmad, M. S. and Abdin, Z., 1988. Effect of wax-coatings on the physiological and bio-chemical aspects of 'Kinnow' fruit. *Pakistan Journal of Scientific and Industrial Research*, 31: 142-145.
- Fidler, J. C. and North, C. J., 1967. The effect of storage on the respiration of apples 1. The effect of

- temperature and concentration of carbon dioxide and oxygen on the production of carbon dioxide and uptake of oxygen. *Journal of Horticultural Science*, 42: 189-206.
- Foust, A.S., Wenzel, L.A., Clump, C.W., Maus, L. and Andersen, L.B., 1980. Principles of unit operations. 2nd edition. John Wiley, New York, 768 pp.
- Frenkel, C. and Patterson, M. E., 1973. Effect of carbon dioxide on activity of succinic dehydrogenase in 'Bartlett' pears during cold storage. *HortScience*, 8: 395-396.
- Gennadios, A., Brandenburg, A. H., Weller, C. L. and Testin, R. F., 1993. Effect of pH on properties of wheat gluten and soy protein isolate films. *Journal of Agricultural and Food Chemistry*, 41: 1835-1839.
- Gennadios, A., McHugh, T. H., Weller, C. L. and Krochta, J. M., 1994. Edible coatings and films based on proteins. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Lancaster, Basel, Technomic Publishing Company, Inc., pp. 201-277.
- Glenn, G. M., Rom, C. R., Rasmussen, H. P. and Poovaiah, B. W., 1990. Influence of cuticular structure on the appearance of artificially waxed 'Delicious' apple fruit. *Scientia Horticulturae*, 42: 289-297.
- Gontard, N., Guilbert, S. and Cuq, J-L., 1993. Water and glycerol as plasticizers affect mechanical and water vapour barrier properties of an edible wheat gluten film. *Journal of Food Science*, 58: 206-211.
- Gontard, N., Duchez, C., Cuq, J. L. and Guilbert, S., 1994. Edible composite films of wheat gluten and lipids: water vapour permeability and other physical properties. *International Journal of Food Science and Technology*, 29: 39-50.
- Gontard, N., Thibault, R., Cuq, B. and Guilbert, S., 1996. Influence of relative humidity and film composition on oxygen and carbon dioxide permeabilities of edible films. *Journal of Agricultural and Food Chemistry*, 44: 1064-1069.
- Gorny, J. R. and Kader, A. A., 1996a. Controlled-atmosphere suppression of ACC synthase and ACC oxidase in 'Golden Delicious' apples during long-term cold storage. *Journal of the American Society for Horticultural Science*, 121: 751-755.
- Gorny, J. R. and Kader, A. A., 1996b. Regulation of ethylene biosynthesis in climacteric apple fruit by elevated CO₂ and reduced O₂ atmospheres. *Postharvest Biology and Technology*, 9: 311-323.
- Hagenmaier, R. D. and Baker, R. A., 1993a. Reduction in gas exchange of citrus fruit by wax coatings. *Journal of Agricultural and Food Chemistry*, 41: 283-287.
- Hagenmaier, R. D. and Baker, R. A., 1993b. Cleaning method affects shrinkage rate of citrus fruit. *HortScience*, 28: 824-825.
- Hagenmaier, R. D. and Baker, R. A., 1993c. Citrus fruit with single or layered coatings compared with

packinghouse-coated fruit. *Proceedings of the Florida State Horticultural Society*, 106: 238-240.

Hagenmaier, R. D. and Baker, R. A., 1994a. Wax microemulsions and emulsions as citrus coatings. *Journal of Agricultural and Food Chemistry*, 42: 899-902.

Hagenmaier, R. D. and Baker, R. A., 1994b. Internal gases, ethanol content and gloss of citrus fruit coated with polyethylene wax, carnauba wax, shellac or resin at different application levels. *Proceedings of the Florida State Horticultural Society*, 107: 261-265.

Hagenmaier, R. D. and Baker, R. A., 1995. Layered coatings to control weight loss and preserve gloss of citrus fruit. *HortScience*, 30: 296-298.

Hagenmaier, R. D. and Baker, R. A., 1996. Edible coatings from candelilla wax microemulsions. *Journal of Food Science*, 61: 562-565.

Hagenmaier, R. D. and Shaw, P. E., 1990. Moisture permeability of edible films made with fatty acid and (hydroxypropyl)methylcellulose. *Journal of Agricultural and Food Chemistry*, 38: 1799-1803.

Hagenmaier, R. D. and Shaw, P. E., 1991a. Permeability of shellac coatings to gases and water vapour. *Journal of Agricultural and Food Chemistry*, 39: 825-829.

Hagenmaier, R. D. and Shaw, P. E., 1991b. Permeability of coatings made with emulsified polyethylene wax. *Journal of Agricultural and Food Chemistry*, 39: 1705-1708.

Hagenmaier, R. D. and Shaw, P. E., 1992. Gas permeability of fruit coating waxes. *Journal of the American Society for Horticultural Science*, 117: 105-109.

Hall, D. J., 1989. Postharvest treatment of Florida fresh market tomatoes with fungicidal wax to reduce decay. *Proceedings of the Florida State Horticultural Society*, 102: 365-367.

Hallman, G. J., 1994. Modified atmospheres. In: R. E. Paull and J. W. Armstrong (Editors), *Insect Pests and Fresh Horticultural Products: Treatments and Responses*. CAB International, Wallingford, pp. 121-136.

Hallman, G. J., Nisperos-Carriedo, M. O., Baldwin, E. A. and Campbell, C. A., 1994. Mortality of Caribbean fruit fly (Diptera: Tephritidae) immatures in coated fruit. *Journal of Economic Entomology*, 87: 752-757.

Hallman, G. J., McGuire, R. G., Baldwin, E. A. and Campbell, C. A., 1995. Mortality of feral Caribbean fruit fly (Diptera: Tephritidae) immatures in coated guavas. *Journal of Economic Entomology*, 88: 1353-1355.

Hallman, G. J. and Foos, J. F., 1996. Coating combined with dimethoate as a quarantine treatment against fruit flies (Diptera: Tephritidae). *Postharvest Biology and Technology*, 7: 177-181.

Hardenburg, R. E., 1967. Wax and Related Coatings for Horticultural Products. A Bibliography. *Agricultural Research Bulletin* 51-15. Washington DC, USA; United States Department of Agriculture.

- Hernandez, E. 1994. Edible coatings from lipids and resins. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Lancaster, Basel, Technomic Publishing Company, Inc., pp. 279-303.
- Hess, B., Ke, D. and Kader, A. A., 1993. Changes in intracellular pH, ATP, and glycolytic enzymes in 'Hass' avocado in response to low O₂ and high CO₂ stresses. *Proceedings from the Sixth International Controlled Atmosphere Research Conference*, Cornell University, Ithaca, New York. pp. 1-9.
- Hitz, C. W. and Haut, I. C., 1938. Effect of certain waxing treatments at time of harvest upon the subsequent storage quality of Grimes Golden and Golden Delicious apples. *Proceedings of the American Society for Horticultural Science*, 36: 440-447.
- Huber, S. C., 1986. Fructose 2,6-bisphosphate as a regulatory metabolite in plants. *Annual Review of Plant Physiology*, 37: 233-246.
- Hubner, G. R. W. and Shellenberger, A., 1978. The mechanism of substrate activation of pyruvate decarboxylase: a first approach. *European Journal of Biochemistry*, 92: 175-181.
- Hulme, A. C., 1956. Carbon dioxide injury and the presence of succinic acid in apples. *Nature*, 178: 218-219.
- Johnston, J. W. and Banks, N. H., 1998. Selection of a surface coating and optimisation of its concentration for use on 'Hass' avocado fruit. *New Zealand Journal of Crop and Horticultural Science* (submitted).
- Joles, D. W., Cameron, A. C., Shirazi, A., Petracek, P. D. and Beaudry, R. M., 1994. Modified-atmosphere packaging of 'Heritage' red raspberry fruit: Respiratory response to reduced oxygen, enhanced carbon dioxide, and temperature. *Journal of the American Society for Horticultural Science*, 119: 540-545.
- Kader, A. A., 1986. Biochemical and physiological basis for effects of controlled and modified atmospheres on fruits and vegetables. *Food Technology*, 40: 99-100, 102-104.
- Kader, A. A., 1989. Mode of action of oxygen and carbon dioxide on postharvest physiology of 'Bartlett' pears. *Acta Horticulturae*, 258: 161-167.
- Kader, A. A., 1995. Regulation of fruit physiology by controlled/modified atmospheres. *Acta Horticulturae*, 398: 59-70.
- Kader, A. A., Zagory, D. and Kerbel, E. L., 1989. Modified atmosphere packaging of fruits and vegetables. *Critical Reviews in Food Science and Nutrition*, 28: 1-30.
- Kamper, S. L. and Fennema, O., 1984a. Water vapour permeability of edible bilayer films. *Journal of Food Science*, 49: 1478-1481, 1485.
- Kamper, S. L. and Fennema, O., 1984b. Water vapor permeability of an edible, fatty acid, bilayer film.

Journal of Food Science, 49: 1482-1485.

- Kato-Noguchi, H. and Watada, A. E., 1996. Low-oxygen atmosphere increases fructose 2,6-bisphosphate in fresh-cut carrots. *Journal of the American Society for Horticultural Science*, 121: 307-309.
- Ke, D., and Kader, A. A., 1992. External and internal factors influence fruit tolerance to low-oxygen atmospheres. *Journal of the American Society for Horticultural Science*, 117: 913-918.
- Ke, D., van Gorsel, H. and Kader, A. A., 1990. Physiological and quality response of 'Bartlett' pears to reduced O₂ and enhanced CO₂ levels and storage temperature. *Journal of the American Society for Horticultural Science*, 115: 435-439.
- Ke, D., Rodriguez-Sinobas, L. and Kader, A. A., 1991. Physiology and prediction of fruit tolerance to low-oxygen atmospheres. *Journal of the American Society for Horticultural Science*, 116: 253-260.
- Ke, D., Mateos, M. and Kader, A. A., 1993. Regulation of fermentative metabolism in fruits and vegetables by controlled atmospheres. *Proceedings from the Sixth International Controlled Atmosphere Research Conference, Cornell University, Ithaca, New York.* pp. 63-77.
- Ke, D., Yahia, E., Mateos, M. and Kader, A. A., 1994. Ethanolic fermentation of 'Bartlett' pears as influenced by ripening stage and atmospheric composition. *Journal of the American Society for Horticultural Science*, 119: 976-982.
- Ke, D., Yahia, E., Hess, B., Zhou, L. and Kader, A. A., 1995. Regulation of fermentative metabolism in avocado fruit under oxygen and carbon dioxide stresses. *Journal of the American Society for Horticultural Science*, 120: 481-490.
- Kerbel, E. L., Kader, A. A. and Romani, R. J., 1988. Effects of elevated CO₂ concentrations on glycolysis in intact 'Bartlett' pear fruit. *Plant Physiology*, 86: 1205-1209.
- Kerbel, E. L., Mitchell, F. G., Kader, A. A. and Mayer, G., 1989. Effects of "Semperfresh" coating on postharvest life, internal atmosphere modification and quality maintenance of 'Granny Smith' apples. *Proceedings from the Fifth International Controlled Atmosphere Research Conference, Wenatchee, Washington*, 1: 247-254.
- Kerbel, E. L., Kader, A. A. and Romani, R. J., 1990. Respiratory and glycolytic response of suspension-cultured 'Passe Crassane' pear fruit cells to elevated CO₂ concentrations. *Journal of the American Society for Horticultural Science*, 115: 111-114.
- Kester, J.J., and Fennema, O.R., 1986. Edible films and coatings: a review. *Food Technology*, 40: 47-59.
- Kester, J. J. and Fennema, O., 1989a. Resistance of lipid films to oxygen transmission. *Journal of the American Oil Chemists' Society*, 66: 1129-1138.
- Kester, J.J. and Fennema, O., 1989b. Resistance of lipid films to water vapor transmission. *Journal of*

- the American Oil Chemists' Society, 66: 1139-1146.
- Kester, J. J. and Fennema, O., 1989c. The influence of polymorphic form on oxygen and water vapor transmission through lipid films. *Journal of the American Oil Chemists' Society*, 66: 1147-1153.
- Kester, J. J., and Fennema, O., 1989d. Tempering influence on oxygen and water vapor transmission through a stearyl alcohol film. *Journal of the American Oil Chemists' Society*, 66: 1154-1157.
- Kester, J. J. and Fennema, O., 1989e. An edible film of lipids and cellulose ethers: barrier properties to moisture vapor transmission and structural evaluation. *Journal of Food Science*, 54: 1383-1389.
- Knee, M., 1991. Fruit metabolism and practical problems of fruit storage under hypoxia and anoxia. In: M. B. Jackson, D. D. Davies and H. Lambers (Editors), *Plant Life Under Oxygen Deprivation*. SPB Academic Publishing bv, The Hague, The Netherlands, pp. 229-243.
- Koelsch, C., 1994. Edible water vapor barriers: properties and promise. *Trends in Food Science & Technology*, 5: 76-81.
- Köksal, A. I., Dumanoglu, H. and Tuna, N., 1994. The effect of Semperfresh on the storage of Williams pear and Starkspur Golden Delicious apple cultivars. *Acta Horticulturae*, 368: 793-801.
- Kuai, J. and Dilley, D., 1992. Extraction and partial purification and characterization of 1-aminocyclopropane-1-carboxylic acid oxidase from apple fruit. *Postharvest Biology and Technology*, 1: 203-211.
- Kubo, Y., Inaba, A. and Nakamura, R., 1990. Respiration and C₂H₄ production in various harvested crops held in CO₂-enriched atmospheres. *Journal of the American Society for Horticultural Science*, 111: 975-978.
- Kumins, C. A., 1965. Transport through polymer films. *Journal of Polymer Science, Part C*, 10: 1.
- Lakshminarayana, S., Sarmiento, L., Ortiz, J. I. and Siade, G., 1974. Extension of storage life of citrus fruit by application of candelilla wax emulsion and comparison of its efficiency with Tag and Flavorseal. *Proceedings of the Florida State Horticultural Society*, 87: 325-330.
- Lau, O. L. and Yastremski, R., 1991. Retention of quality of 'Golden Delicious' apples by controlled- and modified-atmosphere storage. *HortScience*, 26: 564-566.
- Lau, O. L. and Meheriuk, M., 1994. The effect of edible coatings on storage quality of McIntosh, Delicious and Spartan apples. *Canadian Journal of Plant Science*, 74: 847-852.
- Lerdthanangkul, S. and Krochta, J. M., 1996. Edible coating effects on postharvest quality of green bell peppers. *Journal of Food Science*, 61: 176-179.
- Leshuk, J. A. and Saltveit, M. E., 1991. Effects of rapid changes in oxygen concentration on the respiration of carrot roots. *Physiologia Plantarum*, 82: 559-568.
- Li, Z., Liu, Y., Dong, J., Xu, R. and Zhu, M., 1983. Effect of low oxygen and high carbon dioxide on the levels of ethylene and 1-aminocyclopropane-1-carboxylic acid in ripening apple fruits. *Journal of*

Plant Growth Regulators, 2: 81-87.

- Lidster, P. D., 1981. Some effects of emulsifiable coatings on weight loss, stem discoloration, and surface damage disorder in 'Van' sweet cherries. *Journal of the American Society for Horticultural Science*, 106: 478-480.
- Lieberman, E. R. and Gilbert, S. G., 1973. Gas permeation of collagen films as affected by cross-linkage, moisture and plasticizer content. *Journal of Polymer Science*, 41: 33-43.
- Lowings, P. H. and Cutts, D. G., 1982. The preservation of fresh fruits and vegetables. Proceedings of the Institute of Food Science and Technology. Annual Symposium, July, 1981, Nottingham, UK, pp. 52.
- Magness, J. R. and Diehl, H. C., 1924. Physiological studies on apples in storage. *Journal of Agricultural Research*, 27: 1-38.
- Maguire, K.M., 1998. Factors affecting mass loss of apples. PhD Dissertation, Massey University, Palmerston North, New Zealand. 231 pp.
- Mannheim, C. H. and Soffer, T., 1996. Permeability of different wax coatings and their effect on citrus fruit quality. *Journal of Agricultural and Food Chemistry*, 44: 919-923.
- Martín-Polo, M., Voilley, A., Blond, G., Colas, B., Mesnier, M. and Floquet, N., 1992. Hydrophobic films and their efficiency against moisture transfer. 2. Influence of the physical state. *Journal of Agricultural and Food Chemistry*, 40: 413-418.
- McGuire, R. G., 1997. Market quality of guavas after hot-water quarantine treatment and application of carnauba wax coating. *HortScience*, 32: 271-274.
- McGuire, R. G. and Baldwin, E. A., 1994. Composition of cellulose coatings affect populations of yeasts in the liquid formulation and on coated grapefruits. *Proceedings of the Florida State Horticultural Society*, 107: 293-297.
- McGuire, R. G. and Hallman, G. J., 1995. Coating guavas with cellulose- or carnauba-based emulsions interferes with postharvest ripening. *HortScience*, 30: 294-295.
- McHugh, T. H. and Krochta, J. M., 1994a. Permeability properties of edible films. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Lancaster, Basel, Technomic Publishing Company, Inc., pp. 139-187.
- McHugh, T. H. and Krochta, J. M., 1994b. Sorbitol- vs glycerol-plasticized whey protein edible films: integrated oxygen permeability and tensile property evaluation. *Journal of Agricultural and Food Chemistry*, 42: 841-845.
- Meheriuk, M., 1990. Skin color in 'Newtown' apples treated with calcium nitrate, urea, diphenylamine, and a film coating. *HortScience*, 25: 775-776.
- Meheriuk, M. and Porritt, S. W., 1972. Effects of waxing on respiration, ethylene production, and other

- physical and chemical changes in selected apple cultivars. *Canadian Journal of Plant Science*, 52: 257-259.
- Meheriuk, M. and Lau, O. L., 1988. Effect of two polymeric coatings on fruit quality of 'Bartlett' and 'd'Anjou' pears. *Journal of the American Society for Horticultural Science*, 113: 222-226.
- Mellenthin, W. M., Chen, P. M. and Borgic, D. M., 1982. In-line application of porous wax coating materials to reduce friction discolouration of 'Bartlett' and 'd'Anjou' pears. *HortScience*, 17: 215-217.
- Miszczak, A., 1994. Effect of Pro-long treatment on quality of stored apples. *Acta Horticulturae*, 368: 552-557.
- Mohamed, S., Kyi, K. M. M. and Yusof, S., 1994. Effect of various surface treatments on the storage life of guava (*Psidium guajava* L.) at 10°C. *Journal of the Science of Food and Agriculture*, 66: 9-11.
- Nanos, G. D. and Kader, A. A., 1993. Low O₂-induced changes in pH and energy charge in pear fruit tissue. *Postharvest Biology and Technology*, 3: 285-291.
- Nanos, G. D., Romani, R. J. and Kader, A. A., 1992. Metabolic and other responses of 'Bartlett' pear fruit and suspension-cultured 'Passa Crassane' pear fruit cells held in 0.25% O₂. *Journal of the American Society for Horticultural Science*, 117: 934-940.
- Nanos, G. D., Romani, R. J. and Kader, A. A., 1994. Respiratory metabolism of pear fruit and cultured cells exposed to hypoxic atmospheres: associated change in activities of key enzymes. *Journal of the American Society for Horticultural Science*, 119: 288-294.
- Nisperos-Carriedo, M. O., 1994. Edible coatings and films based on polysaccharides. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Lancaster, Basel, Technomic Publishing Company, Inc., pp. 305-335.
- Nisperos-Carriedo, M. O. and Baldwin, E. A., 1996. Edible coatings for whole and minimally processed fruits and vegetables. *Food Australia*, 48: 27-31.
- Nisperos-Carriedo, M. O., Shaw, P. E. and Baldwin, E. A., 1990. Changes in volatile flavor components of pineapple orange juice as influenced by the application of lipid and composite films. *Journal of Agricultural and Food Chemistry*, 38: 1382-1387.
- Nisperos-Carriedo, M. O., Baldwin, E. A. and Shaw, P. E., 1991. Development of an edible coating for extending postharvest life of selected fruits and vegetables. *Proceedings of the Florida State Horticultural Society*, 104: 122-125.
- Norman, S.M., Fouse, D.C. and Croft, C.C., 1972. Thiabendazole residues on and in citrus. *Journal of Agricultural and Food Chemistry*, 20:1227-1230.
- Palet, A. M., Ribas-Carbo, J. M. A. and Azcon-Bieto, J., 1991. Short-term effects of carbon dioxide on

- carnation callus cell respiration. *Plant Physiology*, 96: 467-472.
- Paredes-López, O., Camargo-Rubio, E. and Gallardo-Navarro, Y., 1974. Use of coatings of candelilla wax for the preservation of limes. *Journal of the Science of Food and Agriculture*, 25: 1207-1210.
- Park, H. J., Chinnan, M. S. and Shewfelt, R. L., 1994. Edible coating effects on storage life and quality of tomatoes. *Journal of Food Science*, 59: 568-570.
- Pascat, B., 1985. Study of some factors affecting permeability. In: J. Comyn (Editor), *Polymer Permeability*. Elsevier Applied Science Publishing, New York, pp. 7-24.
- Paull, R. E. and Chen, N. J., 1989. Waxing and plastic wraps influence water loss from papaya fruit during storage and ripening. *Journal of the American Society for Horticultural Science*, 114: 937-942.
- Peppelenbos, H. W. and van't Leven, J., 1996. Evaluation of four types of inhibition for modelling the influence of carbon dioxide on oxygen consumption of fruits and vegetables. *Postharvest Biology and Technology*, 7: 27-40.
- Peppelenbos, H. W., van't Leven, J., van Zwol, B. H. and Tijsskens, L. M. M., 1993. The influence of O₂ and CO₂ on the quality of fresh mushrooms. *Proceedings from the Sixth International Controlled Atmosphere Research Conference*, Cornell University, Ithaca, New York. pp. 746-758.
- Peppelenbos, H. W., Tijsskens, L. M. M., van't Leven, J. and Wilkinson, E. C., 1996. Modelling oxidative and fermentative carbon dioxide production of fruits and vegetables. *Postharvest Biology and Technology*, 9: 283-295.
- Poneleit, L. S. and Dilley, D. R., 1993. Carbon dioxide activation of 1-aminocyclopropane-1-carboxylate (ACC) oxidase in ethylene biosynthesis. *Postharvest Biology and Technology*, 3: 191-199.
- Postharvest News and Information, 1993. Cold air for waxed pears. *Postharvest News and Information*, 4: 73N.
- Potjewijd, R., Nisperos, M. O., Burns, J. K., Parish, M. and Baldwin, E. A., 1995. Cellulose-based coatings as carriers for *Candida guilliermondii* and *Debaryomyces* sp. in reducing decay of oranges. *HortScience*, 30: 1417-1421.
- Pusey, P. L., 1989. Use of *Bacillus subtilis* and related organisms as biofungicides. *Pesticide Science*, 27: 133-140.
- Reyneke, J. and Stubbings, W. A. K., 1940. Oil sprays in relation to the development of scald in Bon Chretien pears. *Farming in South Africa*, 15: 313-324.
- Rico-Peña, D. C. and Torres, J. A., 1990. Oxygen transmission rate of an edible methylcellulose-palmitic acid film. *Journal of Food Process Engineering*, 13: 125-133.
- Risse, L. A., Chun, D., McDonald, R. E. and Miller, W. R., 1987. Volatile production and decay during

- storage of cucumbers waxed, imazalil-treated, and film-wrapped. *HortScience*, 22: 274-276.
- Roberts, J. K. M., Chang, K., Webster, C., Callis, J., Wemmer, D. and Walbot, V., 1989. Dependence of ethanolic fermentation, cytoplasmic pH regulation and viability on the activity of alcohol dehydrogenase in hypoxic maize root tips. *Plant Physiology*, 98: 1275-1278.
- Rohrbach, K. G. and Paull, R. E., 1982. Incidence and severity of chilling induced internal browning of waxed 'Smooth Cayenne' pineapple. *Journal of the American Society for Horticultural Science*, 107: 453-457.
- Rose, P., 1992. Never mind the food, the packaging tastes great. *Food Manufacture International*, 9: 27, 29-30.
- Santerre, C. S., Leach, T. F. and Cash, J. N., 1989. The influence of the sucrose polyester, Semperfresh™, on the storage of Michigan grown "McIntosh" and "Golden Delicious" apples. *Journal of Food Processing and Preservation*, 13: 293-305.
- Siriphanich, J. and Kader, A. A., 1986. Changes in cytoplasmic and vacuolar pH in harvested lettuce tissues as influenced by CO₂. *Journal of the American Society for Horticultural Science*, 111: 73-77.
- Smith, S. M. and Stow, J. R., 1984. The potential of a sucrose ester coating material for improving the storage and shelf-life qualities of Cox's Orange Pippin apples. *Annals of Applied Biology*, 104: 383-391.
- Smith, S., Geeson, J. and Stow, J., 1987. Production of modified atmospheres in deciduous fruits by the use of films and coatings. *HortScience*, 22: 772-776.
- Smock, R. M., 1935. Certain effects of wax treatments on various varieties of apples and pears. *Proceedings of the American Society for Horticultural Science*, 33: 284-289.
- Solomos, T., 1982. Effects of low oxygen concentration on respiration: nature of the respiratory diminution. In: D.G. Richardson and M. Meheriuk (Editors), *Controlled Atmospheres for Storage and Transport of Perishable Agricultural Commodities*. Oregon State University School of Agriculture, Symposium Series 1, pp. 161-170.
- Solomos, T., 1985. Interaction between O₂ levels, rates of respiration and gas diffusion in five apple varieties. In: S. M. Blankenship (Editor), *Proceedings from the Fourth National Controlled Atmosphere Research Conference*, North Carolina State University, Raleigh, NC, pp. 10-19.
- Solomos, T., 1994. Some biological and physical principals underlying modified atmosphere packaging. In: R. C. Wiley (Editor), *Minimally Processed Refrigerated Fruits and Vegetables*. Chapman and Hall, Inc., New York, pp. 183-225.
- Sriyook, S., Siriatiwat, S. and Siriphanich, J., 1994. Durian fruit dehiscence - water status and ethylene. *HortScience*, 29: 1195-1198.

- Sümnü, G. and Bayindirli, L., 1994. Effect of Semperfresh and Johnfresh fruit coatings on poststorage quality of "Ankara" pears. *Journal of Food Processing and Preservation*, 18: 189-199.
- Sümnü, G. and Bayindirli, L., 1995a. Effects of sucrose polyester coating on fruit quality of apricots (*Prunus armeniaca* (L)). *Journal of the Science of Food and Agriculture*, 67: 537-540.
- Sümnü, G. and Bayindirli, L., 1995b. Effects of coatings on fruit quality of Amasya apples. *Lebensmittel Wissenschaft Und Technologie*, 28: 501-505.
- Thomas, M. and Fidler, J. C. 1933. Studies in zymasis. VI. Zymasis by apples in relation to O₂ concentration. *Biochemical Journal*, 27: 1629-1642.
- Trout, S. A., Hall, E. G. and Sykes, S. M., 1953. Effects of skin coatings on the behaviour of apples in storage: I. Physiological and general investigations. *Australian Journal of Agricultural Research*, 4: 57-81.
- Tucker, M.L. and Laties, G.G., 1985. The dual role of oxygen in avocado fruit respiration: Kinetic analysis and computer modelling of diffusion-affected respiratory oxygen isotherms. *Plant, Cell and Environment*, 8: 117-127.
- Tugwell, G.L., 1973. Postharvest fungicides. *Journal of the Australian Institute of Agricultural Science*, 39: 167-173.
- Turner, J. F. and Turner, D. H., 1980. The regulation of glycolysis and the pentose phosphate pathway. In: D.D. Davies (Editor), *The Biochemistry of Plants: A Comprehensive Treatise*, Vol. 2, Academic Press, New York. pp. 279-316.
- Van Zyl, H. J. and Wagner, J. W., 1986. Keeping quality and shelf life of Bon Chretien pears as affected by calcium, Alar and Semperfresh. *Acta Horticulturae*, 194: 223-228.
- Van Zyl, H. J., Tormann, H. and Von Mollendorff, L. J., 1987. Effect of wax treatment on fruit quality of pears, apples, plums and nectarines after cold storage. *Deciduous Fruit Grower*, 37: 169-172.
- Wild, B. L., 1991. Postharvest factors governing the development of peteca rind pitting on 'Meyer' lemons. *HortScience*, 26: 287-289.
- Wong, D. W. S., Gastineau, F. A., Gregorski, K. S., Tillin, S. J. and Pavlath, A. E., 1992. Chitosan-lipid films: microstructure and surface energy. *Journal of Agricultural and Food Chemistry*, 40: 540-544.
- Wong, D. W. S., Camirand, W. M. and Pavlath, A. E., 1994. Development of edible coatings for minimally processed fruits and vegetables. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Lancaster, Basel, Technomic Publishing Company, Inc., pp. 65-88.
- Yang, S.F., 1985. Biosynthesis and action of ethylene. *HortScience*, 20: 41-45.
- Yearsley, C. W., N. H. Banks, S. Ganesh, and D. J. Cleland. 1996. Determination of lower oxygen limits for apple fruit. *Postharvest Biology and Technology*, 8: 95-109.

- Yearsley, C. W., Banks, N. H. and Ganesh, S., 1997a. Temperature effects on the internal lower oxygen limits of apple fruit. *Postharvest Biology and Technology* 11: 73-83.
- Yearsley, C. W., Banks, N. H. and Ganesh, S., 1997b. Effect of carbon dioxide on the internal lower oxygen limits of apple fruit. *Postharvest Biology and Technology* 12: 1-13.
- Yip, W., Jiao, X. and Yang, S. F., 1988. Dependence of the *in vivo* ethylene production rate on 1-aminocyclopropane-1-carboxylic acid content and oxygen concentrations. *Plant Physiology*, 88: 553-558.
- York, G. M., 1994. An evaluation of two experimental polysaccharide Nature Seal coatings in delaying the post-harvest browning of the lychee pericarp. *Proceedings of the Florida State Horticultural Society*, 107: 350-351.
- Young, R. E., Romani, R. J. and Biale, J. B., 1962. Carbon dioxide effects on fruit respiration. II. Response of avocados, bananas and lemons. *Plant Physiology*, 37: 416-422.
- Yuniarti and Suhardi, 1992. Ripening retardation of Arumanis mango. *ASEAN Food Journal*, 7: 207-208.
- Zhang, D. and Qhantick, P. C., 1997. Effects of chitosan coating on enzymatic browning and decay during postharvest storage of litchi (*Litchi chinensis* Sonn.) fruit. *Postharvest Biology and Technology*, 12: 195-202.

Ripening Behaviour, Postharvest Quality and Physiological Disorders of Coated Pears

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3.1 Abstract

Pear (*Pyrus communis* L.) cultivars 'Bartlett', 'Bosc', 'Comice', and 'Packham's' were treated at harvest or after cold storage with a water-based carnauba wax emulsion at concentrations of 0, 5, 10, 20, 40, and 100% (v/v) of the commercial formulation. Fruit coated at harvest were assessed for ripening and physiological disorders during shelf life at 20°C and 60-70% RH. Fruit coated after cold storage were only assessed for physiological disorders. A canonical discriminant analysis showed that increasing coating concentration substantially suppressed ripening of all cultivars. This multivariate technique also indicated a more powerful effect of respiration than firmness and skin colour in separating coating treatments. This is attributed to the large variability of the last two attributes for fruit treated with the same coating concentration. For cultivars having a high natural gloss, increasing the coating concentration improved the finish of the skin. Only 'Bosc' developed off-flavours and this occurred only when fruit were treated with the full strength coating. Increasing coating concentration reduced the incidence of senescent breakdown. 'Comice' pears treated at harvest with a coating concentration $\geq 40\%$ and cold stored for six months had delayed ripening, no senescent scald and no internal disorders after a seven days shelf life period. Besides their effects in delaying ripening and reducing the incidence

of physiological disorders associated with senescence, coatings may predispose some cultivars to internal disorders. 'Bartlett' and 'Bosc' treated at harvest with high coating concentrations developed an internal disorder possibly associated with excessive internal atmosphere modification during low temperature storage. They did not develop the disorder when treated after cold storage. These findings show that cultivar differences must be taken into account in the optimisation of surface coatings for pears.

Keywords: Pear; *Pyrus communis* L.; cultivar; modified atmosphere; surface coating; wax; character of cover; respiration; softening; skin colour; gloss; flavour; senescent breakdown; senescent scald; internal disorder; gas injury; low temperature injury.

3.2 Introduction

Controlled atmosphere (CA) and modified atmosphere (MA) storage techniques are used as supplements to refrigeration to preserve postharvest quality of fruits and vegetables (Kader et al., 1989; Kader, 1995). During the past few years, more attention has been paid to the use of surface coatings to generate a modification of the internal atmosphere of bulky organs to achieve similar beneficial effects of CA/MA storage (Amarante et al., 1998b; Baldwin, 1994; Banks et al., 1993; Banks et al., 1997; Meheriuk and Lau, 1988; Hagenmaier and Baker, 1993 and 1994; Hagenmaier and Shaw, 1992; Smith et al., 1987), reduce water loss (Amarante et al., 1998a; Hagenmaier and Baker, 1993 and 1995; Hagenmaier and Shaw, 1992), and improve the gloss of the skin (Glenn et al., 1990; Hagenmaier and Baker, 1994 and 1995; Johnston and Banks, 1998). Coating materials, by providing differential changes in skin permeance to O₂ and CO₂, can create different levels of modification of internal O₂ and CO₂ partial pressures, depending on the chemical nature (Hagenmaier and Baker, 1993 and 1994; Hagenmaier and Shaw, 1992), thickness (Ben-Yehoshua, 1967; Hagenmaier and Baker, 1993) and character of surface cover (Amarante et al., 1998a; Banks et al., 1993). These characteristics are also important in determining the

potential of a coating in reducing water loss (Amarante et al., 1998a; Ben-Yehoshua, 1967; Hagenmaier and Baker, 1993; Hagenmaier and Shaw, 1992).

Pear fruit treated with coatings exhibit a suppression of respiration and ethylene production, with retention of flesh firmness, green colour, acidity, soluble solids and vitamin C (Elson et al., 1985; Farooqi and Hall, 1973; Köksal et al., 1994; Meheriuk and Lau, 1988; Smock, 1935; Sümnü and Bayindirli, 1994; Van Zyl et al., 1987). Coatings can also reduce the incidence of physiological disorders associated with senescence, such as senescent scald (Köksal et al., 1994; Meheriuk and Lau, 1988) and senescent breakdown (Meheriuk and Lau, 1988; Van Zyl et al., 1987). Other benefits of coating pears are the reduction of weight loss (Amarante et al., 1998b; Farooqi and Hall, 1973; Sümnü and Bayindirli, 1994) and of the skin susceptibility to friction discolouration (Amarante et al., 1998c; Mellenthin et al., 1982).

Coating may improve retention of some aspects of quality in pears, but it appears to predispose the fruit to disorders and ripening problems (Meheriuk and Sholberg, 1990). Coated fruit left in cool storage for long periods of time (Elson et al., 1985) or treated with a very thick coating layer (Smock, 1935) may fail to ripen at room temperature. Coated pears, despite softening, tend to show uneven green-yellow colouration during shelf life (Farooqi and Hall, 1973; Meheriuk and Lau, 1988; Sümnü and Bayindirli, 1994; Van Zyl et al., 1987) and may be induced to ferment and to produce off-flavours (Smock, 1935; Van Zyl et al., 1987).

Effects of coating treatments for individual ripening attributes can be compared using univariate analysis of variance. However, more powerful insight into the holistic interaction between fruit ripening and coating concentrations might be achieved with multivariate statistical techniques, such as canonical discriminant analysis (CDA). CDA can be used to identify differences among treatments (coating concentration) and improve understanding of the relationships among the ripening attributes measured within those treatments. CDA produces linear functions of quantitative attributes, called canonical discriminant functions (CDFs), that maximally separate two or more treatments while keeping variation within treatments as small as possible (Cruz-

Castillo et al., 1994). CDA provides standardized canonical coefficients (SCC), which are used to rank attributes in order of their contribution and to characterise the CDFs, and canonical correlation (r) between the CDFs and the original attributes. While SCC provide information about the attributes contributing jointly (multivariate contribution), r shows the importance of each attribute independent of the others (univariate contribution) to the separation of the treatment groups (Cruz-Castillo et al., 1994). Alternative measures of importance of attributes in distinguishing between group treatments have been recently considered, in an attempt to alleviate the confusion between the interpretation of SCC and r values and to combine the information provided by both. Tomas (1992) suggested the use of parallel discriminant ratio coefficient (DRC), defined as the product of SCC and r . For each CDF, the DRC sum is one. This facilitates judgments of relative importance of attributes in a CDF, with attributes having large and positive DRC's having more power in discriminating treatment groups. The applications of CDA for the multivariate analysis of ripening behaviour of coated pears and the interpretation of SCC, r and DRC results are explored in this paper.

The objective of this study was to investigate the effects of increasing concentrations of a wax coating on ripening behaviour, sensory attributes, skin gloss and physiological disorders of pears.

3.3 Materials and methods

Pear (*Pyrus communis* L.) cultivars 'Bartlett', 'Beurre Bosc', 'Doyenne du Comice', and 'Packham's Triumph' (with average weight of 181 ± 15.0 g, 207 ± 19.2 g, 229 ± 22.9 g, and 176 ± 21.2 g, respectively) were harvested at commercial maturity in 1997, based on ENZA New Zealand (International) maturity index charts. 'Bartlett' was harvested on February 17, from a commercial orchard near Palmerston North and the other three cultivars were harvested on March 11, from the Fruit Crops Unit at Massey University. Actual fruit maturity at harvest for each cultivar is presented in Table 3.1.

Table 3.1 Fruit maturity at harvest of ‘Bartlett’, ‘Bosc’, ‘Comice’ and ‘Packham’s’ pears. Values are average (\pm SD) of 20 single fruit replicates.

Cultivar	Respiration ($\text{nmol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)	Hue angle (h°)	‘Kiwifirm’ firmness (arbitrary units)	Penetrometer firmness ^a (N)	Soluble Solids ($^\circ$ Brix)	Starch Index ^b
‘Bartlett’	100 \pm 18.2	110.5 \pm 2.6	7.0 \pm 0.28	97.4 \pm 10.4	11.0 \pm 0.85	4.4 \pm 1.00
‘Bosc’	80 \pm 8.5	93.0 \pm 4.5	6.7 \pm 0.32	57.0 \pm 4.3	11.1 \pm 0.73	3.6 \pm 0.68
‘Comice’	86 \pm 11.3	109.8 \pm 1.1	6.4 \pm 0.28	47.6 \pm 2.7	14.1 \pm 0.63	2.0 \pm 0.92
‘Packham’s’	93 \pm 11.6	112.7 \pm 0.7	6.7 \pm 0.20	68.4 \pm 3.9	12.6 \pm 0.80	3.8 \pm 0.52

^a Using a 7.9 mm penetrometer tip.

^b Based on ENZA New Zealand (International) index charts; 0 = completely stained (high starch content), 6 = no staining (least starch content).

Fruit free of defects (uniform shape and with no blemishes) were treated with 100 ppm of sodium hypochlorite and randomly allocated to 12 groups of 15 fruit. Six groups were treated at harvest and another six groups were treated after removal from cold storage. Fruit were coated by dipping, with Capsicum/Zucchini Wax[®] (water-based carnauba wax emulsion, Castle Chemicals, Australia) at concentrations of 0, 5, 10, 20, 40 or 100% (v/v) of the commercial formulation. Fruit were stored at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH for at least the period necessary to achieve the chilling requirements for ripening of each cultivar (one month for ‘Bartlett’ and ‘Bosc’, two months for ‘Comice’ and three months for ‘Packham’s’), as described by Richardson and Gerasopoulos (1993), and then transferred to 20°C and 60-70% RH. Fruit coated at harvest were assessed for ripening and physiological disorders, whereas fruit coated after chilling treatment were only assessed for physiological disorders. Ripening was assessed by estimating respiration, firmness and skin colour during shelf life. Internal disorders (senescent breakdown and high CO_2 and/or low O_2 damage) and sensory quality were assessed after a shelf life of 8, 11, 15 and 17 days for ‘Bartlett’, ‘Bosc’, ‘Comice’, and ‘Packham’s’, respectively. Skin gloss was measured 48 h after removal from cold storage with a gloss-meter (Glossgard II, Pacific Scientific, Silver Spring,

MD 20910, USA) by taking the average of readings from four positions along the equator of each fruit replicate.

Respiration rates (r_{CO_2} , $\text{nmol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$) were determined by measurement of the change in partial pressure of CO_2 within $2 \times 10^{-3} \text{ m}^3$ black containers over 30 min using a miniature infra-red transducer (Analytical Development Company, Hoddesdon, UK), with O_2 -free N_2 as a carrier gas (flow rate $580 \text{ mm}^3\cdot\text{s}^{-1}$). The hue angle (h°) of skin colour at the equator of the non-blushed side of each fruit was determined with a chromameter (model CR-200; Minolta Corp., Japan) that had been calibrated to a standard green reflective plate (set CR-A47), connected to a lap top computer (Fig. 3.1). Measurements were taken across an 8 mm diameter area with diffuse illumination at a viewing angle of 0° under CIE illuminant C lighting condition (McGuire, 1992). Firmness (f , arbitrary units) was assessed non-destructively by means of a device designed by Industrial Research Limited, Auckland, New Zealand, and registered as 'Kiwifirm' (Fig. 3.2). By applying a known quantum of energy to the fruit surface through a small, non-penetrating tip, the in-built processor of the device converts characteristics of the resulting collision to display the firmness on an arbitrary scale from 0 to 10 (for 'Kiwifirm', a value of 5.4 is approximately equivalent to 9.8 N, measured with an Effegi penetrometer with a 7.9 mm diameter tip).

The fruit were assessed for sensory quality by more than ten non-trained panelists who put marks on 0.15 m line scales (Meilgaard et al., 1991). The sensory attributes assessed included flavour (bland to intense), off-flavour (none to intense) and texture (hard to soft). The panelists were blocked, with the analysis of sensory scores following a completely randomized block design.

The potential of coatings to delay ripening and reduce the risk of physiological disorders after long-term storage was investigated by coating 'Comice' pears at harvest with the wax concentrations described above and leaving the fruit in cold storage for six months. During seven days shelf life, fruit were assessed for changes in firmness and colour as described above. At the end of this period, fruit were subjectively evaluated for senescent scald and senescent breakdown. Senescent scald was assessed



Figure 3.1 Skin colour assessment with a chromameter connected to a lap top computer.

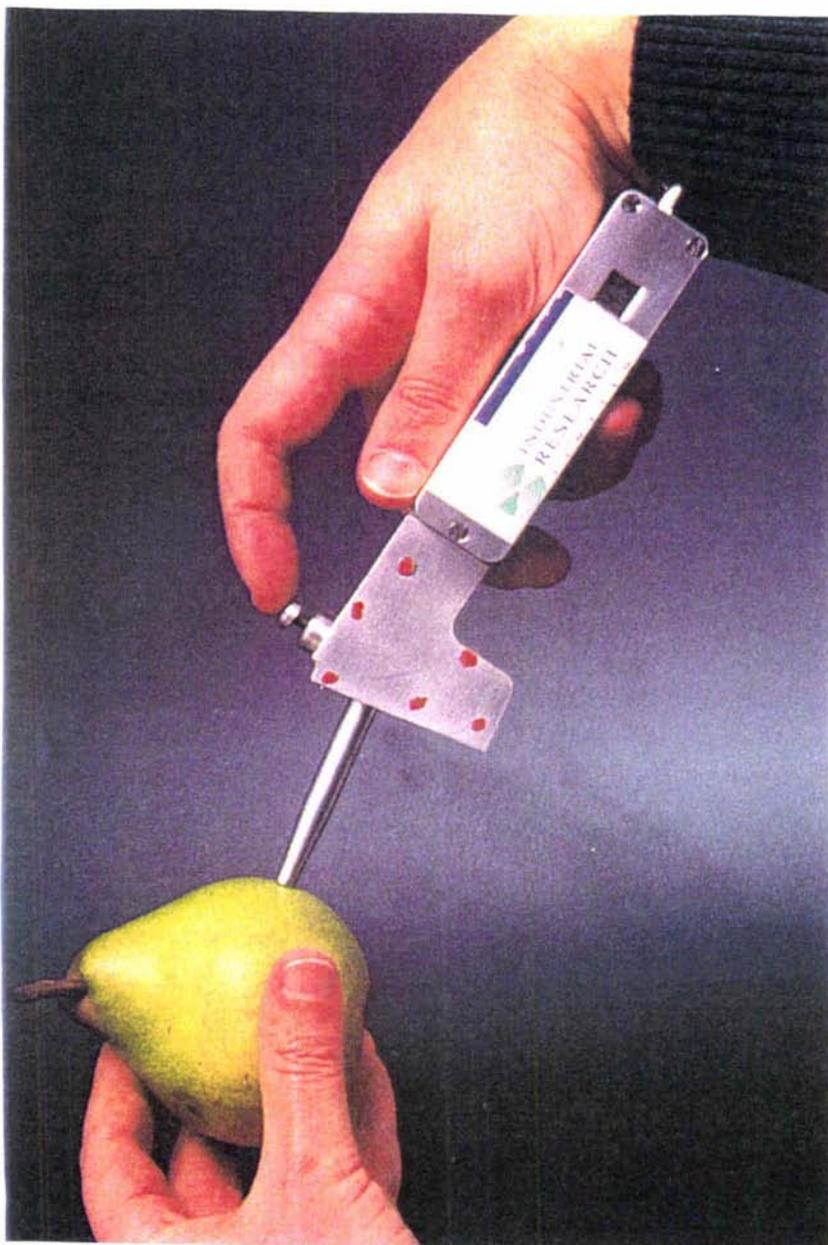


Figure 3.2 'Kiwifirm' for non-destructive assessment of firmness.

by means of a scale from 0 (= none) to 9 (= very high; Fig. 3.3). Senescent breakdown was assessed for percentage of fruit flesh affected by the disorder. Sixteen single fruit and eight single layer carton replicates (20 fruit per carton) per treatment were used to assess ripening and disorders, respectively.

Statistical analysis of the data was performed using the SAS system (SAS, 1990). Analysis of variance (ANOVA) was performed using the PROC GLM procedure; best fit was achieved using the PROC REG or PROC NLIN procedures; CDA was performed using the PROC CANDISC procedure to discriminate between coating treatments and to categorize the ripening attributes for power in discriminating between coating treatments. The ripening processes (r_{CO_2} and the derivatives of f [df/dt] and h° [dh/dt] with respect to time) were taken at 4, 5, 6 and 7 days of shelf life for 'Bartlett', 'Bosc', 'Comice', and 'Packham's', respectively (corresponding to about the respiratory climacteric peak of each cultivar).

3.4 Results

The ripening behaviour of coated pears is presented in Fig. 3.4. 'Bartlett' pear had the highest rates of respiration, softening and change in skin colour, and the shortest shelf life of all cultivars. The respiratory climacteric occurred at about 4, 5, 6, and 7 days of shelf life for 'Bartlett', 'Bosc', 'Comice' and 'Packham's', respectively (Fig. 3.4). 'Comice' pears continued to increase in respiration rate after onset of the climacteric. Increasing coating concentration substantially suppressed ripening of all cultivars. The most dramatic effect of coating concentration was on skin colour. Increasing the coating concentration substantially suppressed the change in colour of all pear cultivars (Figs. 3.4 and 3.5). Fruit coated with high coating concentrations could still soften, while skin colour change was almost totally inhibited, with the exception of 'Bosc', that had softening greatly impaired when coated with the undiluted coating formulation (Fig. 3.4). 'Bartlett' and 'Bosc', both cultivars with no or a low chilling requirement, respectively, had faster ripening with a linear change in

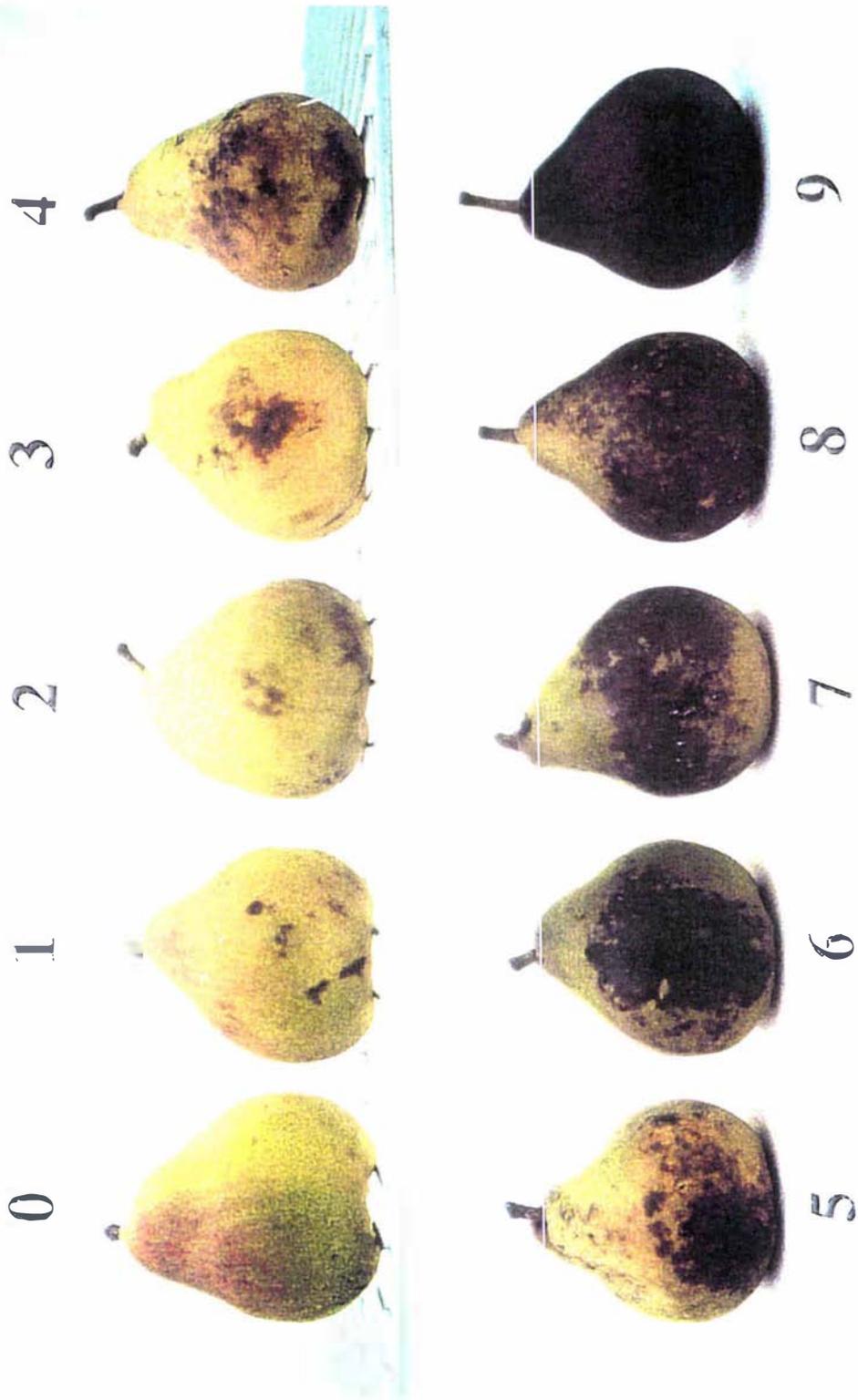


Figure 3.3 Scale for senescent scald assessment.

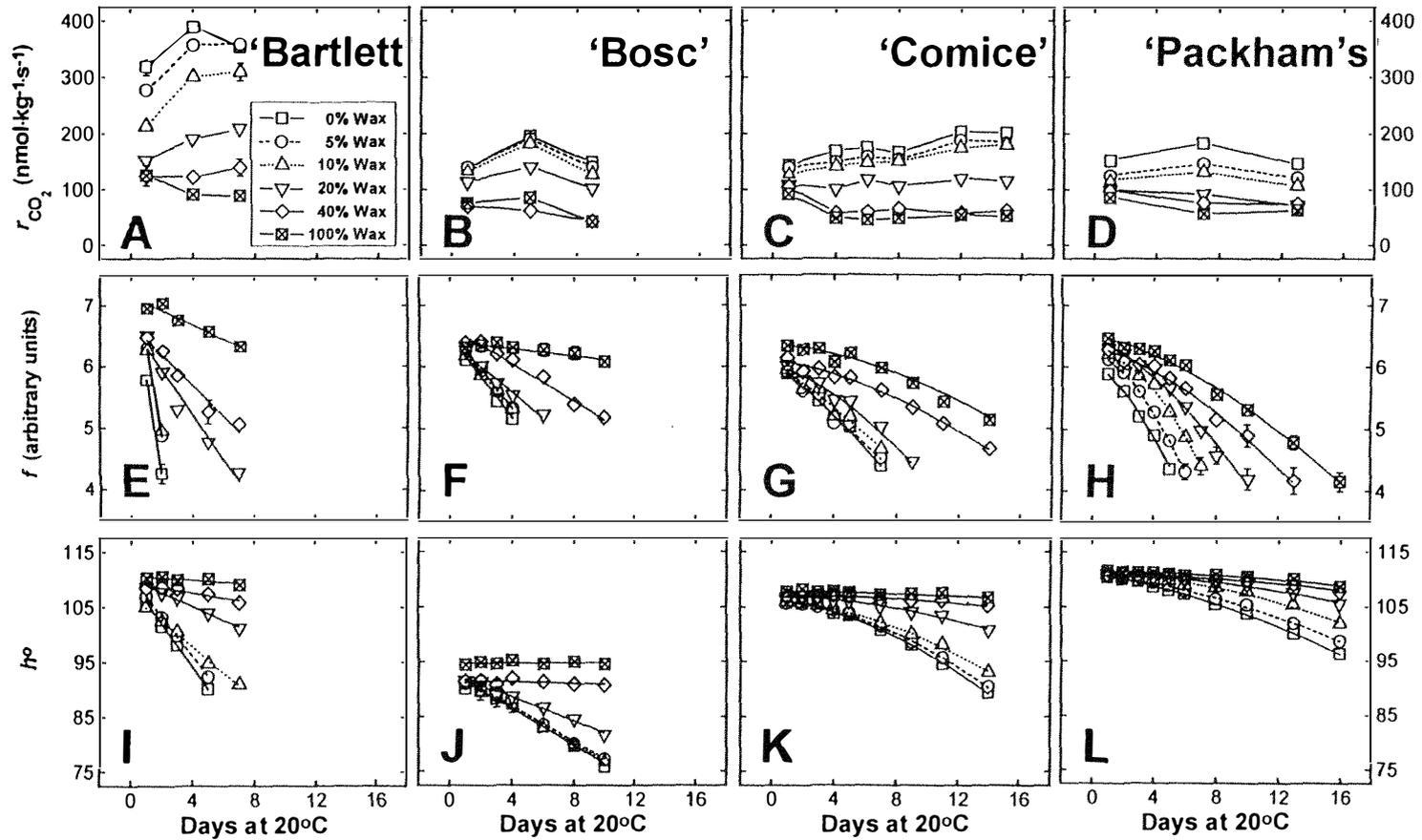


Figure 3.4 Respiration rate (r_{CO_2} ; A, B, C, and D), firmness (f ; E, F, G, and H) and hue angle (h° ; I, J, K, and L) during the shelf life at 20°C and 60-70 % RH of 'Bartlett', 'Bosc', 'Comice' and 'Packham's' pears. Bars represent standard errors of the means (n = 15). Lines represent the best fit for f and h° .

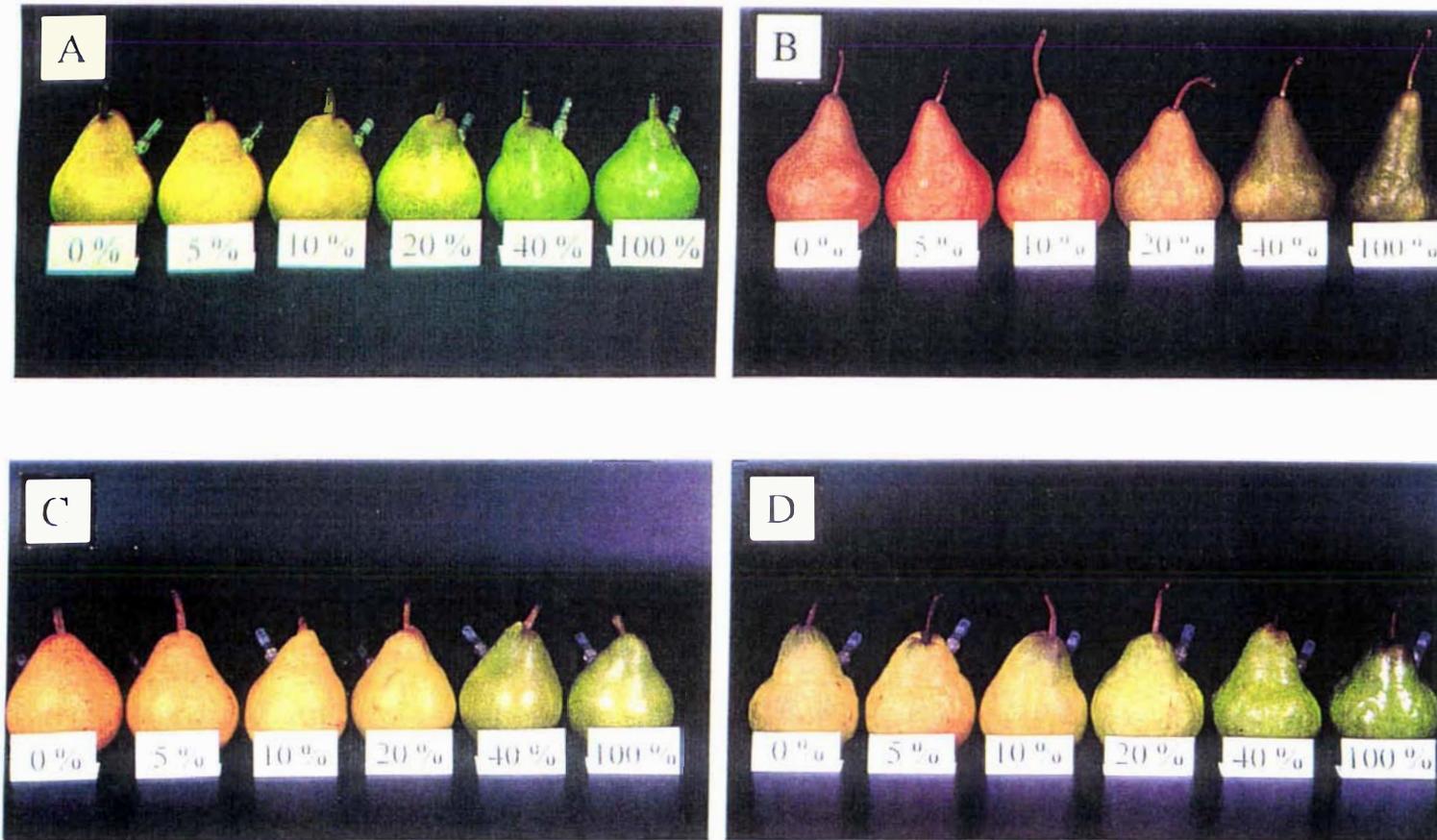


Figure 3.5 Fruit colour at the end of shelf life period of 'Bartlett' (A), 'Bosc' (B), 'Comice' (C) and 'Packham's' (D) pears treated with different coating concentrations.

firmness and skin colour during shelf life. ‘Comice’ and ‘Packham’s’, having a higher chilling requirement, had slower ripening and a quadratic change in firmness and skin colour, increasing in ripening rate with prolonged shelf life. ‘Packham’s’ was the only cultivar affected by skin blotchiness during ripening, when treated with coating concentrations between 20-40% (Fig. 3.6).

The ANOVA results showed highly significant ($P < 0.0001$) differences between treatments with respect to r_{CO_2} , df/dt and dh/dt (not shown). The CDA multivariate technique showed a canonical correlation between 0.88-0.98 for the first canonical discriminant function (CDF_1) and the first eigenvalue explained more than 90% of total variation for all cultivars. This indicates not only that the association between the ripening attributes (r_{CO_2} , df/dt and dh/dt) and the coating concentrations was high, but that it was dominated by CDF_1 . It means that almost all the separation between coating concentrations can be accounted for along CDF_1 (Fig. 3.7). The Wilks’ Lambda multivariate statistic test indicated a highly significant ($P < 0.0001$) difference between coating concentrations. Respiration had positive and the largest values for SCC and r , df/dt small and negative values while dh/dt presented the smallest values (positive or negative; Table 3.2). Therefore, almost all of the separation between coating treatments could be accounted for by a contrast between r_{CO_2} and df/dt , but with a stronger individual effect of r_{CO_2} (with the largest absolute SCC and r values). As a result of largest and positive DRC values for r_{CO_2} , this attribute had the most power in separating coating treatments along CDF_1 for all cultivars. For cultivars having long shelf life (‘Comice’ and ‘Packham’s’) the power of r_{CO_2} was greater and dh/dt became a suppressive attribute (negative DRC value), tending to bring the treatments together along CDF_1 . For ‘Packham’s’ almost all separation between treatments was attributable to r_{CO_2} (largest DRC value). Since most of total data variation was explained by CDF_1 , to facilitate the discrimination between coating treatments, the SCC of CDF_1 were submitted to ANOVA and compared using Tukey’s test (Table 3.3), as suggested by Cruz-Castillo et al. (1994). For all cultivars, increasing the coating concentration from 0% to 20% resulted in significant suppression of fruit

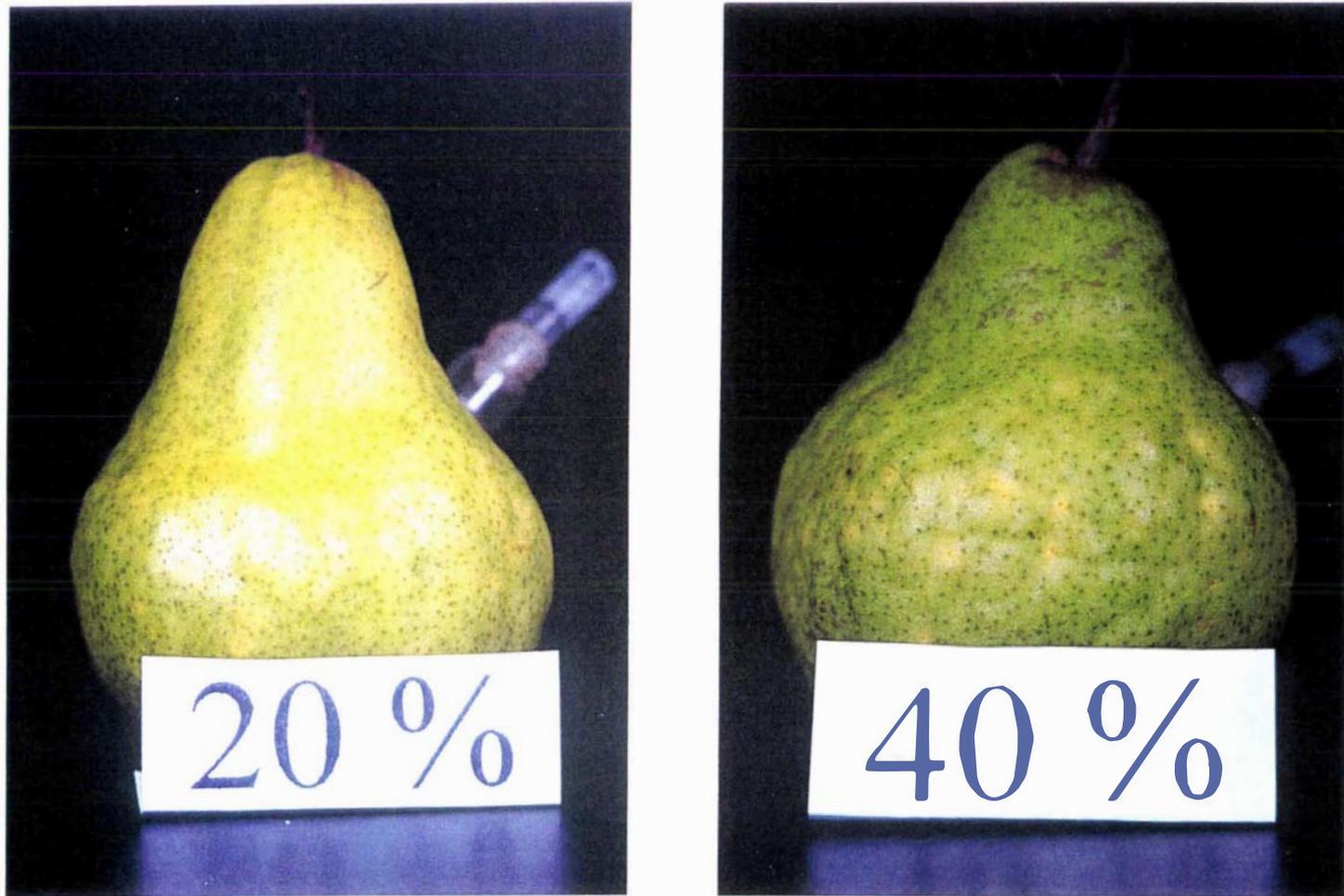


Figure 3.6 Skin blotchiness of 'Packham's' pears treated with coating concentrations of 20% and 40% after ripening at 20°C and 60-70% RH.

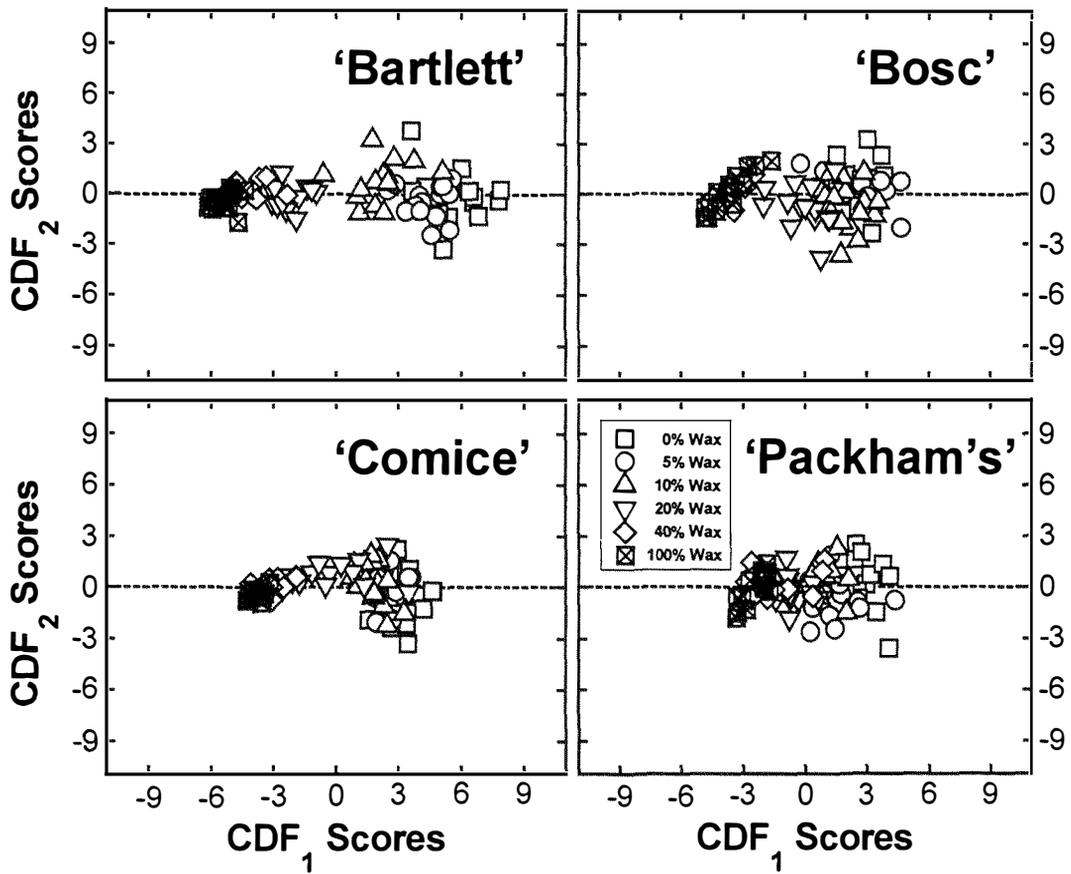


Figure 3.7 Standardized canonical scores of the first two canonical discriminant functions (CDFs) of pear cultivars treated with different coating concentrations.

Table 3.2 Standardized canonical coefficients (SCC), correlation coefficients (r), and parallel discriminant ratio coefficient (DRC) between the first canonical discriminant function (CDF_1) and ripening variables of four pear cultivars.

Cultivar	r_{CO_2}			df/dt			dh/dt		
	SCC	r	DRC	SCC	r	DRC	SCC	r	DRC
'Bartlett'	0.60	0.80	0.48	-0.47	-0.57	0.27	-0.37	-0.70	0.26
'Bosc'	0.60	0.83	0.50	-0.42	-0.70	0.30	-0.32	-0.67	0.20
'Comice'	0.84	0.86	0.72	-0.52	-0.56	0.29	0.02	-0.47	-0.01
'Packham's'	0.99	0.99	0.98	-0.12	-0.68	0.08	0.14	-0.49	-0.07

Table 3.3 Means of standardized canonical scores of the first canonical discriminant function (CDF_1) of four pear cultivars treated with different coating concentrations.

Wax Concentration (%)	Cultivar			
	'Bartlett'	'Bosc'	'Comice'	'Packham's'
0	5.71 a	2.59 a	3.05 a	2.90 a
5	4.38 b	2.33 a	2.30 ab	1.22 b
10	2.13 c	2.17 a	1.81 b	0.68 b
20	-2.41 d	0.03 b	-0.33 c	-0.77 c
40	-4.43 e	-3.46 c	-3.02 d	-1.65 cd
100	-5.37 e	-3.66 c	-3.81 d	-2.39 d

Means within the same column followed by the same letter are not significantly different by Tukey's test ($P < 0.05$).

ripening, with more substantial effect achieved by increasing the coating concentration to 40-100%. There was no difference between 40% and 100% coating concentrations for any cultivar. Smaller effects were achieved by increasing the coating concentration from 0% to 10%. Even treating the fruit with a coating concentration as low as 5% significantly suppressed ripening of 'Bartlett' and 'Packham's' pears.

Skin gloss increased linearly ($P < 0.01$) with coating concentration for all cultivars (Fig. 3.8). 'Bartlett' and 'Comice' both had high natural gloss and also developed larger increases in skin gloss with increasing coating concentration than the other cultivars. 'Packham's' had lower levels of natural gloss and a smaller increase in gloss was achieved by increasing coating concentration than the former cultivars. 'Bosc' had the least natural gloss and increasing coating concentration had only a small effect on enhancing surface finish.

Off-flavour scores were significantly different between treatments for 'Bartlett', 'Bosc', and 'Packham's', but not for 'Comice' (Fig. 3.9). 'Bosc' had significantly higher off-flavours for fruit treated with 100% coating concentration. 'Bartlett' and 'Packham's' had higher off-flavours in the controls and for fruit treated with 5% coating concentration, probably as a result of advanced senescence. Increasing coating concentration from 0% to 40% significantly suppressed softening of all cultivars (Fig. 3.9). For 'Bartlett' and 'Packham's', an increase in coating concentration from 0% to 20% significantly delayed softening. Flavour (Fig. 3.9) was not significantly affected by coating concentration for 'Comice' and 'Packham's'. 'Bartlett' and 'Bosc' flavours were improved by coating concentrations between 10-100% and 5-20%, respectively.

'Bartlett' and 'Bosc' had internal disorders associated with high CO₂ and/or low O₂ when coated at harvest before cold storage, but not when the fruit were coated after cold storage (Figs. 3.10 and 3.11). The disorder was similar to that described by Meheriuk et al. (1994) for CO₂ injury, which was characterised by browning of the interior carpel walls and of the tissue adjacent to the carpels as the disorder progressed. In more advanced stages, cavities had developed that, in some cases, were small and

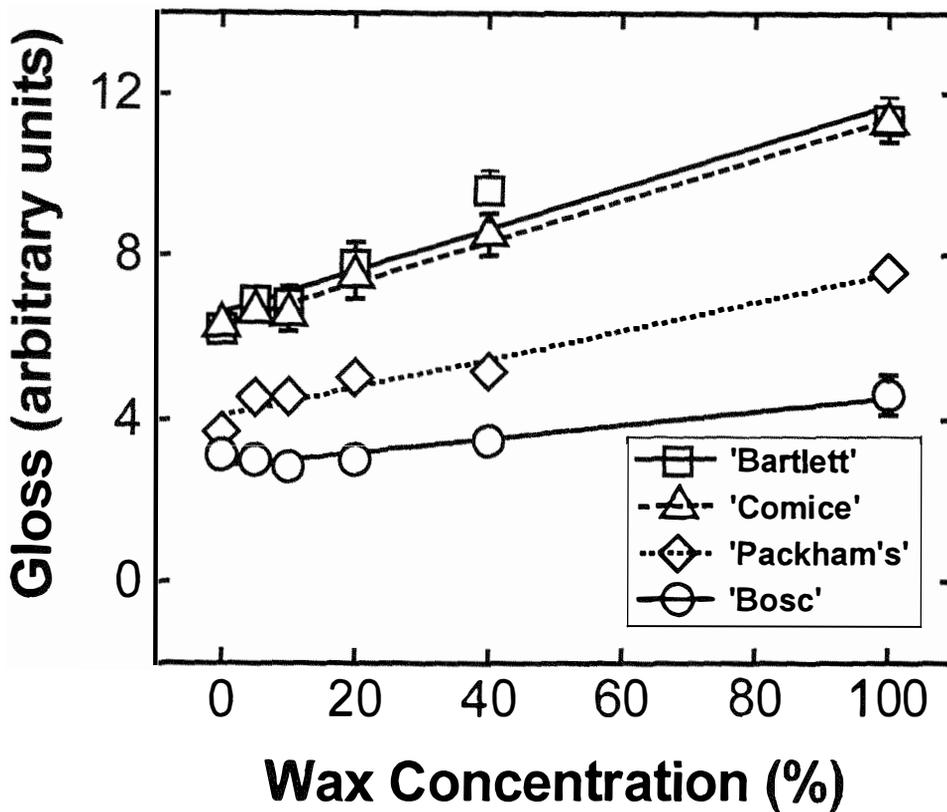


Figure 3.8 Skin gloss of pears treated with different coating concentrations. Bars represent standard error of the means ($n = 15$). Lines represent the best fit for 'Bartlett' [$y = 6.60 (\pm 0.31) + 0.051 (\pm 0.007) x$; $R^2 = 93.23\%$; $P < 0.001$], 'Bosc' [$y = 2.87 (\pm 0.10) + 0.017 (0.002) x$; $R^2 = 92.78\%$; $P < 0.01$], 'Comice' [$y = 6.31 (\pm 0.10) + 0.051 (\pm 0.002) x$; $R^2 = 99.23\%$; $P < 0.001$], and 'Packham's' [$y = 4.10 (\pm 0.16) + 0.034 (\pm 0.004) x$; $R^2 = 95.62\%$; $P < 0.001$] pears.

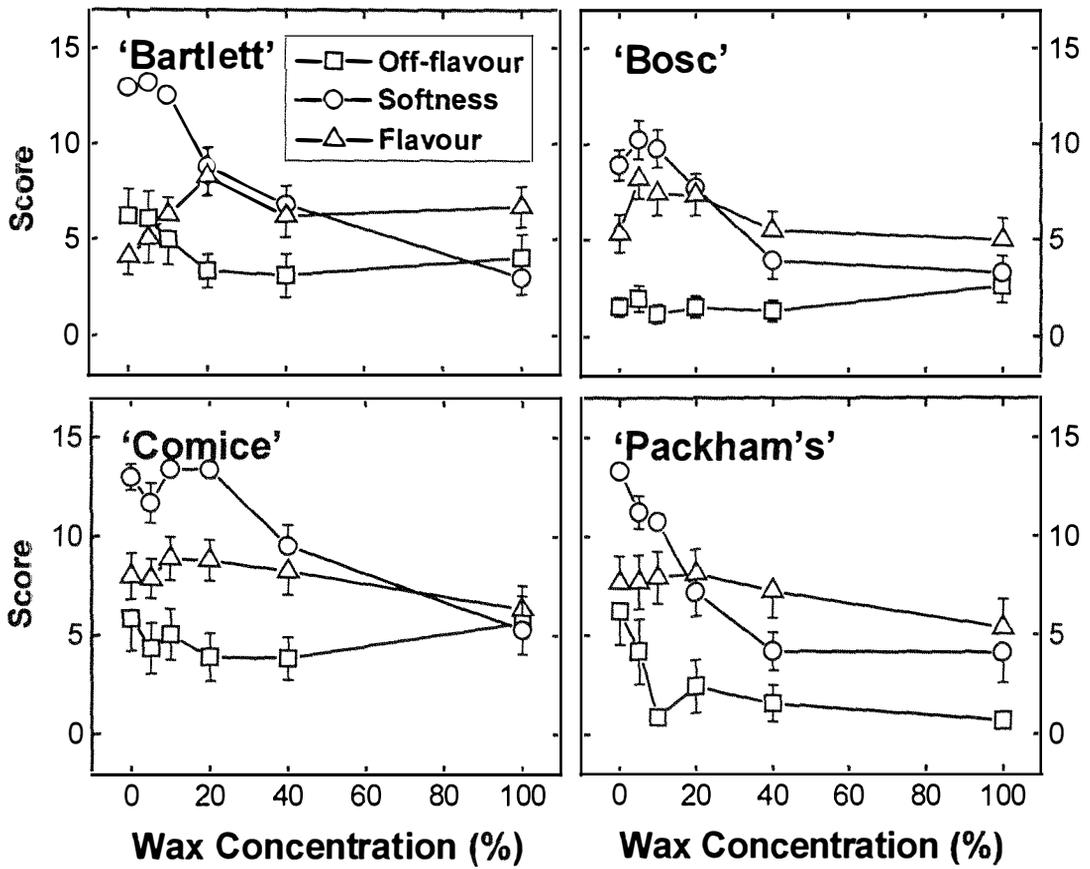


Figure 3.9 Sensory analysis scores of pear cultivars treated with different coating concentrations after ripening at 20°C and 60-70% RH. Bars represent standard errors of the means (n = 10).

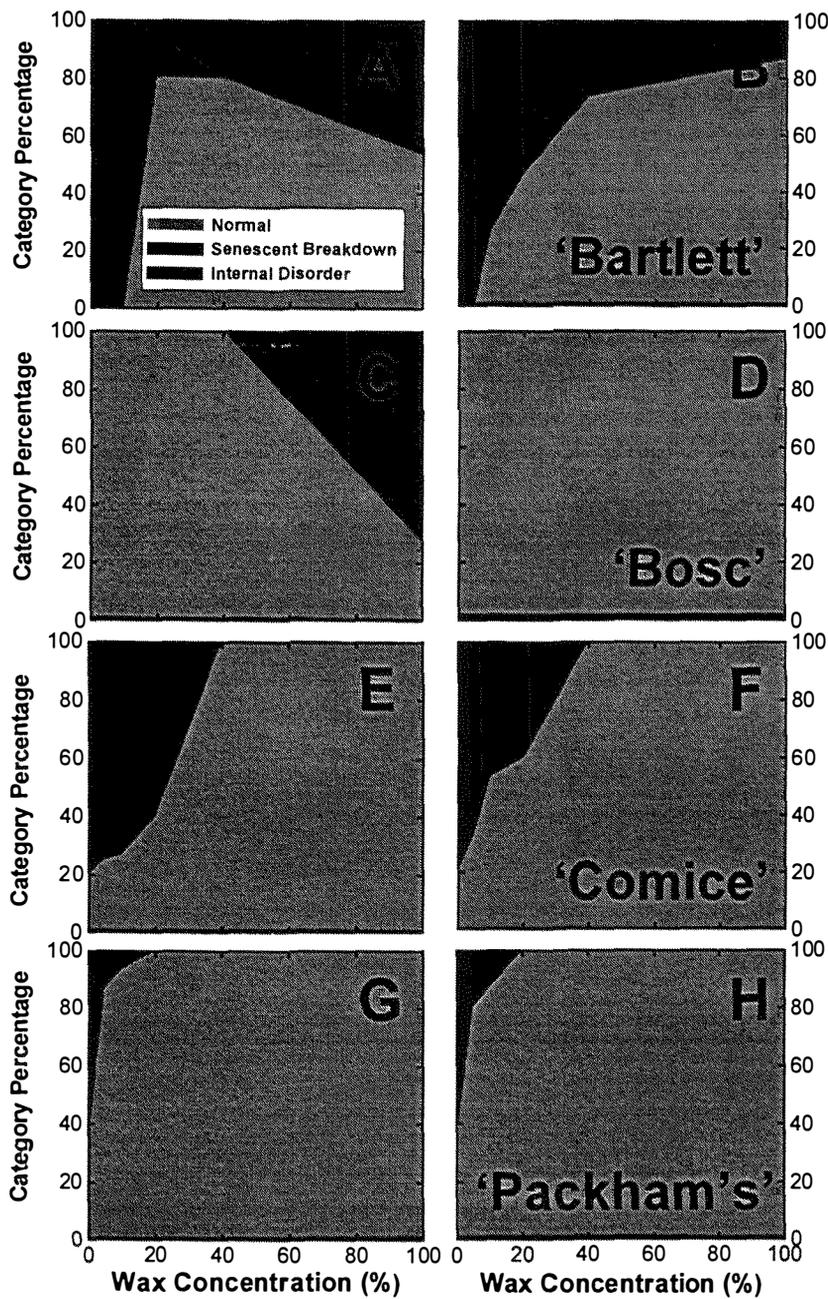


Figure 3.10 Occurrence of internal disorders and senescent breakdown after ripening at 20°C and 60-70% RH of pears coated with different coating concentrations at harvest (left column: A, C, E, and G) or after cold storage (right column: B, D, F, and H), cultivars 'Bartlett' (A and B), 'Bosc' (C and D), 'Comice' (E and F) and 'Packham's' (G and H).

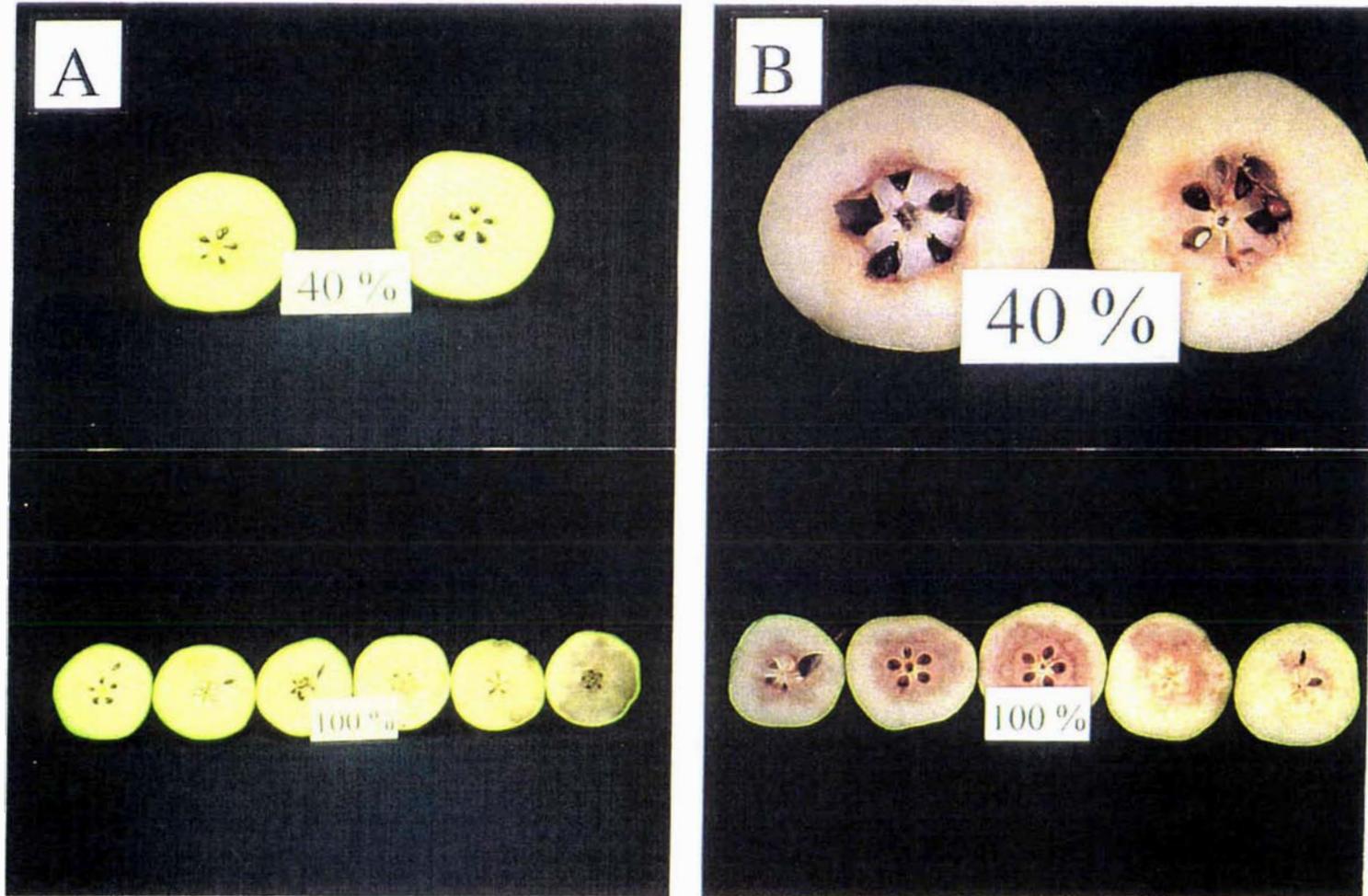


Figure 3.11 Internal disorder of 'Bartlett' (A) and 'Bosc' (B) pears induced by high CO₂ and/or low O₂ of fruit treated with high coating concentrations at harvest before cold storage.

scattered (Fig. 3.11) or, in others, large enough for a depression on the surface to occur (Figs. 3.12). High coating concentrations increased the disorder severity (Fig. 3.11). 'Bartlett' developed the disorder when treated with coating concentrations as low as 20%, with about 45% of fruit having the disorder when treated with undiluted coating (Fig. 3.10A). More than 70% of 'Bosc' fruit left in cold storage for two months developed the disorder when coated with 100% coating concentration (Fig. 3.10B). However, 'Bosc' pears treated with 40% coating concentration and left in cold storage for four or more months also developed the disorder (Fig. 3.11). 'Comice' (Figs. 3.10E and 3.10F) and 'Packham's' (Figs. 3.10G and 3.10H) did not have this internal disorder.

Increasing the coating concentration substantially suppressed the manifestation of senescent breakdown of 'Bartlett', 'Comice' and 'Packham's' pears treated at harvest or after cold storage. 'Bosc' had zero incidence of senescent breakdown after shelf life (Figs. 3.10C and 3.10D). However, fruit treated with coating concentrations < 40% before cold storage had delayed ripening but were free of internal disorders (Fig. 3.10C). Non-coated 'Bartlett' pears, with high ripening rates (Fig. 3.4), were 100% affected by senescent breakdown (Figs. 3.10A and 3.10B). This incidence was reduced to less than 20% by increasing the coating concentration from 10% to 20% wax for fruit treated at harvest (Fig. 3.10A). For fruit treated after cold storage, increasing coating concentration substantially reduced the incidence of senescent breakdown, but fruit treated with undiluted coating formulation still had about 10% of the fruit affected by the disorder (Fig. 3.10B). 'Comice' had a moderate susceptibility to the disorder, that was successfully controlled by coating concentrations $\geq 40\%$ (Figs. 3.10E and 3.10F). 'Packham's' had low susceptibility to senescent breakdown, with complete control of the disorder with coating concentration $\geq 20\%$ (Figs. 3.10G and 3.10H).

Results of fruit ripening, and control of senescent scald and senescent breakdown of 'Comice' pears coated at harvest and left in cold storage for six months are presented in Figs. 3.13, 3.14 and 3.15. Fruit coated with high coating concentration had greater firmness upon removal from cold storage but, at the end of seven days shelf life, there

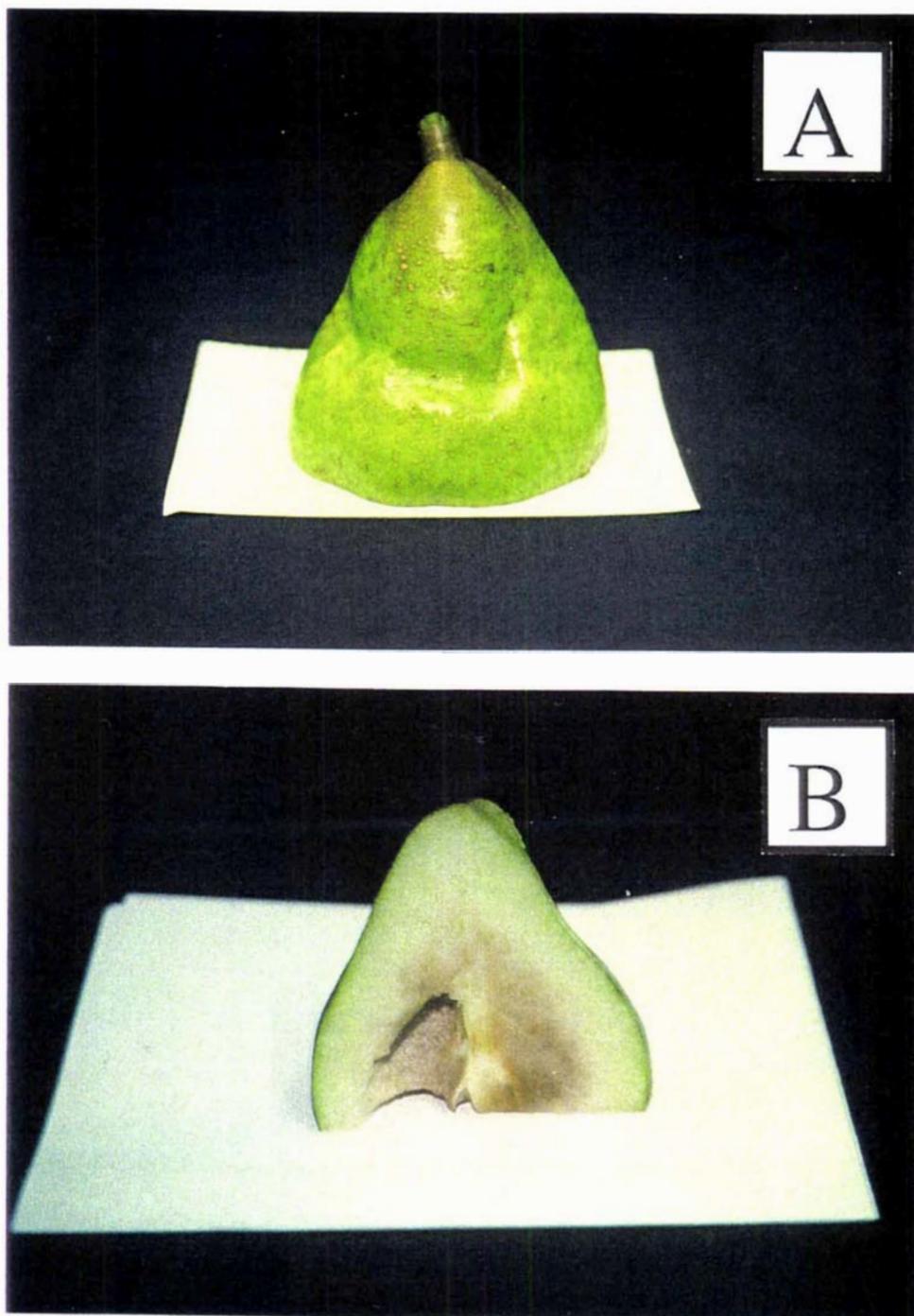


Figure 3.12 Depression on the surface (A) as a result of internal cavities (B) induced by high CO₂ and/or low O₂ and low temperature in ‘Bartlett’ pears.

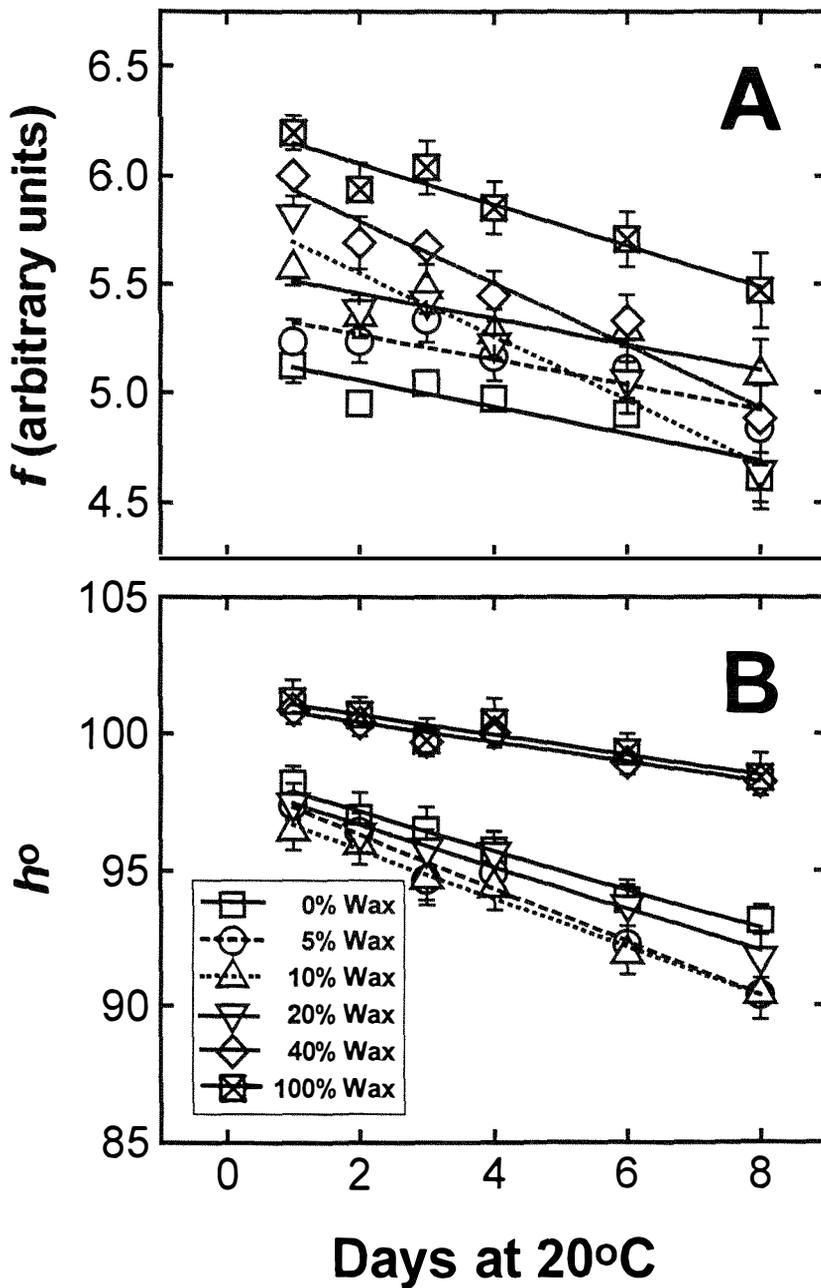


Figure 3.13 Firmness (f ; A) and skin colour (h° ; B) during shelf life at 20°C and 60-70% RH of 'Comice' pears treated at harvest with different coating concentrations and stored for six months at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH. Bars represent standard errors of the means ($n = 15$). Lines represent the best fit.

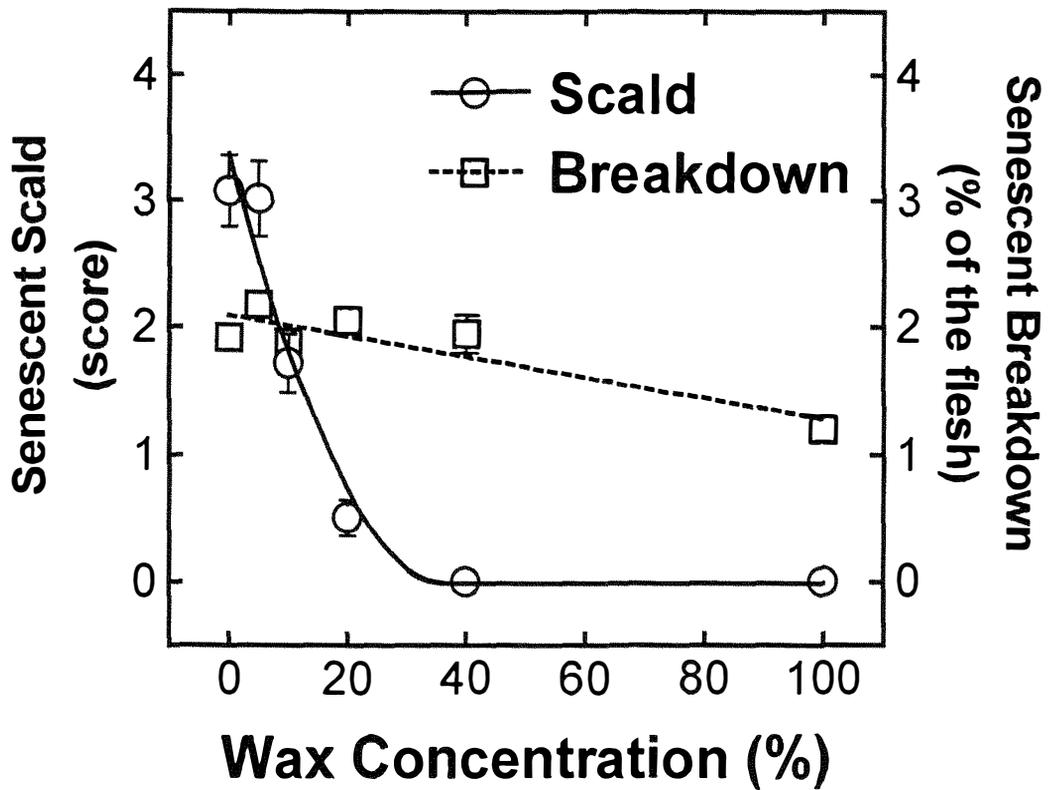


Figure 3.14 Incidence of senescent breakdown (% of fruit flesh affected by the disorder) and senescent scald (score from 0 to 9; Fig. 3.3) after seven days shelf life at 20°C and 60-70% RH of 'Comice' pears treated at harvest with different coating concentrations and stored for six months at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH. Standard errors of the means ($n = 8$) are smaller than symbols. Lines represent the best fit for senescent scald [—; fitted using the segmented model: $y = 3.37 (\pm 0.30) - 0.184 (\pm 0.04) x + 0.0025 (\pm 0.001) x^2$ for $x \leq 36.80\%$ and $y = -0.0247 (\pm 0.003)$ for $x \geq 36.80\%$; $R^2 = 96.33\%$] and senescent breakdown [---; $y = 2.09 (\pm 0.09) - 0.0081 (\pm 0.0020) x$; $R^2 = 80.00\%$].

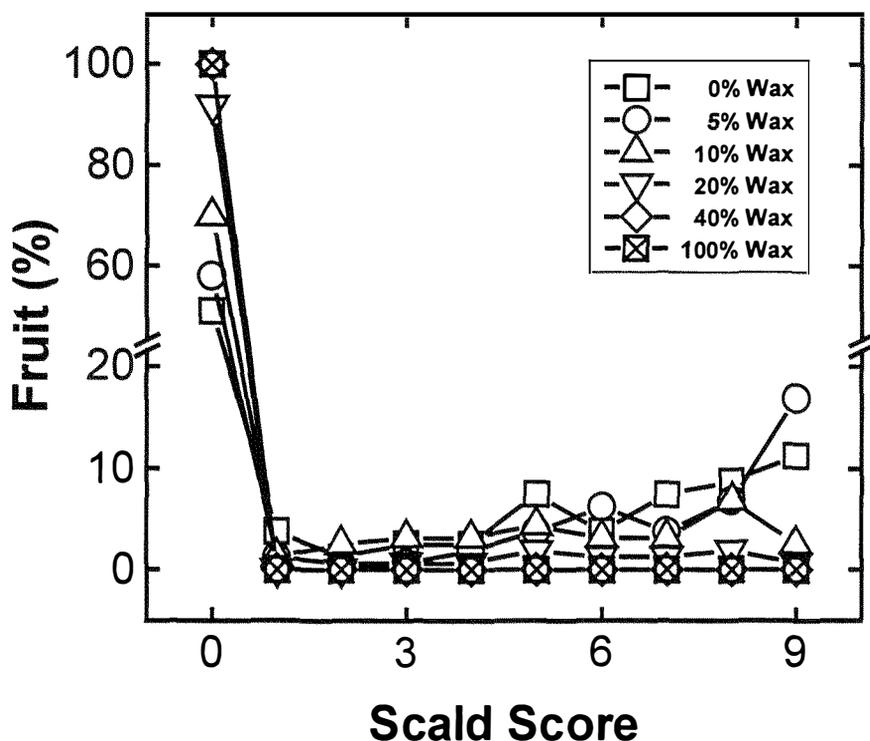


Figure 3.15 Plot of scald score and percentage of fruit affected by the disorder of 'Comice' pears treated at harvest with different coating concentrations and stored for six months at $0 \pm 0.5^{\circ}\text{C}$ and 95-98% RH. Standard errors of the means ($n = 8$) are smaller than symbols.

was no difference between treatments, except for fruit treated with full strength coating, which were firmer (Fig. 3.13A). Coatings had a dramatic effect upon retention of skin colour (Fig. 3.13B). Fruit treated with coating concentrations $\geq 40\%$ were greener, with a better colour retention during the shelf life, while there was no significant difference between the other treatments. An informal sensory analysis did not reveal any off-flavours in coated fruit. Incidence of senescent breakdown after a seven days shelf life period was linearly related to coating concentration ($P < 0.05$; Fig. 3.14). The relationship between senescent scald and coating concentration was

adjusted by fitting a segmented model, made of quadratic and linear equations (Fig. 3.14). The fitted model adjusted nil senescent scald incidence for coating concentrations $\geq 36.80\%$. For lower coating concentrations there was a quadratic relationship, with larger reductions of senescent scald with small increases in coating concentration. With coating concentrations of 0%, 5%, 10%, 20%, and 40-100%, about 51%, 58%, 70%, 92%, and 100% of fruit were unaffected by the disorder, respectively (senescent scald score zero, Fig. 3.15). Increasing coating concentration substantially reduced the average senescent scald score (Fig. 3.14) by reducing the percentage of fruit with high senescent scald levels (Fig. 3.15). No internal disorders caused by high CO_2 and/or low O_2 were noted. Increasing coating concentration had a larger beneficial effect in reducing senescent scald than senescent breakdown (Fig. 3.14).

3.5 Discussion

Highly significant effects of coating concentration in suppressing r_{CO_2} , df/dt and dh/dt were detected by ANOVA. However, with the univariate analysis of variance it is not possible to identify how fruit treated with different coating concentrations compare with respect to all attributes considered together, or how these attributes may be interrelated. CDA simultaneously examines differences between coating treatments, and indicates the relative contribution of each ripening attribute for treatment discrimination (Cruz-Castillo et al., 1994). The CDA results confirmed observations made by Amarante et al. (1998b) that respiration presents less variability within treatment groups relative to between treatment groups than firmness and skin colour. The previous authors observed a larger spread of values for df/dt and dh/dt at a given level of internal O_2 partial pressure (p_{O_2}) than for r_{CO_2} . CDA finds linear combinations of the original attributes that best separate the means of the treatment groups relative to within-group variation (Cruz-Castillo et al., 1994). On this basis, respiration would be expected to have more power in discriminating coating treatments than firmness and skin colour. This was confirmed by the DRC values of each attribute shown in Table

3.3. This raises an important issue about the quality of coated pears: fruit treated with a single coating concentration would have variable quality in terms of firmness and colour change. This is especially important for fruit treated with intermediate levels of coating concentrations, which generate more variable permeance to O_2 (Amarante et al., 1998a) resulting in variable p'_{O_2} (Amarante et al., 1998b; Banks et al., 1997). This may result in variable ripening behaviour, especially for change in skin colour (Fig. 3.16), which is strongly suppressed by any reduction of p'_{O_2} (Amarante et al., 1998b).

For 'Bosc' low coating concentrations (up to 10-20% concentration) only slightly suppressed ripening; high coating concentrations ($\geq 40\%$) had a more substantial effect (Table 3.3). The skin of 'Bosc' contains lignified epidermal cells. The permeance to gases of the epidermis is very low and most of the gas exchange occurs through the large and shallow lenticels, which have a rough internal surface comprised of small stone cells (Amarante et al., 1998b). Low coating concentrations can not effectively block these large lenticels of the skin, resulting in small modification of permeance to gases (Amarante et al., 1998a) and small modification of fruit internal atmosphere (Amarante et al., 1998b), resulting in small suppression of fruit ripening. For the other three cultivars, coating concentrations as low as 5-10% were enough to significantly delay ripening (Table 3.3). These cultivars have a smooth skin with small lenticels and small increases in coating concentration can substantially block pores in the skin, reducing skin permeance to gases (Amarante et al., 1998a) and greatly modifying the fruit internal atmosphere (Amarante et al., 1998b), resulting in substantial suppression of fruit ripening.

The potential to improve skin gloss by coating was shown to be dependent on coating concentration (Fig. 3.8) or, in another words, on the total amount of coating wax left on the skin. Similar results were reported by Johnston and Banks (1998) for avocados coated with a polyethylene wax. However, these benefits also depended strongly on skin characteristics of the commodity. Glenn et al. (1990) reported that fruit finish in apples coated with a wax was highly dependent on the extent of fruit cracking on the skin. Fruit cracks were not always completely filled by the wax,



Figure 3.16 Variability in skin colour of 'Comice' pears treated with 20% coating concentration, after 15 days shelf life at 20°C and 60-70% RH.

resulting in lower light reflectance and poor finish quality of coated fruit. This seems to be the case for pears as well, and shows that cultivars with low natural gloss may benefit less from increasing coating concentration in terms of improved skin finish. This was especially the case for 'Bosc', where the presence of stone cells on the skin impaired scope for coating to improve skin finish. Enhancement of skin gloss seems also to be dependent on coating formulation. Hagenmaier and Baker (1994) have shown that citrus fruit treated with shellac and resin-based coatings had higher gloss than fruit treated with polyethylene and carnauba waxes. However, fruit treated with shellac and resin presented a larger decrease in gloss during shelf life as a result of higher water loss than fruit treated with polyethylene and carnauba wax, resulting in no significant difference in gloss between these coating treatments at the end of the shelf life period. Drake and Nelson (1990) also reported no evident difference in skin finish

among apples treated with shellac, carnauba or resin-based waxes after long term cold storage. Since increasing coating concentration reduces skin permeance to water and, consequently, fruit water loss (Amarante et al., 1998a), it is possible that improving the character of cover of the skin by increasing coating concentration may help retain the gloss by reducing shrivel.

All work with optimisation of surface coatings should include assessment of final product quality, especially for sensory attributes and the incidence of physiological disorders, since these will affect fruit acceptability by the consumer. The sensory analysis in the current work shows that, with the exception of 'Bosc' pears that become anaerobic when treated with undiluted coating formulation (Amarante et al., 1998b), increasing coating concentration did not induce off-flavours. Instead, by delaying senescence, increasing coating concentration can reduce the accumulation of senescence-related volatiles that occurs during fruit ageing, as well as improving flavour and firmness retention (Fig. 3.9).

'Bartlett' and 'Bosc' had very high susceptibility to internal disorders associated with high CO₂ and/or low O₂ levels when treated with high coating concentrations before cold storage (Figs. 3.10A, 3.10C, and 3.11). The high susceptibility of these cultivars to internal disorders may be the result of high internal CO₂ partial pressure (p'_{CO_2}) at very low p'_{O_2} for fruit of both cultivars when treated with high coating concentrations, as observed by Amarante et al. (1998b). In the case of 'Bartlett' held at 20° C, p'_{CO_2} was ~ 10 kPa as p'_{O_2} approached 0 kPa presumably as a result of high respiration rate (~ 100 nmol·kg⁻¹·s⁻¹ for fruit treated with coating full strength; Fig. 3.4). 'Bosc' began to ferment when fruit were treated with coating concentrations ≥ 40% and p'_{O_2} dropped below about 2 kPa, and p'_{CO_2} reached up to 25 kPa as p'_{O_2} approached 0 kPa (Amarante et al., 1998b). Neither cultivar developed the disorder if treated after removal from the cold storage, and left at 20°C for the same period (Figs. 3.10B and 3.10D). Although modifications of internal atmosphere would have been less severe at the storage temperature of about 0°C, the effects of coating may have been exacerbated by the enhanced solubility of CO₂ at low temperature. The low

temperature may also have impaired the metabolic repair of the internal gas stress. Amarante et al. (1998b) reported for 'Comice' and 'Packham's' a p'_{CO_2} below 10 kPa when p'_{O_2} was close to 0 kPa for fruit held at 20°C, as a result of reduced respiration rates of both cultivars (below 80 nmol·kg⁻¹·s⁻¹ for fruit treated with coating full strength; Fig. 3.4). These characteristics, coupled with a lower susceptibility to high CO₂ and/or low O₂ levels may have played a role in the absence of the disorder in 'Comice' and 'Packham's'.

Data on physiological disorders presented in Fig. 3.10 were based on assessment of only 15 fruit per treatment, and should therefore be considered as indicative only. Experiments with a larger volume of fruit should be carried out to confirm the results obtained with such small samples of fruit.

By delaying ripening and senescence of 'Comice' pears during long term storage, increasing coating concentration reduced the incidence of senescent scald and senescent breakdown, especially the former disorder. Senescent breakdown develops during long term cold storage (Meheriuk et al., 1994). However, since the modification of internal atmosphere by coatings is modest at low temperature (Amarante et al., 1998b), the beneficial effect of increasing coating concentration in reducing senescent breakdown during long term cold storage was very small. Senescent scald usually develops after long storage periods but mainly after removal from cold storage (Meheriuk et al., 1994). At ambient temperatures increasing coating concentration substantially reduces p'_{O_2} (Amarante et al., 1998b); this could suppress the browning reaction brought about by polyphenol oxidase (Amarante et al., 1998c) and reduce senescence scald during shelf life after long term cold storage. Increasing coating concentration also reduces water loss (Amarante et al., 1998a) that could have helped reduce the incidence of senescence scald by preserving skin integrity.

For 'Comice' and 'Packham's', as well as for 'Bartlett' not subjected to low temperatures, high concentrations of coatings should be preferred to achieve more substantial effects in reducing water loss, delaying ripening and reducing the incidence of senescence physiological disorders (scald and breakdown), with low risk of

developing off-flavours. Coating concentrations between 20-40% should be avoided for 'Packham's' destined for fresh market as they can cause skin blotchiness. High coating concentrations can substantially delay ripening during cold storage, but the fruit may fail to change in colour during shelf life, while still being able to soften. This is the main drawback of high coating treatments for fruit destined for fresh market. However, these treatments have a high potential for fruit destined for the processing industry, since skin colour is not of paramount importance in such fruit and they can still soften. This could reduce storage costs and permit long term preservation of quality for fruit destined for processing.

3.6 Conclusion

In this work, coating pears delayed ripening and reduced the incidence of physiological disorders associated with senescence, e.g. senescent scald and senescent breakdown. However, the optimum levels of surface coatings were strongly dependent on cultivar and treatment period. 'Bartlett' and 'Bosc' coated at harvest developed internal disorder caused by high CO₂ and/or low O₂ during cold storage. 'Comice' and 'Packham's' did not seem to be affected by this disorder and fruit should be coated before cold storage to reduce water loss and delay ripening. 'Bartlett' pears do not have a chilling requirement to ripen so fruit could be coated at harvest before marketing, to reduce water loss and delay ripening. 'Bosc' pears should be treated after cold storage with a coating concentration $\leq 40\%$ to delay ripening and avoid the risk of anaerobiosis and development of off-flavours.

The main drawback of coating treatments was the variability in rates of ripening between individual fruit during shelf life, mainly for changes in skin colour, particularly for fruit treated with coating concentrations $< 40\%$. This problem could be overcome by the use of high coating concentrations, except for 'Bosc' in which fermentation may occur. However, this may result in fruit failing to change in colour while still being able to soften.

3.7 References

- Amarante, C., Banks, N.H. and Ganesh, S., 1998a. Relationship between character of skin cover and permeance to gases of coated pears. *Postharvest Biology and Technology* (in preparation).
- Amarante, C., Banks, N.H. and Ganesh, S., 1998b. Characterising ripening behaviour and the lower oxygen limit in relation to the internal atmosphere of coated pears. *Postharvest Biology and Technology* (in preparation).
- Amarante, C., Banks, N.H. and Ganesh, S., 1998c. Effects of coating concentration, ripening stage, water status and fruit temperature on pear susceptibility to friction discolouration. *Postharvest Biology and Technology* (in preparation).
- Baldwin, E.A., 1994. Edible coatings for fresh fruits and vegetables: past, present, and future. In: J.M. Krochta, E.A. Baldwin, and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Lancaster, Basel, Technomic Publishing Company, Inc., pp. 25-64.
- Banks, N. H., Dadzie, B. K. and Cleland, D. J., 1993. Reducing gas exchange of fruits with surface coatings. *Postharvest Biology and Technology*, 3: 269-284.
- Banks, N. H., Cutting, J. G. M. and Nicholson, S. E., 1997. Approaches to optimising surface coatings for fruits. *New Zealand Journal of Crop and Horticultural Science*, 25: 261-272.
- Ben-Yehoshua, S., 1967. Some physiological effects of various skin coatings on orange fruit. *Israel Journal of Agricultural Research*, 17: 17-27.
- Cruz-Castillo, J.G., Ganeshanandam, S., MacKay, B.R., Lawes, G.S., Lawoko, C.R.O. and Woolley, D.J., 1994. Applications of canonical discriminant analysis in horticultural research. *HortScience*, 29: 1115-1119.
- Drake, S.R. and Nelson, J.W., 1990. Storage quality of waxed and nonwaxed 'Delicious' and 'Golden Delicious' apples. *Journal of Food Quality*, 13: 331-341.
- Elson, C.M., Hayes, E.R. and Lidster, P.D., 1985. Development of the differentially permeable fruit coating "Nutri-Save" for the modified atmosphere storage of fruit. In: S.M. Blankenship (Editor), *Proceedings from the Fourth National Controlled Atmosphere Research Conference*. Horticultural Report North Carolina State University, Raleigh, pp. 248-262.
- Farooqi, W.A. and Hall, E.G., 1973. Effect of wax coatings containing diphenylamine on apples and pears during storage and ripening. *Australian Journal of Experimental Agriculture and Animal Husbandry*, 13: 200-204.
- Glenn, G.M., Rom, C.R., Rasmussen, H.P. and Poovaiah, B.W., 1990. Influence of cuticular structure on the appearance of artificially waxed 'Delicious' apple fruit. *Scientia Horticulturae*, 42: 289-297.

- Hagenmaier, R.D. and Baker, R.A., 1993. Reduction in gas exchange of citrus fruit by wax coatings. *Journal of Agricultural and Food Chemistry*, 41: 283-287.
- Hagenmaier, R.D. and Baker, R.A., 1994. Internal gases, ethanol content and gloss of citrus fruit coated with polyethylene wax, carnauba wax, shellac or resin at different application levels. *Proceedings of the Florida State Horticultural Society*, 107: 261-265.
- Hagenmaier, R.D. and Baker, R.A., 1995. Layered coatings to control weight loss and preserve gloss of citrus fruit. *HortScience*, 30: 296-298.
- Hagenmaier, R. D. and Shaw, P. E., 1992. Gas permeability of fruit coating waxes. *Journal of the American Society for Horticultural Science*, 117: 105-109.
- Johnston, J.W. and Banks, N.H., 1998. Selection of a surface coating and optimisation of its concentration for use on 'Hass' avocado fruit. *New Zealand Journal of Crop and Horticultural Science* (submitted).
- Kader, A. A., 1995. Regulation of fruit physiology by controlled/modified atmospheres. *Acta Horticulturae*, 398: 59-70.
- Kader, A.A., Zagory, D. and Kerbel, E.L., 1989. Modified atmosphere packaging of fruits and vegetables. *Critical Reviews in Food Science and Nutrition*, 28: 1-30.
- Köksal, A.I., Dumanoglu, H. and Tuna, N., 1994. The effect of Semperfresh on the storage of Williams pear and Starkspur Golden Delicious apple cultivars. *Acta Horticulturae*, 368: 793-801.
- Meheriuk, M. and Lau, O. L., 1988. Effect of two polymeric coatings on fruit quality of 'Bartlett' and 'd'Anjou' pears. *Journal of the American Society for Horticultural Science*, 113: 222-226.
- Meheriuk, M. and Sholberg, P., 1990. Postharvest treatments of pears. *Postharvest News and Information*, 1: 441-446.
- Meheriuk, M., Prange, R.K., Lidster, P.D. and Porritt, S.W., 1994. Postharvest disorders of apples and pears. *Agriculture Canada Publication 1737/E*. 67pp.
- Meilgaard, M., Civille, G.V. and Carr, B.T., 1991. *Sensory Evaluation Techniques*. 2nd ed. CRC Press, Boca Raton, Fla., pp. 54-55.
- Mellenthin, W.M., Chen, P.M. and Borgic, D.M., 1982. In-line application of porous wax coating materials to reduce friction discolouration of 'Bartlett' and 'd'Anjou' pears. *HortScience*, 17:215-217.
- McGuire, R.G., 1992. Reporting of objective color measurements. *HortScience*, 27: 1254-1255.
- Richardson, D. G. and Gerasopoulos, D., 1993. Controlled atmosphere recommendations for pear fruits and storage chilling satisfaction requirements for ripening winter pears. *Acta Horticulturae*, 367: 452-454.
- SAS, 1990. SAS Institute INC. Cary, NC.

- Smith, S., Geeson, J. and Stow, J., 1987. Production of modified atmospheres in deciduous fruits by the use of films and coatings. *HortScience*, 22: 772-776.
- Smock, R.M., 1935. Certain effects of wax treatments on various varieties of apples and pears. *Proceedings of the American Society for Horticultural Science*, 33: 284-289.
- Sümnü, G. and Bayindirli, L., 1994. Effect of Semperfresh and Johnfresh fruit coatings on poststorage quality of "Ankara" pears. *Journal of Food Processing and Preservation*, 18: 189-199.
- Thomas, D.R., 1992. Interpreting discriminant functions: a data analytic approach. *Multivariate Behavioral Research*, 27: 335-362.
- Van Zyl, H.J., Tormann, H. and Von Mollendorff, L.J., 1987. Effect of wax treatment on fruit quality of pears, apples, plums and nectarines after cold storage. *Deciduous Fruit Grower*, 37: 169-172.

Relationship Between Character of Skin Cover and Permeance to Gases of Coated Pears

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4.1 Abstract

Pear fruit (*Pyrus communis* L.) with different skin characteristics (non-lignified: 'Bartlett', 'Comice' and 'Packham's'; or with lignified cells in the skin: 'Bosc') were treated at harvest with a water-based carnauba wax emulsion at concentrations of 0, 5, 10, 20, 40, and 100% (v/v) of the commercial formulation and assessed for skin permeance at 20°C and 60-70% RH. 'Bartlett' had the highest natural skin permeance to water vapour and gases, followed by 'Bosc', 'Comice' and 'Packham's'. Small increases in coating concentrations achieved substantial reductions in permeance to H₂O, O₂ and CO₂ in cultivars with non-lignified skin. These cultivars underwent a larger reduction in permeance to O₂ than to CO₂ with increasing coating concentrations. 'Bosc', with lignified cells in the skin, had only small changes in permeance to H₂O with waxing. In addition, permeance to O₂ and CO₂ decreased to a similar extent and more gradually than in the other cultivars with increasing coating concentration, diminishing to close to zero for the undiluted coating. The large decrease in skin permeance of smooth skinned cultivars achieved with small increases in coating concentration were attributable mainly to improved coverage of cracks in the cuticle and blockage of lenticels. The epidermis of 'Bosc', comprising an irregular layer of lignified cells, seemed to have high permeance to H₂O and low permeance to

CO₂. Increasing coating concentration was not effective in covering the lignified cells in the epidermis but did gradually block the lenticels in the skin, resulting in substantial reduction of permeance to O₂ and CO₂ but not of permeance to H₂O. Approaches to optimisation of surface coatings for pears must take into account differences in the nature of the skin. Substantial reduction of skin permeance to water and gases was achieved with small increases in coating concentration only for cultivars without lignified cells in the skin.

Keywords: Pear; *Pyrus communis* L.; cultivar; modified atmosphere; surface coating; wax; character of cover; skin permeance; oxygen; carbon dioxide; water; weight loss.

4.2 Introduction

Surface coatings have been used extensively to modify the internal atmosphere of bulky organs to achieve similar beneficial effects to those of CA/MA storage to delay ripening (Amarante et al., 1998a and 1998b; Baldwin, 1994; Banks et al., 1993; Banks et al., 1997; Smith et al., 1987). Surface coatings can also improve the postharvest quality of horticultural commodities by reducing water loss (Hagenmaier and Baker, 1993 and 1995; Johnston and Banks, 1998), improving the finish of the skin (Amarante et al., 1998a; Glenn et al., 1990; Hagenmaier and Baker, 1994b and 1995; Johnston and Banks, 1998), and reducing skin susceptibility to friction damage (Amarante et al., 1998c; Mellenthin et al., 1982). Surface coatings, by providing differential changes on skin permeance to water vapour, O₂ and CO₂, can create different levels of water loss and modification of commodity internal atmosphere, depending on the chemical nature (Hagenmaier and Baker, 1993 and 1994b; Hagenmaier and Shaw, 1992), thickness (Ben-Yehoshua, 1967; Hagenmaier and Baker, 1993) and character of surface cover (Banks et al., 1993). While hydrophobic coatings (waxes) can substantially modify the fruit internal atmosphere and reduce water loss, hydrophilic coatings (such as polysaccharide and, to a lesser extent, shellac-

based coatings) can sometimes over-restrict gas exchange, causing anaerobiosis, and they have limited potential to reduce water loss (Banks et al., 1997; Hagenmaier and Baker, 1993, 1994b and 1995; Hagenmaier and Shaw, 1990).

Most of the literature about surface coatings does not provide information about the degree of change in permeance to gases in coated bulky organs. A number of authors have published values of permeance (or permeability) to gases and water vapour of coating films (Elson et al., 1985; Gennadios et al., 1994; Hagenmaier and Shaw, 1990, 1991a, 1991b, 1992; Hagenmaier and Baker 1994a and 1996; Mannheim and Soffer, 1996; Martín-Polo et al., 1992; McHugh and Krochta, 1994), with limited published information for coated commodities (Banks, 1984; Banks et al., 1997; Ben-Yehoshua et al., 1985; Hagenmaier and Baker, 1993; Johnston and Banks, 1998; Paull and Chen, 1989). Permeance values of commodities treated with coatings can be very different from the permeance of the coating films themselves.

The published literature about barrier properties of coating films is the result of using several different techniques that were carried out in a range of environmental conditions of temperature, RH and gases partial pressures (McHugh and Krochta, 1994). Unfortunately most of the environmental conditions used (low RH and high temperatures) are quite different from the real situation encountered by the surface coating in intimate contact with the commodity skin and exposed to very diverse environmental conditions during storage of the coated product.

The skin of a fruit consists of a thick cuticle, with a layer of wax on the outside, an epidermis, and a hypodermis of thick walled cells (Pratt, 1989). The skin has several discontinuities represented by cracks in the cuticle and lenticels (Clements, 1935; Kovács et al. 1994). Lenticels originate from openings in the cuticle and epidermis, such as stomates or broken hair bases (Clements, 1935; Pratt, 1989). Lenticels are believed to be the main path for O₂ and CO₂ exchange (Banks et al., 1993 and 1997; Clements, 1935). However, the contribution of cracks in the cuticle to skin permeance to gases has not been explored. Coatings mainly exert their effects on skin permeance to gas by blocking a greater or lesser proportion of discontinuities in the product skin

(Banks et al., 1993 and 1997; Hagenmaier and Baker, 1993). On this basis, it might be expected that fruit with different skin characteristics may have very different responses to a certain coating, based on their interaction with the coating material. This, in association with the respiration rate of each product, determines the level of modification of internal atmosphere and the resultant quality of the product (Banks et al., 1993). Therefore, direct measurement of coated commodity permeance to gases under controlled environmental conditions (temperature, RH and gases partial pressure) should be preferred for optimisation of surface coating for fruits and vegetables (Hagenmaier and Baker 1993).

In this investigation we provide information about the relationships between coating concentration, character of cover of the skin and permeance to H₂O, O₂ and CO₂ of different pear cultivars. The discrimination between treatments for permeance to different gases of coated fruit was investigated in a multivariate sense by using a canonical discriminant analysis (CDA) technique.

4.3 Materials and methods

Pear (*Pyrus communis* L.) cultivars 'Bartlett', 'Beurre Bosc', 'Doyenne du Comice', and 'Packham's Triumph' were harvested at commercial maturity in 1997, based on ENZA New Zealand (International) maturity index charts. Fruit were treated before storage with Capsicum/Zucchini Wax[®] (water-based carnauba wax emulsion, Castle Chemicals, Australia) at concentrations of 0, 5, 10, 20, 40, and 100% (v/v) of the commercial formulation, as described by Amarante et al. (1998a). The average amount of coating applied on the fruit for each coating concentration was determined by measuring the weight gain (wet weight) one minute after dipping the fruit in the coating emulsion. The coating deposit (dry mass in g·m⁻²) of coated fruit was estimated from the wet weight of coating per fruit, the total solids of the coating formulations (g·m⁻³), and fruit area. The surface tension of different dilutions of the commercial coating was estimated by the drop weight method as described by Adamson (1990).

Fruit were stored at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH for at least the period necessary to achieve the chilling requirements for ripening of each cultivar (one month for 'Bartlett' and 'Bosc', two months for 'Comice' and three months for 'Packham's'), as described by Richardson and Gerasopoulos (1993), and then transferred to 20°C and 60-70% RH for assessment of permeance to gases.

Permeance to water ($P'_{\text{H}_2\text{O}}$), CO_2 (P'_{CO_2}) and O_2 (P'_{O_2}) were estimated from the steady-state rate of gas transfer using the equation for Fick's First Law of Diffusion (Banks et al., 1995), assuming that composition of the internal atmosphere was uniform throughout the fruit (Cameron and Yang, 1982):

$$P'_j = \frac{r_j \cdot M}{A \cdot \Delta p_j} \quad [4.1]$$

where:

P'_j = fruit skin permeance to gas j ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$);

r_j = specific rate of transfer of gas j between internal and external atmospheres ($\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$);

M = weight of fruit (kg);

A = surface area of fruit (m^2);

Δp_j = difference in partial pressures of gas j between the internal and the external atmosphere of the fruit (Pa).

Fruit surface area was estimated from weight for each pear cultivar, as proposed by Clayton et al. (1995), using the allometric model:

$$A = a \cdot M^b \quad [4.2]$$

where a and b are constants, and the values of fitted models for each cultivar are presented in Table 4.1.

Table 4.1 Parameter values (\pm SE) and determination coefficients (R^2) for the fitted allometric models of the relationship between weight and area of different pear cultivars.

Cultivar	a	b	R^2 (%)
'Bartlett'	0.0514 \pm 0.0006	0.664 \pm 0.0079	99.89
'Bosc'	0.0511 \pm 0.0010	0.638 \pm 0.0139	99.76
'Comice'	0.0532 \pm 0.0007	0.687 \pm 0.0101	99.37
'Packham's'	0.0524 \pm 0.0010	0.654 \pm 0.0106	99.83

Specific rate of gas transfer was estimated from respiration rates (r_{CO_2} , mol·kg⁻¹·s⁻¹) determined by measurement of the change in partial pressure of CO₂ within 2 x 10⁻³ m³ black containers over 30 min. Any fruit having an O₂ level below the internal lower O₂ limit (LOL^i , kPa; determined from data presented by Amarante et al., 1998b) was eliminated from the estimation of skin permeance to gases; remaining fruit were assumed to have a respiratory quotient of one (rate of CO₂ evolution = rate of O₂ consumption). The internal partial pressures of O₂ (p'_{O_2} , Pa) and CO₂ (p'_{CO_2} , Pa) of fruit were measured non-destructively using the external chamber method, as described by Yearsley et al. (1996), after 72 h equilibration (a period enough for full equilibration between the fruit and chamber internal atmospheres; Appendix 1). To allow satisfactory equilibration between the vial and the fruit internal atmosphere, a small piece of adhesive tape was stuck on the fruit skin (at the equatorial position of the fruit) before applying the coating treatment; it was then removed before the surface chamber was glued in place. Gas samples were removed from surface chambers by gas tight syringe (Hamilton 100 mm³) and the values of p'_{O_2} and p'_{CO_2} were determined using an O₂ electrode (Citicell C/S type, City Technology Ltd., London, UK) in series with a miniature infra-red transducer (Analytical Development Company, Hoddesdon, UK), with O₂-free N₂ as a carrier gas (flow rate 580 mm³·s⁻¹).

Specific rate of water transfer ($r_{\text{H}_2\text{O}}$, $\text{nmol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$) was estimated by measuring rates of weight loss of fruit over a 12 h period in an air stream with average velocity of $3 \text{ m}\cdot\text{s}^{-1}$ and water vapour pressure difference between the fruit and air stream ($\Delta p_{\text{H}_2\text{O}}$), of approximately 0.8 kPa. Average $\Delta p_{\text{H}_2\text{O}}$ was estimated using wet and dry bulb temperatures of the air and the fruit surface using standard psychrometric equations (Campbell, 1977). Estimates of $P'_{\text{H}_2\text{O}}$ were obtained using Eq. 4.1, with $r_{\text{H}_2\text{O}}$ calculated as the difference between rate of total mass loss and rate of carbon loss due to respiration for each individual fruit.

Efficacy of the different coating treatments in reducing weight loss was investigated by weighing 'Comice' pears after coating the fruit at harvest and again 12 h after removal from cold storage of fruit stored for two and a half months at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH in non-lined single layered boxes. Twenty-two single fruit replicates were used per treatment.

The character of cover of 'Bosc' and 'Comice', two cultivars with very distinct skin characteristics (the first with stone cells in the epidermis and the second with smooth skin), treated with different coating concentrations, was examined using a Leica confocal scanning microscope model DMRBE (Leica[®], Switzerland). The nature of the skin was evaluated using an argon/krypton laser source in reflection mode, an optical filter using an excitation of 480 nm, a beam splitter with reflection/transmission rate of 30/70 and a detector for all wave lengths.

Statistical analysis of the data was performed by using the SAS system (SAS, 1990). Analysis of variance (ANOVA) was performed by using the PROC GLM procedure; best fit was achieved by using the PROC REG or PROC NLIN procedures; canonical discriminant analysis (CDA) was performed as described by Amarante et al. (1998a) using the PROC CANDISC procedure to discriminate between coating treatments and to categorize the skin permeance attributes for power in discriminating between coating treatments.

4.4 Results

The relationship between coating concentration and the total coating dry mass left on the skin followed a quadratic model ($P < 0.001$) for all cultivars (Fig. 4.1). The surface tension was drastically reduced from $72.9 \text{ mN}\cdot\text{m}^{-1}$ for distilled water to about $39.5 \text{ mN}\cdot\text{m}^{-1}$ with the commercial coating diluted to a concentration as low as 2.5%, with no substantial change with further increases in coating concentration (Fig. 4.2).

The relationships with coating treatments for $P'_{\text{H}_2\text{O}}$ and fruit weight loss, followed the hyperbolic model:

$$P'_{\text{H}_2\text{O}} = c \cdot \left[1 - \left(\frac{x}{x+d} \right) \right] + e \quad [4.3]$$

where x is the coating concentration (% v/v) or coating deposit (dry mass in $\text{g}\cdot\text{m}^{-2}$) and c , d and e are parameters, with values presented in Tables 4.2 and 4.3 for each cultivar.

For non-coated fruit, 'Bartlett' had the highest $P'_{\text{H}_2\text{O}}$, followed by 'Bosc', 'Comice' and 'Packham's', with a small difference between the latter two cultivars (Fig. 4.3). $P'_{\text{H}_2\text{O}}$ of 'Comice', 'Bartlett' and 'Packham's' underwent a large reduction (about one third) with increases in coating concentration from 0% to 20%; further increases in wax concentration resulted in progressively smaller improvements to a maximum of 40% to 60% reduction for undiluted coating (Fig. 4.3). Fitted values for d indicated that about half of the benefit in reducing $P'_{\text{H}_2\text{O}}$ would be achieved with a wax concentration of 10% to 20% (Table 4.2) or with a coating dry mass of $0.3 \text{ g}\cdot\text{m}^{-2}$ to $0.6 \text{ g}\cdot\text{m}^{-2}$ (Table 4.3). This modification of $P'_{\text{H}_2\text{O}}$ by increasing the wax concentration was reflected by a reduction in loss of saleable weight for 'Comice' pears left in cold storage for two and a half months, mainly as a result of reduced water loss (Fig. 4.3B). The full strength coating reduced the weight loss by ~50%, from about 6% weight loss for the controls to about 3% weight loss for undiluted coating, with a half maximum reduction of weight loss achieved with a 13% coating concentration (Table 4.2) or with a coating dry mass of $0.35 \text{ g}\cdot\text{m}^{-2}$ (Table 4.3). 'Bosc' pears had small changes in $P'_{\text{H}_2\text{O}}$

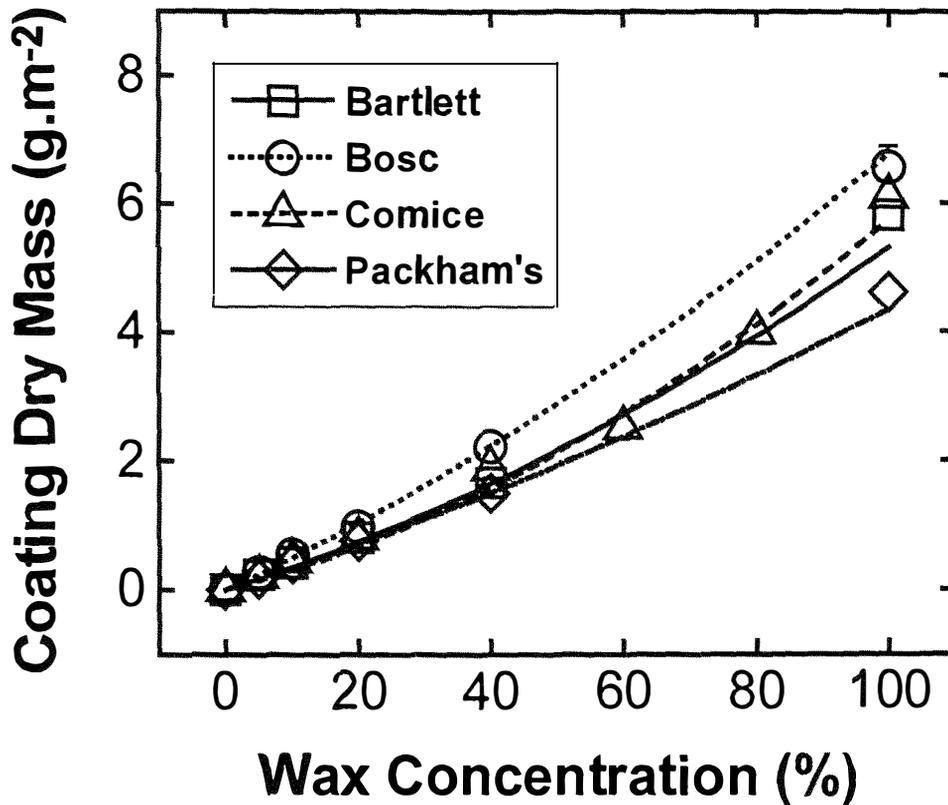


Figure 4.1 Coating deposit on the skin of pear cultivars treated with different coating concentrations. Bars represent standard errors of the means ($n = 5$). Lines represent the best fit for 'Bartlett' [$—$; $y = 0.0331 (\pm 0.002) x + 0.00025 (\pm 0.00002) x^2$; $R^2 = 99.96\%$; $P < 0.001$], 'Bosc' [\cdots ; $y = 0.0477 (\pm 0.0012) x + 0.00018 (\pm 0.00001) x^2$; $R^2 = 99.99\%$; $P < 0.001$], 'Comice' [$- - -$; $y = 0.0274 (\pm 0.0058) x + 0.00032 (\pm 0.00007) x^2$; $R^2 = 99.55\%$; $P < 0.001$], and 'Packham's' [$\cdot\cdot\cdot\cdot\cdot$; $y = 0.0335 (\pm 0.0013) x + 0.00013 (\pm 0.00001) x^2$; $R^2 = 99.98\%$; $P < 0.001$] pears.

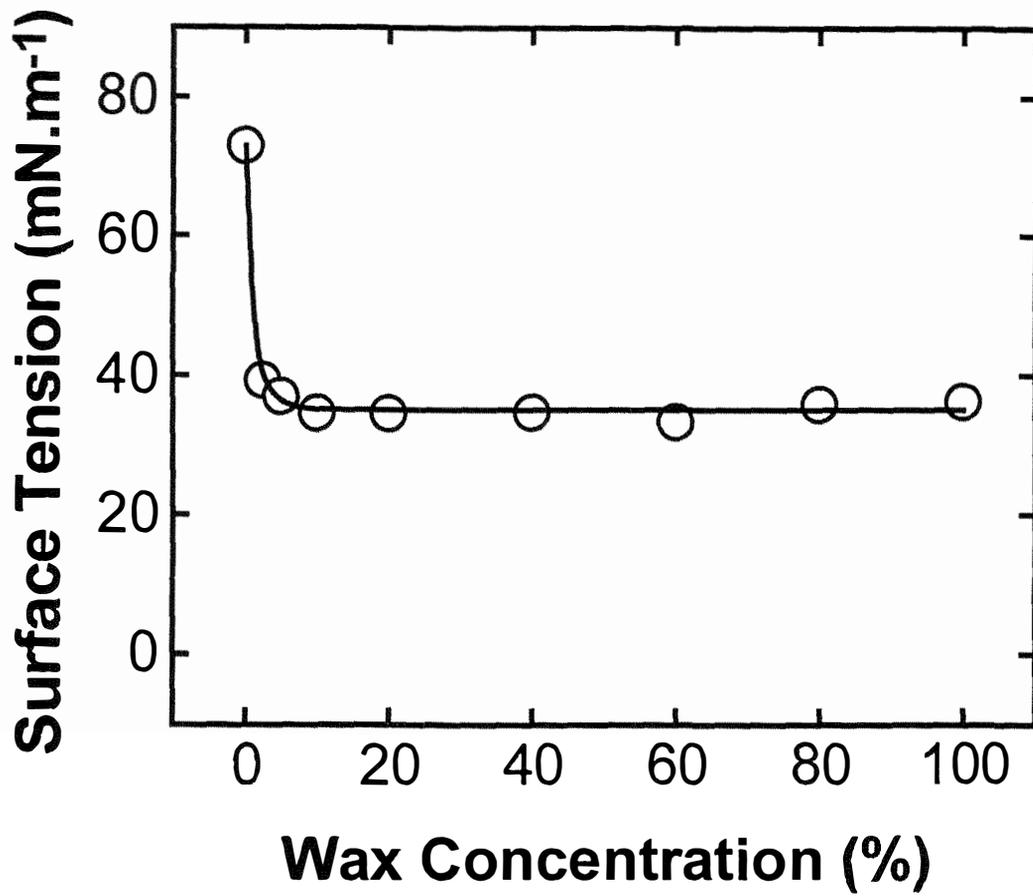


Figure 4.2 Surface tension of different coating concentrations. Standard errors of the means ($n = 20$) are smaller than symbols. Line represents the best fit $\{y = [38.9 (\pm 1.2) \cdot e^{-0.85 (\pm 0.10)x}] + 35.04 (\pm 0.44); R^2 = 99.40\%$.

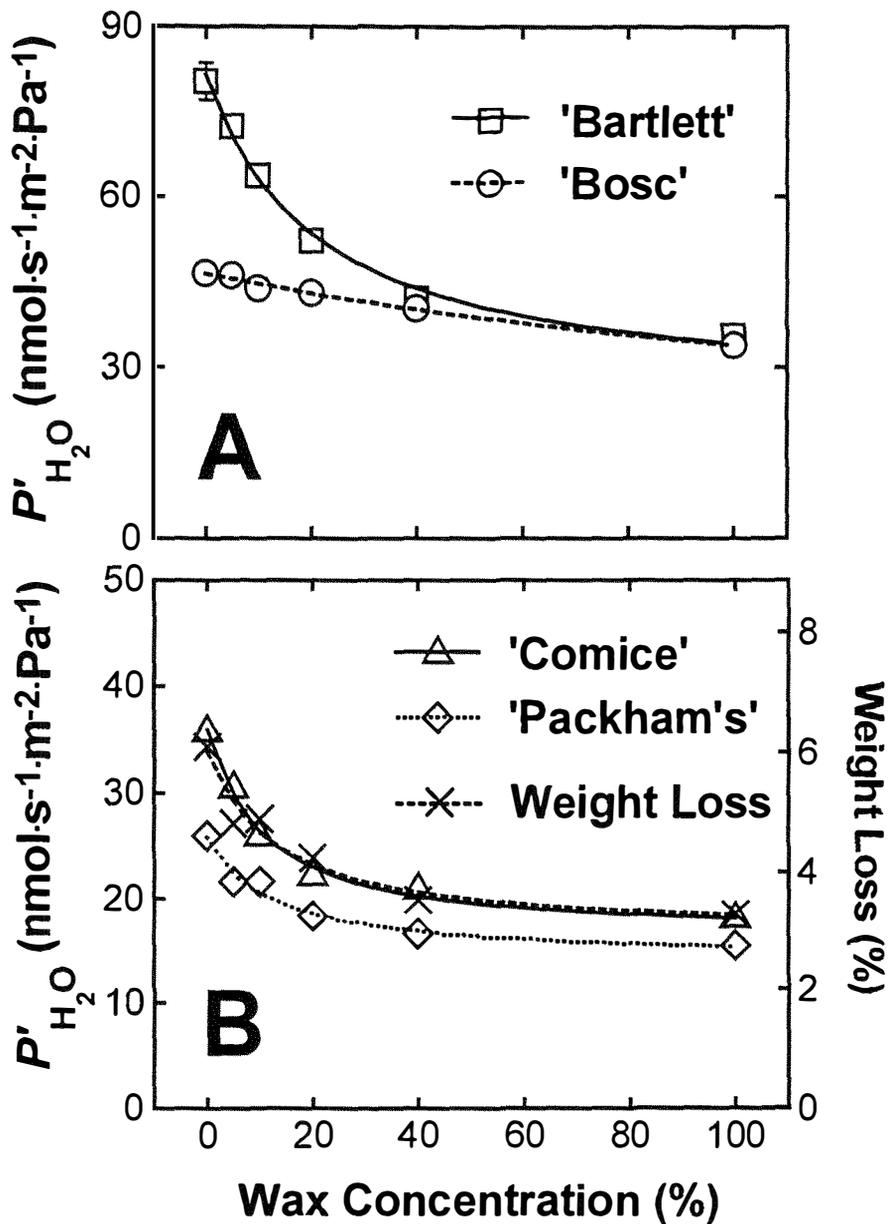


Figure 4.3 Effect of coating concentrations on permeance to H₂O (P'_{H_2O}) at 20°C and 60-70% RH of 'Bartlett' (A), 'Bosc' (A), 'Comice' (B) and 'Packham's' (B) pears, and on weight loss (% of initial weight) of 'Comice' pears (B) after two and a half months storage at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH. Bars represent standard errors of the means ($n = 15$). Lines represent the best fit of the Eq. 4.3, for which parameter values are presented in Table 4.2.

Table 4.2 Parameter values (\pm SE) and determination coefficients (R^2) for the fitted models of the hyperbolic relationship between coating concentration (% v/v) and $P'_{\text{H}_2\text{O}}$ of different pear cultivars, and for weight loss of 'Comice' pears left in cold storage for two and a half months at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH.

Cultivar	c	d	e	R^2 (%)
'Bartlett'	57.1 ± 3.57	20.3 ± 4.3	24.5 ± 3.66	99.18
'Bosc'	37.2 ± 15.28	199.2 ± 122.6	9.1 ± 15.54	99.03
'Comice' ^{/1}	15.0 ± 0.83	10.4 ± 2.0	16.6 ± 0.72	99.19
'Comice' ^{/2}	3.1 ± 0.38	12.8 ± 5.4	2.9 ± 0.35	96.21
'Packham's'	11.9 ± 1.19	12.5 ± 4.3	14.0 ± 1.09	97.44

^{/1} For $P'_{\text{H}_2\text{O}}$

^{/2} For weight loss.

Table 4.3 Parameter values (\pm SE) and determination coefficients (R^2) for the fitted models of the hyperbolic relationship between coating deposit (coating dry mass in $\text{g}\cdot\text{m}^{-2}$) and $P'_{\text{H}_2\text{O}}$ of different pear cultivars, and weight loss of 'Comice' pears left in cold storage for two and a half months at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH.

Cultivar	c	d	e	R^2 (%)
'Bartlett'	53.0 ± 2.70	0.65 ± 0.12	28.5 ± 2.56	99.33
'Bosc'	24.2 ± 5.09	6.45 ± 2.71	22.1 ± 5.32	98.99
'Comice' ^{/1}	14.2 ± 0.71	0.29 ± 0.05	17.5 ± 0.55	99.27
'Comice' ^{/2}	2.9 ± 0.34	0.35 ± 0.15	3.1 ± 0.28	96.08
'Packham's'	11.5 ± 1.12	0.41 ± 0.14	14.3 ± 0.98	97.44

^{/1} For $P'_{\text{H}_2\text{O}}$

^{/2} For weight loss.

with increasing concentrations of wax coating, with a maximum reduction of about 30% for undiluted coating (Fig. 4.3A).

The percentage of total weight loss comprising respiratory weight loss was significantly different between cultivars. ‘Comice’ had the highest percentage of respiratory weight loss ($4.25 \pm 0.73\%$), followed by ‘Packham’s’ ($3.86 \pm 0.61\%$), ‘Bartlett’ ($2.93 \pm 0.89\%$), and ‘Bosc’ ($2.37 \pm 0.57\%$).

The relationships with coating treatments for both P'_{O_2} and P'_{CO_2} were well described by exponential decay curves:

$$P'_j = (f \cdot e^{g \cdot x}) + h \quad [4.4]$$

where x is coating concentration (% v/v) or coating deposit (dry mass in $g \cdot m^{-2}$) and f , g and h are parameters, with values presented in Table 4.4 and Table 4.5 for each cultivar.

For non-coated fruit, as observed for P'_{H_2O} , ‘Bartlett’ had the highest P'_{O_2} and P'_{CO_2} , followed by ‘Bosc’, ‘Comice’ and ‘Packham’s’ (Fig. 4.4). P'_{O_2} was higher than P'_{CO_2} for ‘Bartlett’ but slightly lower for ‘Comice’ and ‘Bosc’ and much lower for ‘Packham’s’. While ‘Bartlett’, ‘Comice’ and ‘Packham’s’ had a more dramatic change in P'_{O_2} and P'_{CO_2} with small increases in coating concentration, ‘Bosc’ had a more gradual change in permeance to both gases with increasing coating concentration (Fig. 4.4). Also, for ‘Bartlett’, ‘Comice’ and ‘Packham’s’ the maximum decline achieved by increasing the coating concentration, was greater for P'_{O_2} than for P'_{CO_2} . For ‘Bosc’, P'_{O_2} and P'_{CO_2} decreased to a similar extent, to a value close to zero for the highest coating concentration. As a result, the P'_{CO_2}/P'_{O_2} ratio was increased by a factor of ~ 3 for ‘Comice’, by a factor of ~ 2 for ‘Bartlett’ and ‘Packham’s’, and only by a factor of ~ 0.4 for ‘Bosc’ with increases in coating concentration from 0% to 100% (Fig. 4.5).

There was an interconnected network of cracks of different sizes, some very large, in the cuticle of ‘Comice’ (Fig. 4.6A). Increasing the amount of coating deposited filled in these cracks (Fig. 4.6) and blocked the lenticels (Fig. 4.7). For ‘Bosc’ with an irregular layer of lignified cells in its skin, low coating concentrations presented little

Table 4.4 Parameter values (\pm SE) and determination coefficients (R^2) for the fitted models of the exponential decay relationship between coating concentration (% v/v) and P'_{O_2} and P'_{CO_2} of different pear cultivars.

Cultivar	P'_j	f	g	h	R^2 (%)
'Bartlett'	P'_{O_2}	0.419 ± 0.028	0.076 ± 0.012	0.1262 ± 0.020	98.69
	P'_{CO_2}	0.560 ± 0.028	0.089 ± 0.011	0.0500 ± 0.019	99.27
'Bosc'	P'_{O_2}	0.422 ± 0.025	0.052 ± 0.008	0.0315 ± 0.021	98.96
	P'_{CO_2}	0.396 ± 0.051	0.046 ± 0.015	0.0073 ± 0.044	95.55
'Comice'	P'_{O_2}	0.252 ± 0.018	0.072 ± 0.013	0.0882 ± 0.013	98.49
	P'_{CO_2}	0.303 ± 0.025	0.082 ± 0.017	0.0248 ± 0.017	97.98
'Packham's'	P'_{O_2}	0.116 ± 0.014	0.107 ± 0.031	0.1086 ± 0.009	95.84
	P'_{O_2}	0.099 ± 0.005	0.086 ± 0.011	0.0327 ± 0.003	99.22

Table 4.5 Parameter values (\pm SE) and determination coefficients (R^2) for the fitted models of the exponential decay relationship between coating deposit (coating dry mass in $g \cdot m^{-2}$) and P'_{CO_2} and P'_{O_2} of different pear cultivars.

Cultivar	P'_j	f	g	h	R^2 (%)
'Bartlett'	P'_{CO_2}	0.412 ± 0.028	2.19 ± 0.37	0.1320 ± 0.019	98.63
	P'_{O_2}	0.553 ± 0.024	2.54 ± 0.27	0.0550 ± 0.016	99.42
'Bosc'	P'_{CO_2}	0.421 ± 0.022	1.01 ± 0.14	0.0308 ± 0.018	99.19
	P'_{O_2}	0.393 ± 0.044	0.88 ± 0.25	0.0082 ± 0.036	96.51
'Comice'	P'_{CO_2}	0.245 ± 0.018	2.36 ± 0.44	0.0930 ± 0.012	98.38
	P'_{O_2}	0.296 ± 0.024	2.65 ± 0.54	0.0288 ± 0.016	97.98
'Packham's'	P'_{CO_2}	0.115 ± 0.014	3.12 ± 0.91	0.1091 ± 0.009	95.63
	P'_{O_2}	0.098 ± 0.005	2.50 ± 0.34	0.0333 ± 0.004	99.06

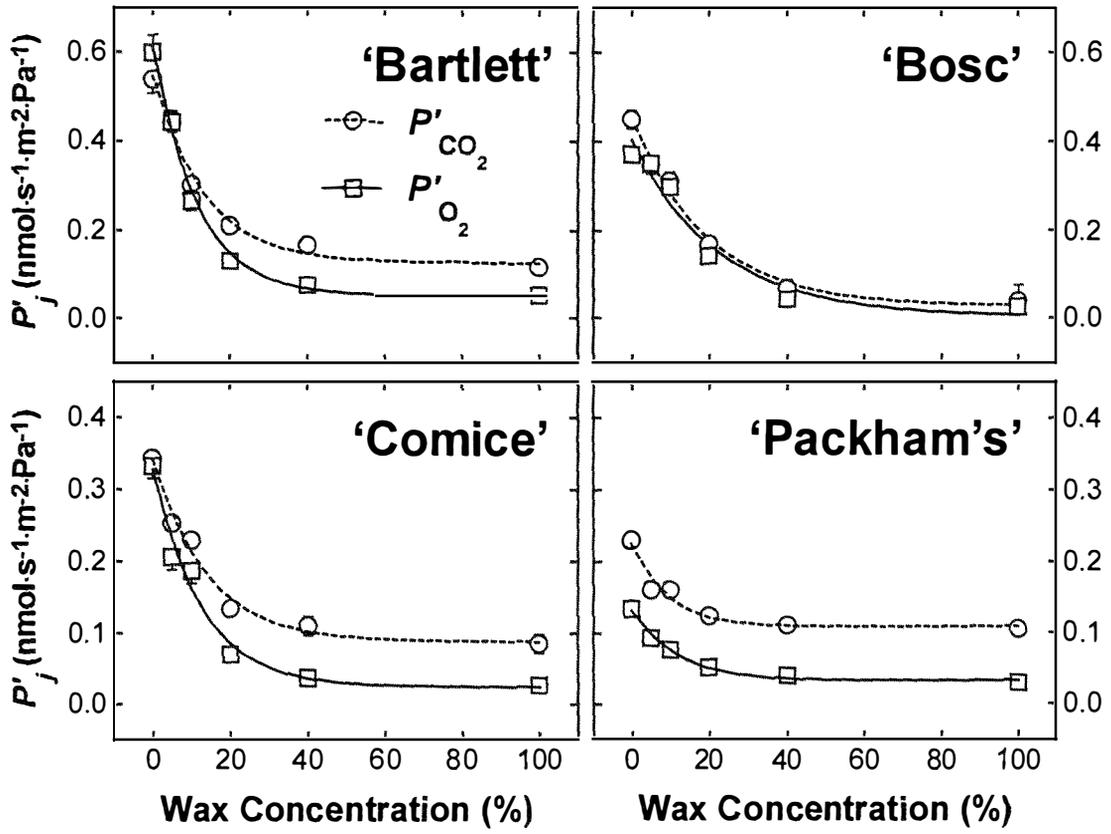


Figure 4.4 Perneance to O₂ (P'_{O_2}) and CO₂ (P'_{CO_2}) at 20°C and 60-70% RH of pear cultivars, treated with different coating concentrations. Bars represent standard errors of the means (n = 15). Lines represent the best fit of the Eq. 4.4, for which parameter values are presented in Table 4.4.

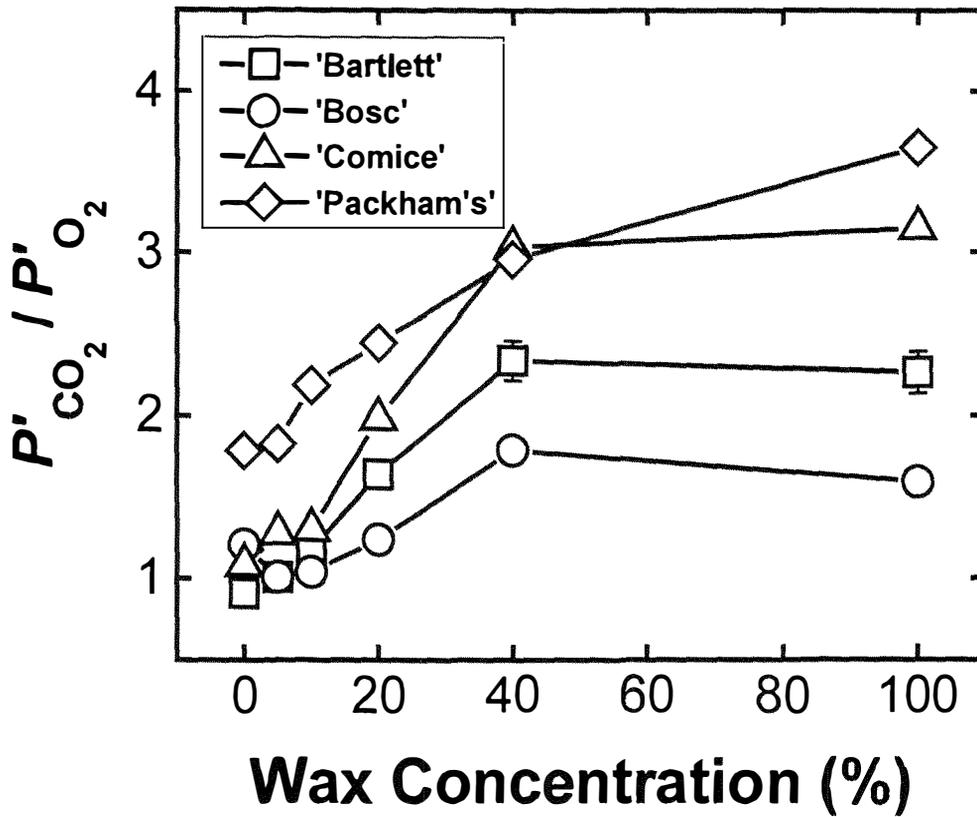


Figure 4.5 Ratio between permeance to CO_2 and permeance to O_2 (P'_{CO_2}/P'_{O_2}) at $20^\circ C$ and 60-70% RH of pear cultivars treated with different coating concentrations. Bars represent standard errors of the means ($n = 15$).

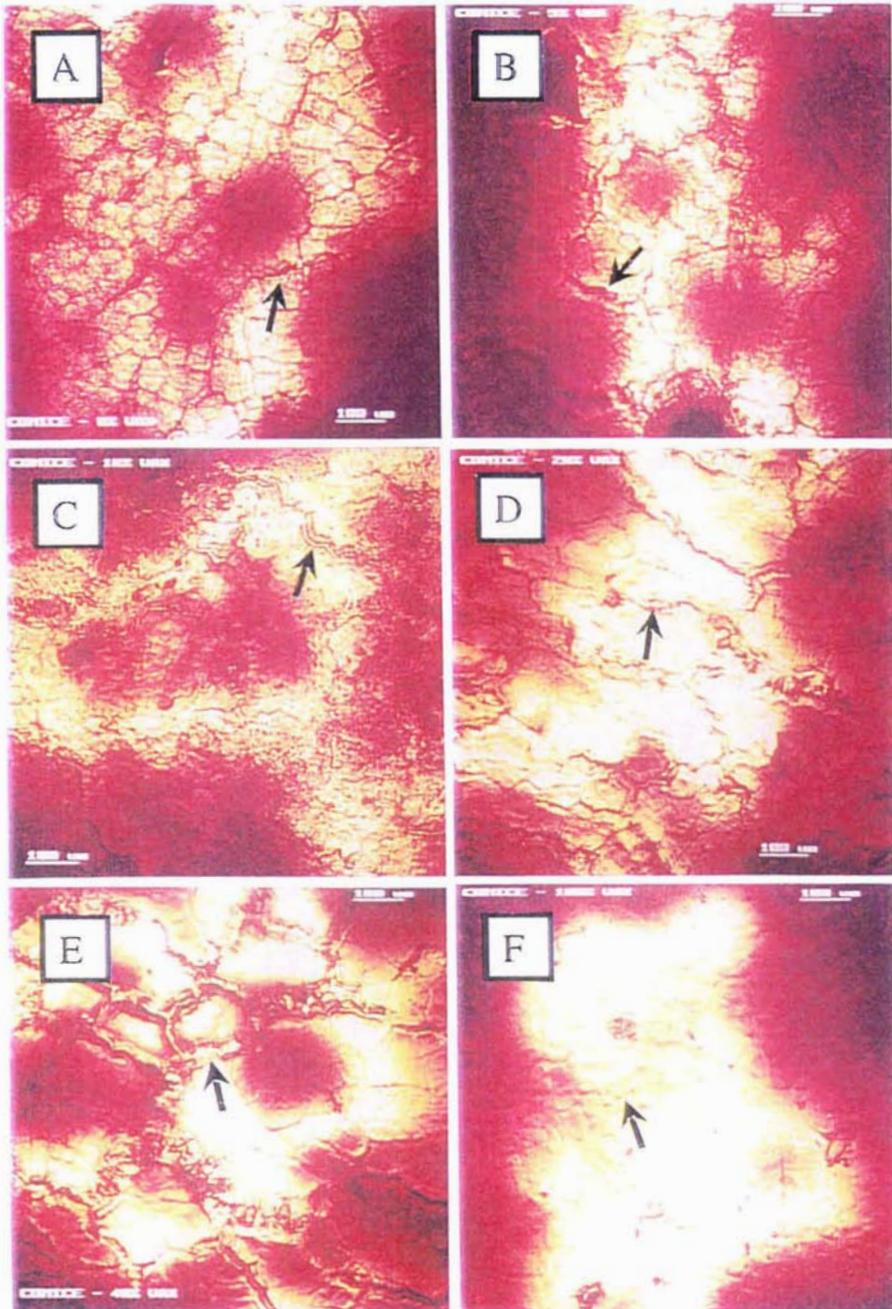


Figure 4.6 Photographs of the surface of 'Comice' pear fruit treated with coating concentrations of 0% (A), 5% (B), 10% (C), 20% (D), 40% (E), and 100% (F) of a commercial coating formulation. Arrows indicate cracks in the cuticle. Observe the substantial blockage of cracks with increases in coating concentration. Photographs magnification represented by the bar size (corresponding to 100 μm).

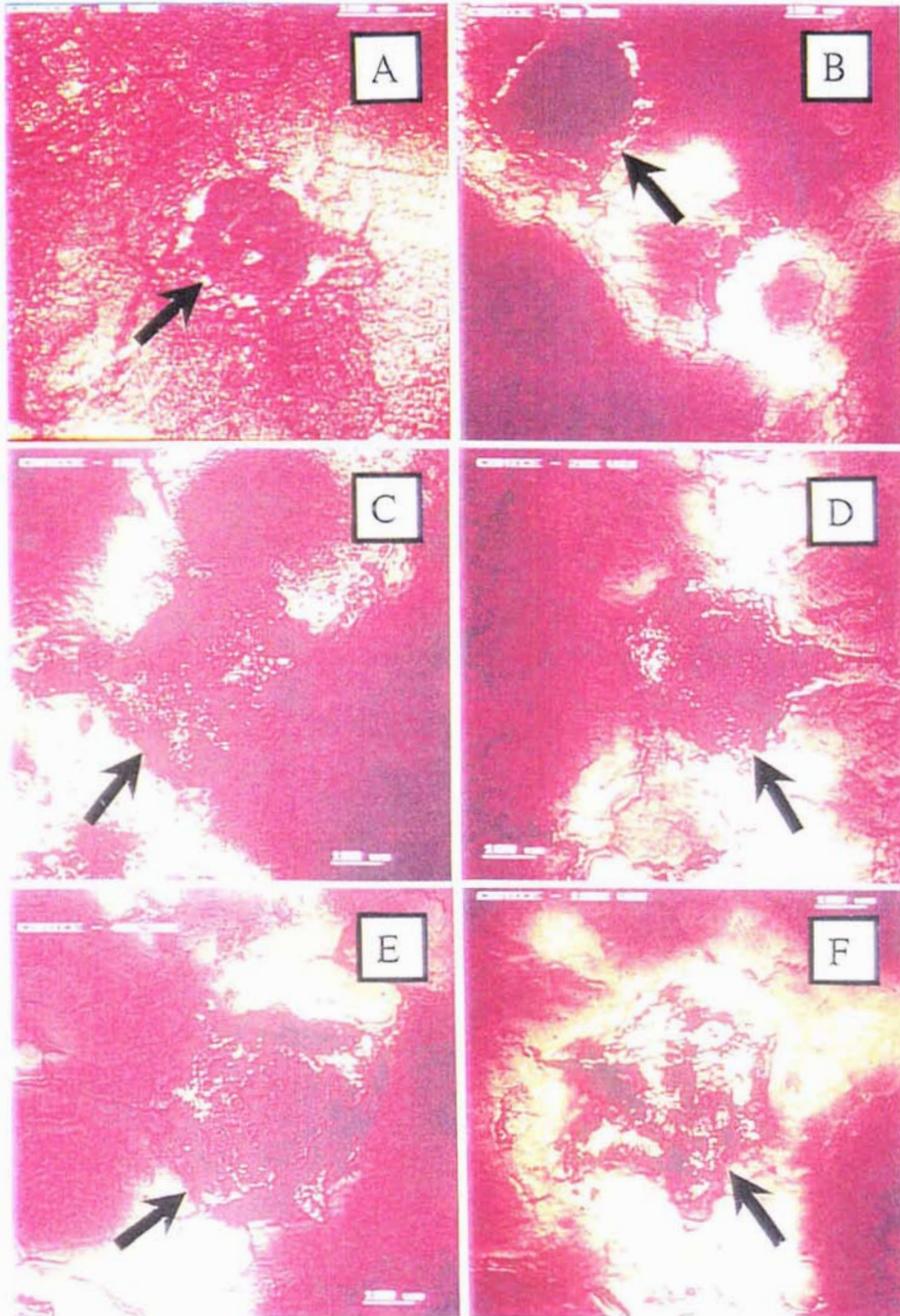


Figure 4.7 Photographs of lenticels of 'Comice' pear fruit treated with coating concentrations of 0% (A), 5% (B), 10% (C), 20% (D), 40% (E), and 100% (F) of a commercial coating formulation. Arrows indicate lenticels in the skin. Observe the substantial blockage of lenticels with increases in coating concentration. Photographs magnification represented by the bar size (corresponding to 100 μm).

scope to cover the lignified cells in the epidermis (Fig. 4.8) and the large lenticels of the skin (Fig. 4.9). Increasing coating concentration and the amount of coating deposited (Fig. 4.1) gradually improved the blockage of lenticels (Fig. 4.9) but had a small effect in filling in the large gaps between the stone cells on the skin (Figs. 4.8 and 4.10).

Highly significant ($P < 0.0001$) differences between treatments with respect to P'_{H_2O} , P'_{O_2} and P'_{CO_2} were revealed by ANOVA for all cultivars (not shown). The CDA multivariate technique showed a canonical correlation between 0.89-0.95 for the first canonical discriminant function (CDF_1) and the first eigenvalue explained more than 89% of total variation for all cultivars. This indicates not only that the association between the permeance attributes and the coating concentrations was strong, but it was dominated by CDF_1 . Almost all the separation between coating concentrations could be accounted for along CDF_1 (Fig. 4.11). The Wilks' Lambda multivariate statistic test indicated a highly significant ($P < 0.0001$) difference between coating concentrations. For P'_{H_2O} , the CDF_1 showed high and positive standardized canonical coefficients (SCC) and correlation coefficients (r) values for 'Bartlett', 'Comice' and 'Packham's', but small values for 'Bosc' (Table 4.6). P'_{H_2O} was important for treatment separation of the former three cultivars but not of 'Bosc'. In a univariate sense (r values), P'_{O_2} and P'_{CO_2} were more important than P'_{H_2O} for separation of coating concentrations for all cultivars. While in a multivariate sense, P'_{H_2O} was still important for treatment separation of 'Bartlett', 'Comice' and 'Packham's' (large SCC values), the same did not happen for P'_{O_2} for 'Bartlett' and 'Comice' and for P'_{CO_2} for 'Packham's'. This is better seen by comparing the DRC values for each permeance attribute for these three cultivars. 'Bartlett' and 'Comice' had higher SCC and DRC values for P'_{CO_2} than for P'_{O_2} . In fact P'_{O_2} was a suppressive attribute in a multivariate sense for 'Comice', which had negative SCC and DRC values. For 'Bartlett' and 'Comice' the separation between coating treatments was mainly due to differences in P'_{H_2O} and P'_{CO_2} , largely the latter. 'Packham's' had higher SCC and DRC for P'_{O_2} than for P'_{CO_2} and, therefore, the separation between coating treatments was mainly due to differences in P'_{H_2O} and P'_{O_2} .

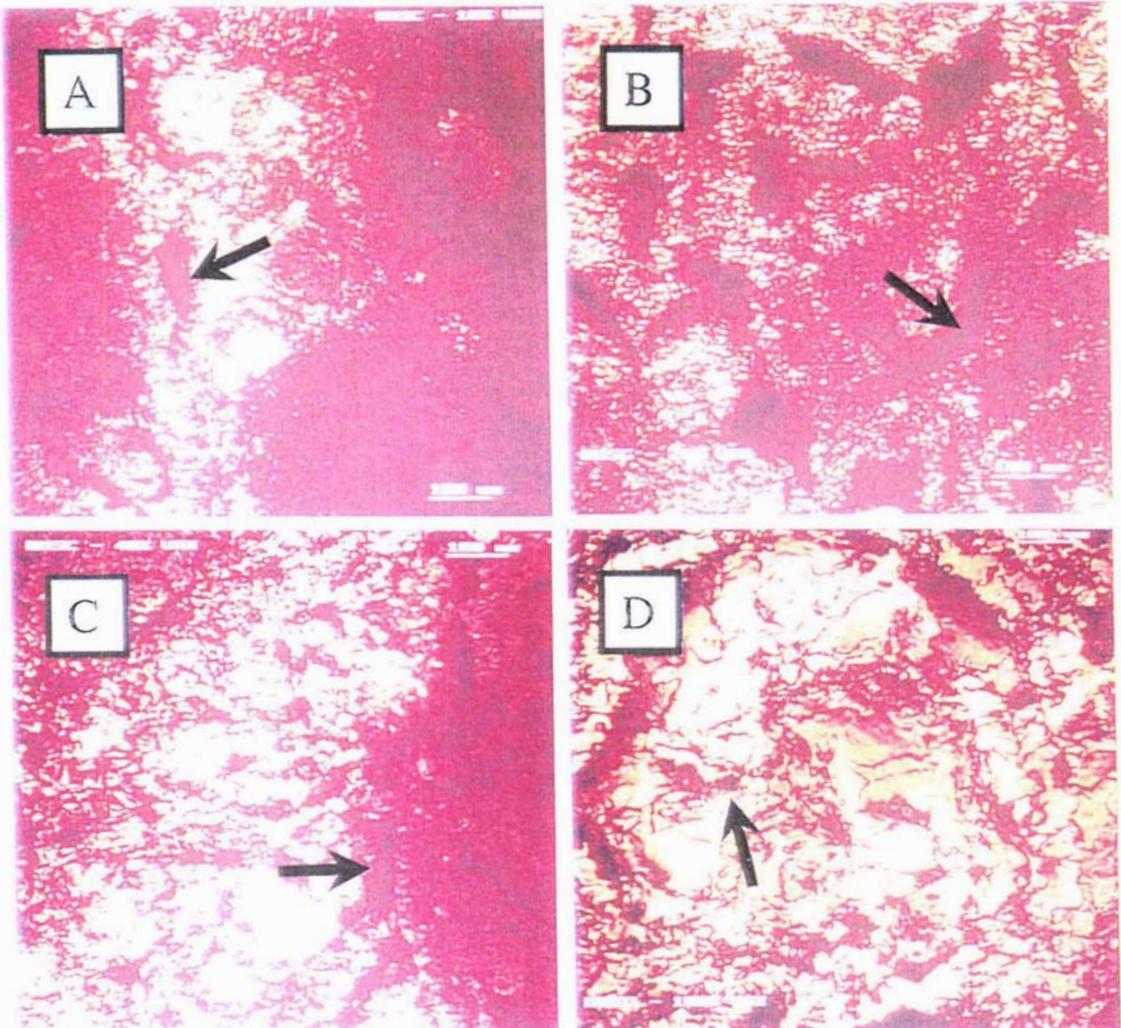


Figure 4.8 Photographs of the surface of 'Bosc' pear fruit treated with coating concentrations of 10% (A), 20% (B), 40% (C), and 100% (D) of a commercial coating formulation. Arrows indicate cracks in the skin. Observe the limited achievement by coating in blocking the large cracks in the skin with increases in concentration. Photographs magnification represented by the bar size (corresponding to 100 μm).

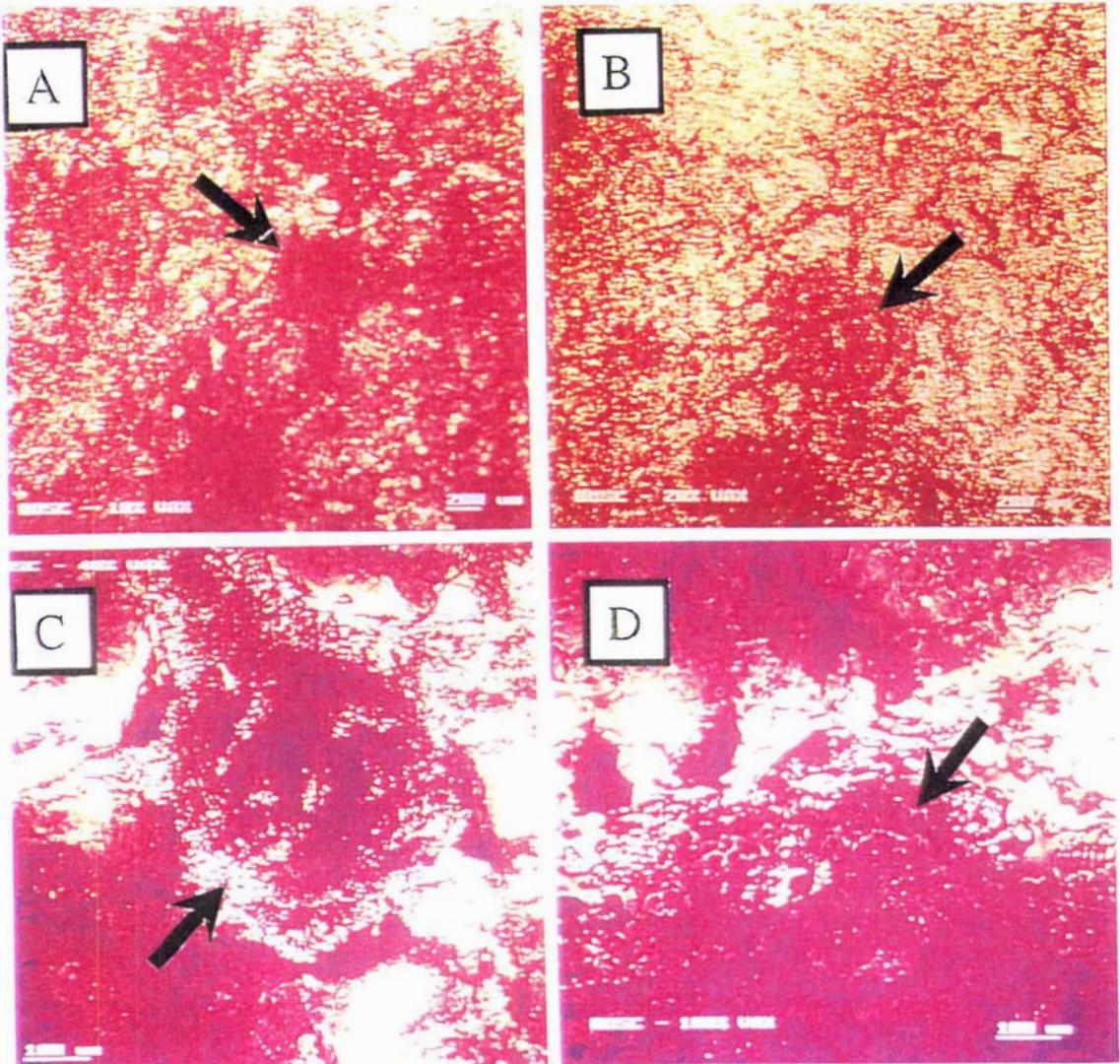


Figure 4.9 Photographs of lenticels of 'Bosc' pear fruit treated with coating concentrations of 10% (A), 20% (B), 40% (C), and 100% (D). Arrows indicate lenticels in the skin. Observe the more substantial blockage of lenticels of fruit treated with coating concentration $\geq 40\%$. Photographs magnification represented by the bar size (corresponding to 200 μm for Figs. A and B and 100 μm for Figs. C and D).

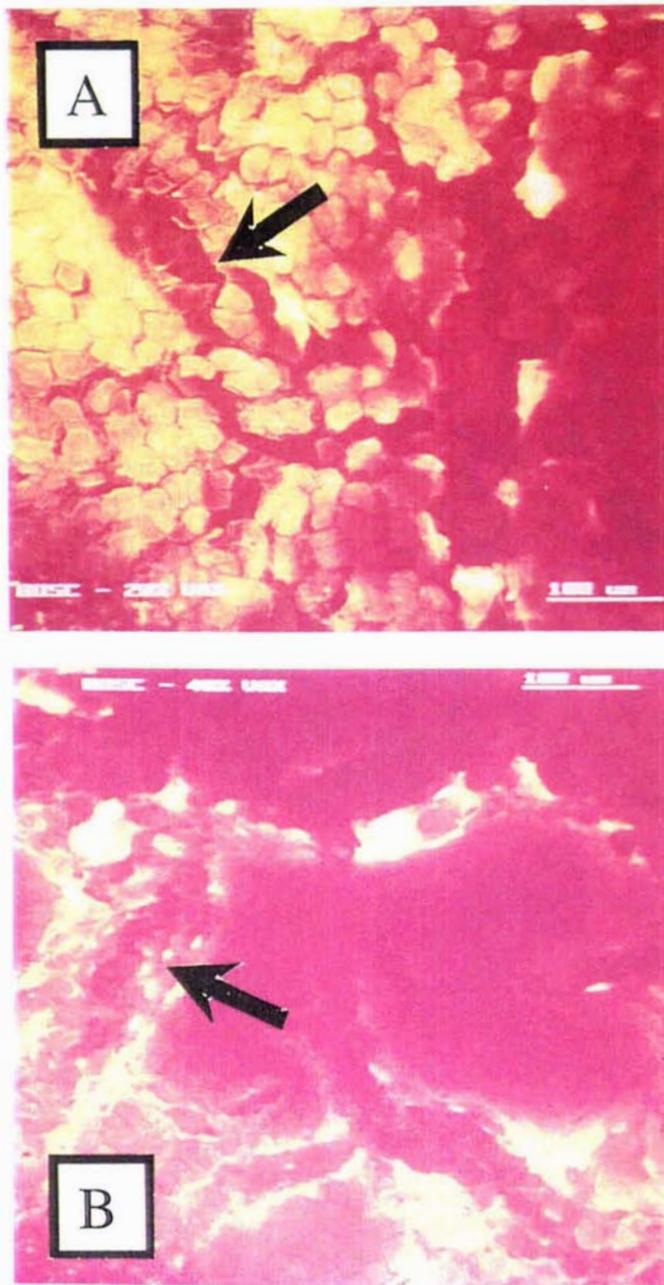


Figure 4.10 Photographs of the surface of 'Bosc' pear fruit treated with coating concentrations of 20% (**A**) and 40% (**B**). Arrows indicate cracks in the skin. Observe the incomplete cover of the gaps between the stone cells in fruit treated with 20% and of the large cracks of fruit treated with 40% coating concentrations. Photographs magnification represented by the bar size (corresponding to 100 μm).

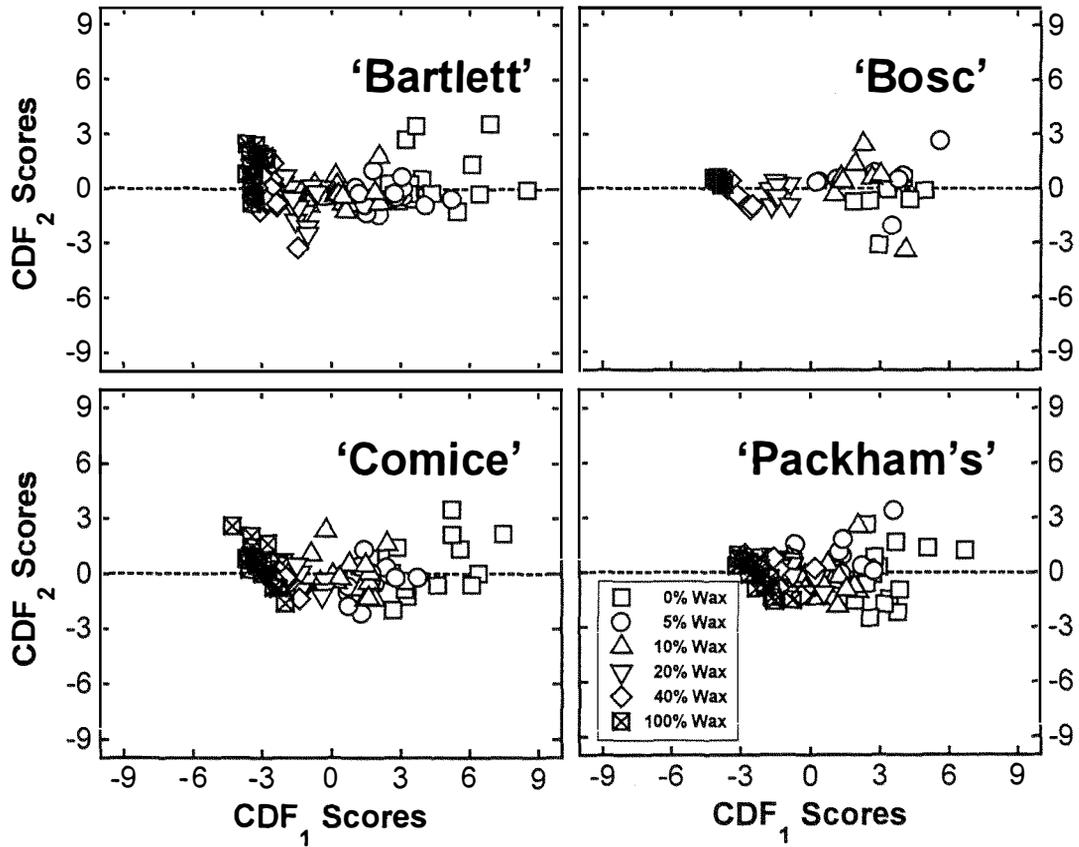


Figure 4.11 Standardized canonical scores of the first two canonical discriminant functions (CDFs) of pear cultivars treated with different coating concentrations.

Table 4.6 Standardized canonical coefficients (SCC), correlation coefficients (r), and parallel discriminant ratio coefficient (DRC) between canonical discriminant function 1 (CDF₁) and permeance attributes of four pear cultivars.

Cultivar	P'_{H_2O}			P'_{CO_2}			P'_{O_2}		
	SCC	r	DRC	SCC	r	DRC	SCC	r	DRC
'Bartlett'	0.52	0.67	0.35	0.56	0.86	0.48	0.20	0.82	0.16
'Bosc'	0.31	0.24	0.07	-0.10	0.69	-0.07	1.05	0.95	1.00
'Comice'	0.59	0.66	0.39	1.30	0.79	1.03	-0.60	0.69	-0.41
'Packham's'	0.58	0.73	0.42	0.17	0.73	0.12	0.56	0.81	0.45

'Bosc' pears had for P'_{CO_2} a negative SCC value, resulting in a negative DRC value, while P'_{O_2} had high and positive SCC and DRC values, contributing mostly for separation between coating treatments.

As most of total data variation was explained by CDF₁, to facilitate the discrimination between coating treatments the SCC scores of CDF₁ were submitted to ANOVA and compared by a Tukey's test (Table 4.7), as suggested by Cruz-Castillo et al. (1994). For all cultivars, increasing the coating concentration from 0% to 20% resulted in significant reductions in skin permeance, with more substantial effects achieved by increasing the coating concentration to 40-100%. There was no significant difference between 40% and 100% coating concentrations for all cultivars. For 'Bartlett', 'Comice' and 'Packham's' treating the fruit with a coating concentration as low as 5% significantly reduced skin permeance, while for 'Bosc' a 20% coating concentration was required to substantially reduce the skin permeance.

Table 4.7 Means of standardized canonical scores of the first canonical discriminant function (CDF_1) of pear cultivars treated with different concentrations of a wax coating.

Wax Concentration (%)	Cultivar			
	'Bartlett'	'Bosc'	'Comice'	'Packham's'
0	4.55 a	3.43 a	4.15 a	3.40 a
5	2.61 b	2.70 a	1.74 b	1.02 b
10	0.42 c	2.23 a	0.89 b	0.51 b
20	-1.52 d	-1.38 b	-1.52 c	-0.96 c
40	-2.67 e	-3.09 c	-2.15 cd	-1.71 cd
100	-3.39 e	-3.90 c	-3.10 d	-2.27 d

Means within the same column followed by the same letter are not significantly different by Tukey's test ($P < 0.05$).

4.5 Discussion

Increasing coating concentration resulted in a quadratic increase in the amount of coating deposit left on the fruit surface (Fig. 4.1), as a result of increasing the total solids concentration and also by possibly increasing coating viscosity rather than by reducing coating surface tension.

Cultivars had different proportional contribution to total weight loss made up by respiration. 'Bartlett' had the highest respiration rate of all four cultivars (Amarante et al., 1998a), but because P'_{H_2O} was also very high (Fig. 4.3A), respiration contributed only a small percentage of total weight loss. 'Bosc', 'Comice' and 'Packham's' have similar respiration rates (Amarante et al., 1998a), but because 'Bosc' had a very high P'_{H_2O} (Fig. 4.3A), this resulted in a smaller percentage of total weight loss made up by respiration than the other two cultivars. These values of respiratory weight loss should not be neglected and always used for a more precise estimation of P'_{H_2O} , especially under situation of low driving force for water loss (i.e. high RH).

Values for $P'_{\text{H}_2\text{O}}$ were about 100 times higher than P'_{O_2} and P'_{CO_2} for all cultivars, and increasing the coating concentration increased these differences as a result of a more substantial effect of coatings in reducing permeance to gases than permeance to water vapour. This is the result of pore blockage in the skin. Gases diffuse mainly through pores, while water moves preferentially by a different pathway, probably through a liquid aqueous phase in the cuticle where water conductance is much higher (Ben-Yehoshua et al., 1985). The gases O_2 and CO_2 are constrained from using the cuticle as the main pathway because their diffusivity in liquid water is 10^4 -fold less than in air (Foust et al., 1980). As a result, waxing the fruit partially or completely plugs pores, restricting mainly the transport of O_2 and CO_2 , and to a lesser extent, of water.

In the current work, we have shown that the nature of the skin greatly affected the character of cover by the surface coatings and gas exchange attributes of coated pears, reflected by changes in permeance with increasing coating concentration. Pears with non-lignified smooth skin ('Bartlett', 'Comice', and 'Packham's') followed the model for effects of coatings on gas exchange presented by Banks et al. (1993), in which coating deposits were predicted to have a greater effect on P'_{O_2} than on P'_{CO_2} , because of the differing solubilities of O_2 and CO_2 in the outer layers of the skin. By increasing coating concentration, the permeance of pores to gases was reduced, with a greater effect on O_2 , since the pores are the main path for this gas, as opposed to CO_2 that is quite soluble in water and the waxy materials of cuticle and wax coating. The parallel decrease in P'_{O_2} and P'_{CO_2} for 'Bosc' with increasing coating concentration may be the result of very low P'_{CO_2} of the lignified cells in the epidermis, constraining CO_2 exchange to occur mainly through the lenticels, as is thought to be the case for O_2 transfer. This cultivar has very large and shallow lenticels, with a rough internal surface made of small stone cells (Fig. 4.9), which may require large increases in coating concentration to effectively block the lenticels and depress both P'_{O_2} and P'_{CO_2} (Fig. 4.6).

The apparently smooth skin of 'Comice' pears has been shown to have an interconnected network of cracks in the cuticle, some very large in size (Fig. 4.6).

These cracks may be expected to have a much higher permeance to water vapour, and possibly other gases, than areas of intact cuticle. For these fruit, coating with a low concentration of a wax might fill in these imperfections, potentially providing a substantial reduction in permeance to water vapour, and possibly other gases, of these areas of the skin. Further increases in coating concentration would then have a small effect on $P'_{\text{H}_2\text{O}}$ by increasing the coating deposit and its thickness (Fig. 4.6). Increasing coating concentration would further block the lenticels (Fig. 4.7), contributing to further reduction in P'_{O_2} and P'_{CO_2} . The same was not observed for 'Bosc', which has a rough skin, presumably because although coating blocked the lenticels (Fig. 4.9), the large gaps between the stone cells in the epidermis were less affected (Figs. 4.8 and 4.10), resulting in steady and similar reductions in P'_{O_2} and P'_{CO_2} , but only a small reduction in $P'_{\text{H}_2\text{O}}$.

Banks et al. (1993) only considered the involvement of pores and not of cracks in the cuticle to model the effects of coatings on permeance to water vapour and gases. Banks et al. (1997) suggested that the permeability of the coating film is much more important than pore blockage in reducing fruit's water loss, and that the modification of fruit internal atmosphere is strongly determined by the proportion of pores blocked by the coating and not by the permeability of the coating film. In contrast, Hagenmaier and Baker (1993) suggested that for both CO_2 and water vapour, the skin permeance of coated fruit was mainly reduced by a coating's tendency to seal pores in the fruit peel, besides the resistance of the coating film by itself. The results of the current work indicate that the involvement of cracks on the cuticle, in addition to lenticels, for permeance to water vapour and gases in non-coated pears should not be disregarded and further refinement of the model presented by Banks et al. (1993) in this way may improve the accuracy with which it is able to predict effects of coating on gas exchange of fruits.

The CDA results showed that improving the character of cover reduced skin permeance of all cultivars. The substantial reductions in $P'_{\text{H}_2\text{O}}$ achieved by increasing coating concentration in 'Bartlett', 'Comice' and 'Packham's' (Fig. 4.3) and the large

and positive SCC, r and DRC values for CDF_1 , meant that this variable contributed strongly to the ability to separate coating treatments in a multivariate sense. In contrast, increasing coating concentration resulted in small changes in P'_{H_2O} for 'Bosc' (Fig. 4.3), providing little scope for treatment separation based on this permeance attribute. The r values for P'_{O_2} and P'_{CO_2} were high for all cultivars, indicating that in a univariate sense, both permeance attributes contributed to the separation of coating concentrations along CDF_1 . The r values for P'_{O_2} and P'_{CO_2} were in fact higher than those of P'_{H_2O} , as expected, since increasing coating concentration had a greater effect in reducing P'_{O_2} and P'_{CO_2} than in reducing P'_{H_2O} (Figs. 4.3 and 4.4). For 'Bartlett' and 'Comice', two cultivars with moderate to high skin permeance, the higher SCC values for P'_{CO_2} than for P'_{O_2} , indicates that increasing the coating concentration might have resulted in variable blockage of cracks and lenticels on the skin, creating smaller between treatment and/or larger within treatment variation in P'_{O_2} than in P'_{CO_2} . For these cultivars small increases in coating concentration had a larger effect in reducing P'_{O_2} than in reducing P'_{CO_2} . This might have created larger variability in P'_{O_2} than in P'_{CO_2} by increasing coating concentration, contributing to the higher power of P'_{CO_2} than P'_{O_2} in separating coating treatments. 'Packham's' had higher SCC and DRC values for P'_{O_2} than for P'_{CO_2} . This indicates that for cultivars with low skin permeance to gases the lenticels may be partially blocked, and increasing the coating concentration results in improved blockage of these pores. This might have resulted in larger between treatment and/or smaller within treatment variation in P'_{O_2} than in P'_{CO_2} , since improving the deposit of coating on the skin can still result in variable P'_{CO_2} through the cuticle. P'_{O_2} and P'_{CO_2} dropped to a similar extent with increasing coating concentration and this may have also contributed to the higher power of P'_{O_2} than of P'_{CO_2} in separating coating treatments. For 'Bosc' with stone cells in the skin, P'_{O_2} had more power to discriminate between coating treatments as a result of its larger variability between treatments and/or smaller variability within treatments than for P'_{CO_2} and P'_{H_2O} . The incomplete cover of the stone cells in the epidermis may have resulted in a small between treatment variability of P'_{H_2O} , while the blockage of the large lenticels resulted in a substantial but large within

treatment variability of P'_{CO_2} and substantial but less variable reduction of P'_{O_2} . In spite of blockage of lenticels, their large pore area may still contribute strongly to CO_2 gas exchange, resulting in variable within treatment P'_{CO_2} .

Recent reports have suggested that the potential for using surface coatings to reduce water loss is rather limited (Banks et al., 1993; Banks et al., 1997), and such treatments have the risk of inducing anaerobic respiration by creating very low internal O_2 if a large proportion of pores in the skin are occluded by the coating (Banks et al., 1997). However, the data presented here indicates that this is not the case for pears with smooth skin, for which substantial reduction in water loss was achieved by treating the fruit with a low wax concentration. If a similar response of $P'_{\text{H}_2\text{O}}$ to low concentration wax coating can be achieved with other fruits, this treatment could represent a technology with a high potential to reduce water loss, without adversely affecting internal atmosphere composition and causing anaerobiosis.

4.6 Conclusion

Only small increases in coating concentration were needed to substantially reduce skin permeance to gases of smooth skinned cultivars. However, cultivars with high skin permeance to gases ('Bartlett' and 'Comice') had variable reduction of P'_{O_2} , that could cause variable internal atmosphere modification and postharvest quality. This was not the case for smooth skinned cultivars with low permeance to gases ('Packham's'), in which small increases in the amount of coating deposited greatly suppressed O_2 exchange and could achieve small variability in fruit internal atmosphere. For all cultivars with smooth skin, very substantial reductions in $P'_{\text{H}_2\text{O}}$ were achieved with small increases in the amount of coating deposited. 'Bosc', with stone cells in the skin, had high $P'_{\text{H}_2\text{O}}$ and low P'_{CO_2} in the epidermis. Improving the character of cover blocked the lenticels and reduced P'_{O_2} , but still provided variable and small changes in $P'_{\text{H}_2\text{O}}$ and substantial but variable changes in P'_{CO_2} . This cultivar may not benefit from reduction in water loss but may benefit from modification of internal

atmosphere to delay ripening, if care is taken to avoid coating concentrations that can cause over-restriction of gas exchange and anaerobiosis.

4.7 References

- Adamson, A.W., 1990. Physical Chemistry of Surfaces. John Wiley, New York, pp. 21-23.
- Amarante, C., Banks, N.H. and Ganesh, S., 1998a. Ripening behaviour, postharvest quality and physiological disorders of coated pears. Postharvest Biology and Technology (in preparation).
- Amarante, C., Banks, N.H. and Ganesh, S., 1998b. Characterising ripening behaviour and the lower oxygen limit in relation to the internal atmosphere of coated pears. Postharvest Biology and Technology (in preparation).
- Amarante, C., Banks, N.H. and Ganesh, S., 1998c. Effects of coating concentration, ripening stage, water status and fruit temperature on pear susceptibility to friction discoloration. Postharvest Biology and Technology (in preparation).
- Baldwin, E.A., 1994. Edible coatings for fresh fruits and vegetables: past, present, and future. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), Edible Coatings and Films to Improve Food Quality. Technomic Publishing Company, Inc., Lancaster, pp. 25-64.
- Banks, N. H., 1984. Some effects of TAL-Prolong coating on ripening bananas. Journal of Experimental Botany, 35: 127-137.
- Banks, N. H., Dadzie, B. K. and Cleland, D. J., 1993. Reducing gas exchange of fruits with surface coatings. Postharvest Biology and Technology, 3: 269-284.
- Banks, N. H., Cleland, D. J., Cameron, A. C., Beaudry, R. M. and Kader, A. A., 1995. Proposal for a rationalized system of units for postharvest research in gas exchange. HortScience, 30: 1129-1131.
- Banks, N. H., Cutting, J. G. M. and Nicholson, S. E., 1997. Approaches to optimising surface coatings for fruits. New Zealand Journal of Crop and Horticultural Science, 25: 261-272.
- Ben-Yehoshua, S., 1967. Some physiological effects of various skin coatings on orange fruit. Israel Journal of Agricultural Research, 17: 17-27.
- Ben-Yehoshua, S., Burg, S. P. and Young, R., 1985. Resistance of citrus fruit to mass transport of water vapor and other gases. Plant Physiology, 79: 1048-1053.
- Cameron, A. C., and Yang, S. F., 1982. A simple method for the determination of resistance to gaseous diffusion in plant organs. Plant Physiology, 70: 21-23.
- Campbell, G. S., 1977. An Introduction to Environmental Biophysics. Springer-Verlag, New York, 159 pp.
- Clayton, M., Amos, N. D., Banks, N. H. and Morton, R. H., 1995. Estimation of apple fruit surface area. New Zealand Journal of Crop and Horticultural Science, 23: 345-349.
- Clements, H.F., 1935. Morphology and physiology of pome lenticels of *Pyrus malus*. Botanical Gazette, 97: 101-117.

- Cruz-Castillo, J.G., Ganeshanandam, S., MacKay, B.R., Lawes, G.S., Lawoko, C.R.O., Woolley, D.J., 1994. Applications of canonical discriminant analysis in horticultural research. *HortScience*, 29: 1115-1119.
- Elson, C.M., Hayes, E.R. and Lidster, P.D., 1985. Development of the differentially permeable fruit coating "Nutri-Save" for the modified atmosphere storage of fruit. In: S.M. Blankership (Editor), *Proceedings from the 4th National Controlled Atmosphere Research Conference*. Horticultural Report North Carolina State University, Raleigh, pp. 248-262.
- Foust, A.S., Wenzel, L.A., Clump, C.W., Maus, L. And Andersen, L.B., 1980. *Principles of Unit Operations*. 2nd edition. John Wiley, New York, 768 pp.
- Gennadios, A., McHugh, T. H., Weller, C. L. and Krochta, J. M., 1994. Edible coatings and films based on proteins. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 201-277.
- Glenn, G.M., Rom, C.R., Rasmussen, H.P. and Poovaiah, B.W., 1990. Influence of cuticular structure on the appearance of artificially waxed 'Delicious' apple fruit. *Scientia Horticulturae*, 42: 289-297.
- Hagenmaier, R.D. and Baker, R.A., 1993. Reduction in gas exchange of citrus fruit by wax coatings. *Journal of Agricultural and Food Chemistry*, 41: 283-287.
- Hagenmaier, R.D. and Baker, R.A., 1994a. Wax microemulsions and emulsions as citrus coatings. *Journal of Agricultural and Food Chemistry*, 42: 899-902.
- Hagenmaier, R.D. and Baker, R.A., 1994b. Internal gases, ethanol content and gloss of citrus fruit coated with polyethylene wax, carnauba wax, shellac or resin at different application levels. *Proceedings of the Florida State Horticultural Society*, 107: 261-265.
- Hagenmaier, R.D. and Baker, R.A., 1995. Layered coatings to control weight loss and preserve gloss of citrus fruit. *HortScience*, 30: 296-298.
- Hagenmaier, R.D. and Baker, R.A., 1996. Edible coatings from candelilla wax microemulsions. *Journal of Food Science*, 61: 562-565.
- Hagenmaier, R. D. and Shaw, P. E., 1990. Moisture permeability of edible films made with fatty acid and (hydroxypropyl)methylcellulose. *Journal of Agricultural and Food Chemistry*, 38: 1799-1803.
- Hagenmaier, R. D. and Shaw, P. E., 1991a. Permeability of shellac coatings to gases and water vapour. *Journal of Agricultural and Food Chemistry*, 39: 825-829.
- Hagenmaier, R. D. and Shaw, P. E., 1991b. Permeability of coatings made with emulsified polyethylene wax. *Journal of Agricultural and Food Chemistry*, 39: 1705-1708.
- Hagenmaier, R. D. and Shaw, P. E., 1992. Gas permeability of fruit coating waxes. *Journal of the American Society for Horticultural Science*, 117: 105-109.

- Johnston, J.W. and Banks, N.H., 1998. Selection of a surface coating and optimisation of its concentration for use on 'Hass' avocado fruit. *New Zealand Journal of Crop and Horticultural Science* (submitted).
- Kovács, E., Kovács, J., Zackel, E. and Genova, J., 1994. Structural and chemical changes of pear skin. *Acta Horticulturae*, 368: 243-250.
- Mannheim, C. H. and Soffer, T., 1996. Permeability of different wax coatings and their effect on citrus fruit quality. *Journal of Agricultural and Food Chemistry*, 44: 919-923.
- Martín-Polo, M., Voilley, A., Blond, G., Colas, B., Mesnier, M. and Floquet, N., 1992. Hydrophobic films and their efficiency against moisture transfer. 2. Influence of the physical state. *Journal of Agricultural and Food Chemistry*, 40: 413-418.
- Mellenthin, W.M., Chen, P.M. and Borgic, D.M., 1982. In-line application of porous wax coating materials to reduce friction discolouration of 'Bartlett' and 'd'Anjou' pears. *HortScience*, 17:215-217.
- McHugh, T. H. and Krochta, J. M., 1994. Permeability properties of edible films. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 139-187.
- Paull, R. E. and Chen, N. J., 1989. Waxing and plastic wraps influence water loss from papaya fruit during storage and ripening. *Journal of the American Society for Horticultural Science*, 114: 937-942.
- Pratt, C., 1988. Apple flower and fruit: morphology and anatomy. *Horticultural Reviews*, 10: 273-308.
- Richardson, D. G. and Gerasopoulos, D., 1993. Controlled atmosphere recommendations for pear fruits and storage chilling satisfaction requirements for ripening winter pears. *Acta Horticulturae*, 367: 452-454.
- SAS, 1990. SAS Institute INC. Cary, NC.
- Smith, S., Geeson, J. and Stow, J., 1987. Production of modified atmospheres in deciduous fruits by the use of films and coatings. *HortScience*, 22: 772-776.
- Yearsley, C.W., Banks, N.H., Ganesh, S. and Cleland, D.J., 1996. Determination of lower oxygen limits for apple fruit. *Postharvest Biology and Technology*, 8: 95-109.

Characterising Ripening Behaviour and the Lower Oxygen Limit in Relation to the Internal Atmosphere of Coated Pears

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5.1 Abstract

Pear (*Pyrus communis* L.) cultivars ‘Bartlett’, ‘Bosc’, ‘Comice’, and ‘Packham’s’ were treated at harvest or after cold storage with a water-based carnauba wax emulsion at concentrations of 0, 5, 10, 20, 40, and 100% (v/v) of the commercial formulation. Coated fruit were assessed for ripening behaviour and internal atmosphere composition at 0°C/95-98% RH and 20°C/60-70% RH. At low temperatures, coatings had a more substantial effect in delaying softening than colour change; firmness retention seemed to be related to increase of internal partial pressure of CO₂ (p'_{CO_2}), while the limited suppression of colour change seemed to be related to small reductions of internal partial pressure of O₂ (p'_{O_2}). For all cultivars ripening at ambient temperature, respiration rates, softening and colour change followed a Michaelis-Menten model when plotted against p'_{O_2} , while p'_{CO_2} had virtually no explanatory power for these variables. Canonical correlation analysis showed a high correlation between the first pair of canonical variables of gas composition (p'_{O_2} and p'_{CO_2}) and ripening attributes (respiration, softening and colour), with a much higher standardised coefficient for p'_{O_2} than for p'_{CO_2} for the gas composition canonical variable. This supports the notion that modification of p'_{O_2} rather than p'_{CO_2} is the principal means by which coating achieves its effects on ripening behaviour of pears during shelf life.

Michaelis-Menten constant values (K_m) for respiration and softening were lower than those for colour change for all cultivars at ambient temperatures. This resulted in colour change being retarded by any level of depression in p'_o , created by coating, while firmness was substantially reduced only at much lower p'_o , during shelf life. Plots of p'_{CO_2} and respiration versus p'_o for fruit coated either pre-climacteric or entering the climacteric, indicated that 'Comice' and 'Packham's' were tolerant to hypoxia whereas, with 'Bartlett' and 'Bosc', tolerance reduced with advancing ripening, and the latter cultivar was the least tolerant of all four cultivars. Optimisation of surface coatings for pears must account for differences between cultivars and ripening stage at which fruit are coated.

Keywords: Pear; *Pyrus communis* L.; cultivar; modified atmosphere; surface coating; wax; optimisation; internal atmosphere; storage temperature; respiration; hypoxia; anaerobiosis; ripening stage; softening; skin colour; oxygen; carbon dioxide.

5.2 Introduction

Surface coatings have been used extensively on many fruits and vegetables to delay ripening (Amarante et al., 1998a; Baldwin, 1994; Banks et al., 1993; Banks et al., 1997; Smith et al., 1987), reduce water loss (Amarante et al., 1998b; Hagenmaier and Baker, 1993 and 1994), improve the finish of the skin (Amarante et al., 1998a; Hagenmaier and Baker, 1994), and reduce skin susceptibility to friction damage (Amarante et al., 1998c; Mellenthin et al., 1982). The optimisation of surface coatings involves the selection of both type and amount of coating that results in maximum level of benefits in delaying ripening and retaining postharvest quality, with acceptable levels of risk, to avoid fermentation and physiological disorders (Amarante et al., 1998a; Banks et al., 1997). The type of coating formulation affects the permeance of the coating film and the character of skin cover (pore blockage), both important in modifying skin permeance of coated commodities. While hydrophobic coatings

(waxes) can substantially modify the fruit internal atmosphere and reduce water loss, hydrophilic coatings (such as polysaccharide and, to a lesser extent, shellac-based coatings) can achieve the first purpose, sometimes over-restricting gas exchange and causing anaerobiosis, with limited potential for reducing water loss (Banks et al., 1997; Hagenmaier and Baker, 1993 and 1994).

Much of the work with surface coatings for fruits and vegetables has been largely empirical, describing the changes in quality that occur as a result of application of a particular coating treatment. The published literature has not provided a mechanistic model for the physiological mode of action of coatings in delaying ripening, based on the extent of internal atmosphere modification in the commodity. Also, little is known about the relationship between the extent of internal atmosphere modification of coated commodities and different physiological ripening processes, such as respiration, softening and skin colour change, during cold storage and shelf life.

Generally, the effect of reduced O₂ and/or elevated CO₂ on reducing respiration rate and processes linked to respiration, as well as ethylene synthesis and action, have been assumed to be the primary reasons for the beneficial effects of CA/MA on fruits and vegetables (Kader, 1989; Kader et al., 1989). The majority of literature concerning optimisation of CA/MA storage has focused on the effects of low O₂ concentration, since a smaller and also less consistent effect of high CO₂ has been reported on respiratory metabolism of fruits and vegetables (Boersig et al., 1988; Dadzie et al., 1996; Gran and Beaudry, 1993; Peppelenbos et al., 1996; Yearsley et al., 1997b). However, for coated commodities, the relative contribution of low O₂ and high CO₂ in delaying ripening during cold storage and shelf life remains unclear (Magness and Diehl, 1924; Smith and Stow, 1984; Smith et al., 1987).

For the optimisation of CA/MA storage, the main focus has been to characterise the relationship between external partial pressure of O₂ ($p_{O_2}^e$) and respiration, to reveal the shape of this relationship and to identify the external lower O₂ limit of the commodity (LOL^e ; Gran and Beaudry, 1993; Cameron et al., 1994; Peppelenbos et al., 1996).

However, it is the gas concentrations in the cytosol, close to equilibrium with the partial pressure of gases in the intracellular air spaces that directly affect physiological processes (Dadzie et al., 1996). Therefore, for coated commodities, the main interest should be to characterise ripening behaviour with respect to the internal partial pressure of gases and also to identify the commodity's internal lower O_2 limit (LOL^i). Yearsley et al. (1996) proposed that both internal anaerobic compensation point (ACP^i) and internal fermentation threshold (FT^i) could be useful ways to estimate LOL^i . ACP^i was estimated from plots of internal partial pressure of CO_2 (p'_{CO_2}) versus internal partial pressure of O_2 (p'_{O_2}), in which the increase in p'_{CO_2} that occurred when p'_{O_2} approached to 0 kPa was related to anaerobic activity. The FT^i was described in terms of plots of respiratory quotient (FT^i_{RQ}) and internal ethanol concentration (FT^i_{EtOH}) versus p'_{O_2} . For coated fruit, Banks et al. (1997) have proposed the use of ACP^i described by Yearsley et al. (1996) to identify the LOL^i . This approach, in addition to FT^i_{RQ} and FT^i_{EtOH} , can be used in identifying the LOL^i to optimise the use of surface coatings for fresh fruits and vegetables. In addition, plots of respiratory CO_2 production (r_{CO_2}) versus p'_{O_2} can be used to identify the LOL^i of coated commodities.

The LOL depends on commodity (Ke and Kader, 1992), cultivar (Yearsley et al. 1997a), physiological age (Boersig et al., 1988; Ke et al., 1993; Nanos et al., 1992), temperature (Ke et al., 1993; Yearsley et al. 1997b), and duration of exposure (Boersig et al., 1988; Ke et al., 1993). However, none of these aspects has been extensively investigated for the estimation of LOL^i and optimisation of surface coatings for fruits and vegetables.

In this investigation we have characterised ripening behaviour during cold storage and shelf life with respect to the internal partial pressure of gases and the LOL^i of pear cultivars treated with different concentrations of a commercial coating. The effect of ripening stage on LOL^i was investigated by coating fruit at harvest (pre-climacteric) or after the chilling requirement for each cultivar (entering the climacteric).

5.3 Materials and methods

Pear (*Pyrus communis* L.) cultivars 'Bartlett', 'Beurre Bosc', 'Doyenne du Comice', and 'Packham's Triumph' were harvested at commercial maturity in 1997, based on ENZA New Zealand (International) maturity index charts. Fruit were treated at harvest or after removal from cold storage with Capsicum/Zucchini Wax[®] (water-based carnauba wax emulsion, Castle Chemicals, Australia) at concentrations of 0, 5, 10, 20, 40, and 100% (v/v) of the commercial formulation, as described by Amarante et al. (1998a). Fruit were stored at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH for at least the period necessary to achieve the chilling requirements for ripening of each cultivar (one month for 'Bartlett' and 'Bosc', two months for 'Comice' and three months for 'Packham's'), as described by Richardson and Gerasopoulos (1993), and then transferred to 20°C and 60-70% RH, for assessment of fruit ripening and internal atmosphere.

Respiration rates (r_{CO_2} , $\text{nmol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$) were determined by measurement of the change in partial pressure of CO_2 within $2 \times 10^{-3} \text{ m}^3$ black containers over 30 min. The hue angle (h°) of skin colour at the equator of the non-blushed side of each fruit was determined with a chromameter (model CR-200; Minolta Corp., Japan) and the firmness (f , arbitrary units) was assessed non-destructively by means of a 'Kiwifirm' device, as described by Amarante et al. (1998a).

Internal partial pressure values for O_2 (p'_{O_2} , Pa) and CO_2 (p'_{CO_2} , Pa) were determined non-destructively using the external chamber method (Fig. 5.1), as described by Amarante et al. (1998b) after 72 h equilibration. The modification of internal atmosphere of coated 'Comice' pears stored at 0°C for two months and during equilibration at 20°C was investigated using the cannulation method (Fig. 5.1) described by Banks (1983). Gas samples were removed from surface chambers or cannulae by gas tight syringe (Hamilton 100 mm^3) and the values of p'_{O_2} and p'_{CO_2} were determined using an O_2 electrode (Citicell C/S type, City Technology Ltd., London, UK) in series with a miniature infra-red transducer (Analytical Development Company, Hoddesdon, UK), with O_2 -free N_2 as a carrier gas (flow rate $580 \text{ mm}^3\cdot\text{s}^{-1}$).

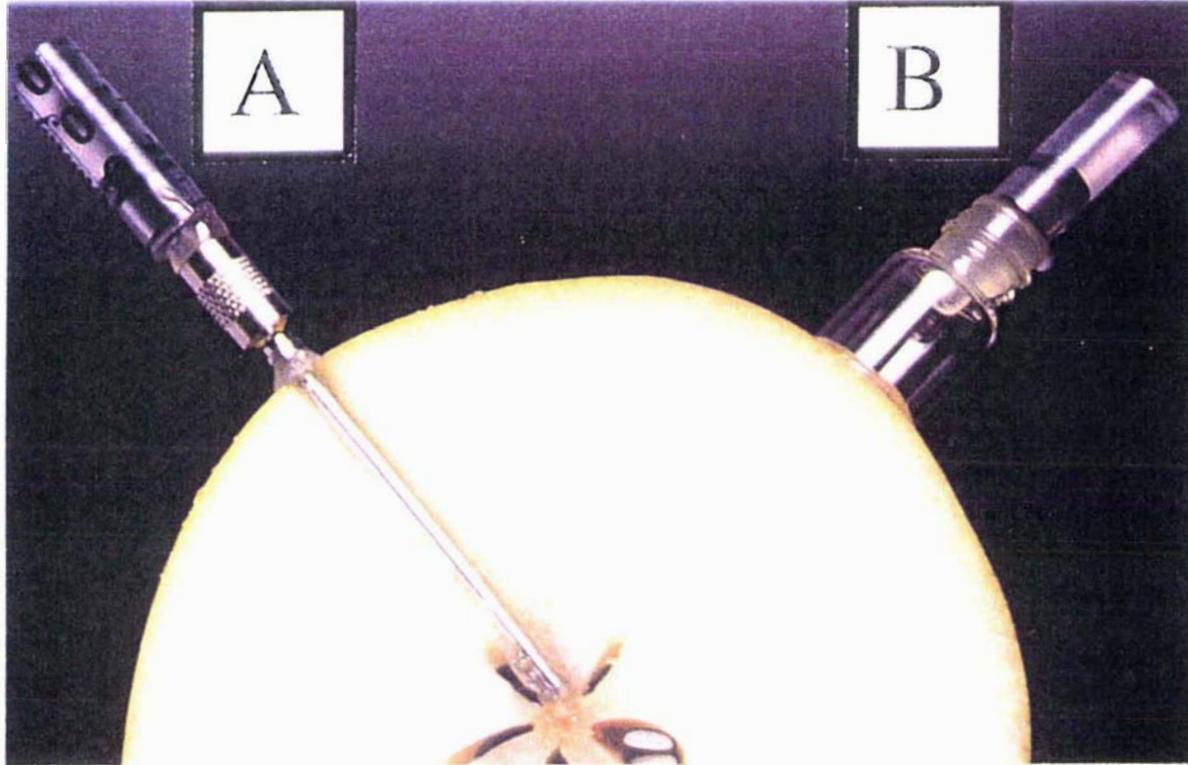


Figure 5.1 Cannulae (A) and surface chamber (B) for sampling internal gas composition in pears.

The potential of coatings for delaying ripening during long-term storage was investigated for ‘Comice’ pears coated at harvest with the wax concentrations described above and removed from cold storage after two and six months for estimation of skin colour and firmness. The estimation of skin colour and firmness at time zero after removal from cold storage was made from fitted regression lines of ripening changes during shelf life for each individual fruit (from data presented by Amarante et al., 1998a).

Statistical analysis of the data was performed by using the SAS system (SAS, 1990). Analysis of variance (ANOVA) was performed by using the PROC GLM procedure; lines of best fit were identified by using the PROC REG or PROC NLIN procedures; canonical correlation analysis was performed by using the PROC CANCORR procedure to assess the degree of association between internal gas composition (p'_{O_2} and p'_{CO_2}) and ripening attributes (r_{CO_2} , f and h^o), and also to identify the gas more strongly associated with the ripening behaviour of coated pears. For the canonical correlation analysis, attributes associated with rate of ripening (r_{CO_2} and the derivatives of f [df/dt] and h^o [dh/dt] with respect to time at ambient temperature) of fruit coated at harvest were taken at four, five, six and seven days of shelf life for ‘Bartlett’, ‘Bosc’, ‘Comice’, and ‘Packham’s’, respectively (corresponding to about the respiratory climacteric peak of each cultivar).

5.4 Results

Relationships with p'_{O_2} for df/dt (Fig. 5.2 and Table 5.1), dh/dt (Fig. 5.3 and Table 5.1), and aerobic r_{CO_2} (Figs. 5.4 and 5.5 and Table 5.2) were reasonably described by Michaelis-Menten equations while p'_{CO_2} had virtually no explanatory power for these variables for all cultivars (Figs. 5.2-5.5). The canonical correlation analysis showed a high correlation between the first pair of canonical variables of ripening attributes (r_{CO_2} , df/dt and dh/dt) and gas composition (p'_{O_2} and p'_{CO_2}), with much higher standardized coefficient for p'_{O_2} than for p'_{CO_2} for the gas composition canonical variable (Fig. 5.6).

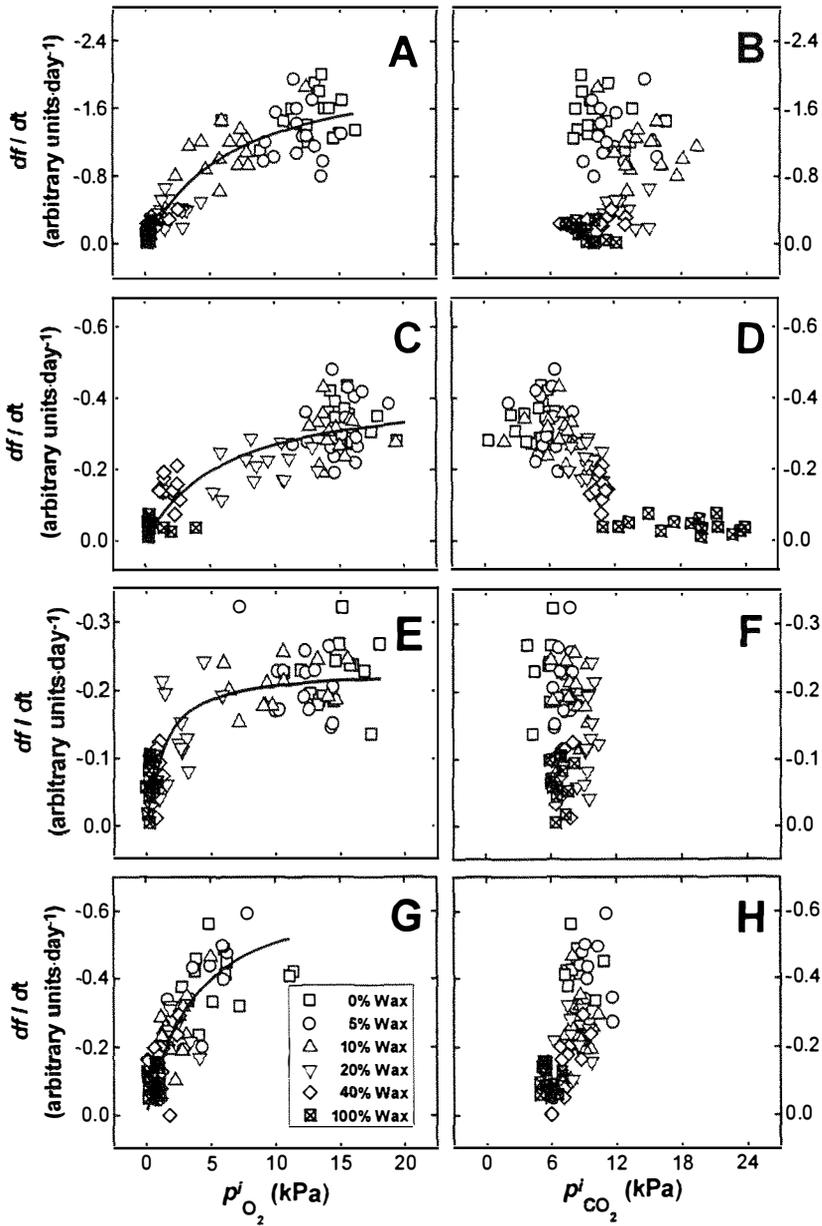


Figure 5.2 Scatter plots of internal partial pressure of O_2 (p'_{O_2}) or CO_2 (p'_{CO_2}) and the derivatives of firmness with respect to time (df/dt) at $20^\circ C$ for 'Bartlett' (A and B), 'Bosc' (C and D), 'Comice' (E and F), and 'Packham's' (G and H) pears treated at harvest with different coating concentrations. Lines represent the best fit for p'_{O_2} plots.

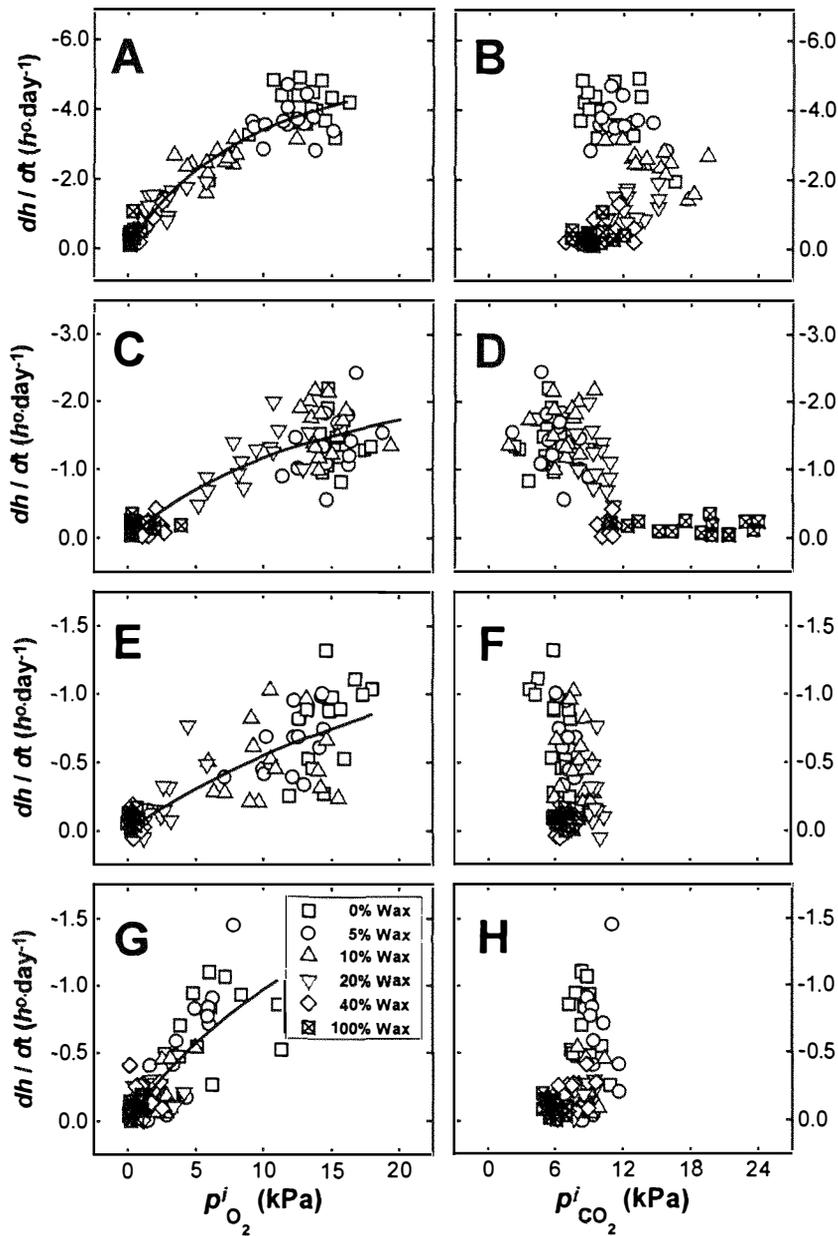


Figure 5.3 Scatter plots of internal partial pressure of O_2 (p'_{O_2}) or CO_2 (p'_{CO_2}) and the derivatives of skin hue angle with respect to time (dh/dt) at $20^{\circ}C$ for 'Bartlett' (A and B), 'Bosc' (C and D), 'Comice' (E and F), and 'Packham's' (G and H) pears treated at harvest with different coating concentrations. Lines represent the best fit for p'_{O_2} plots.

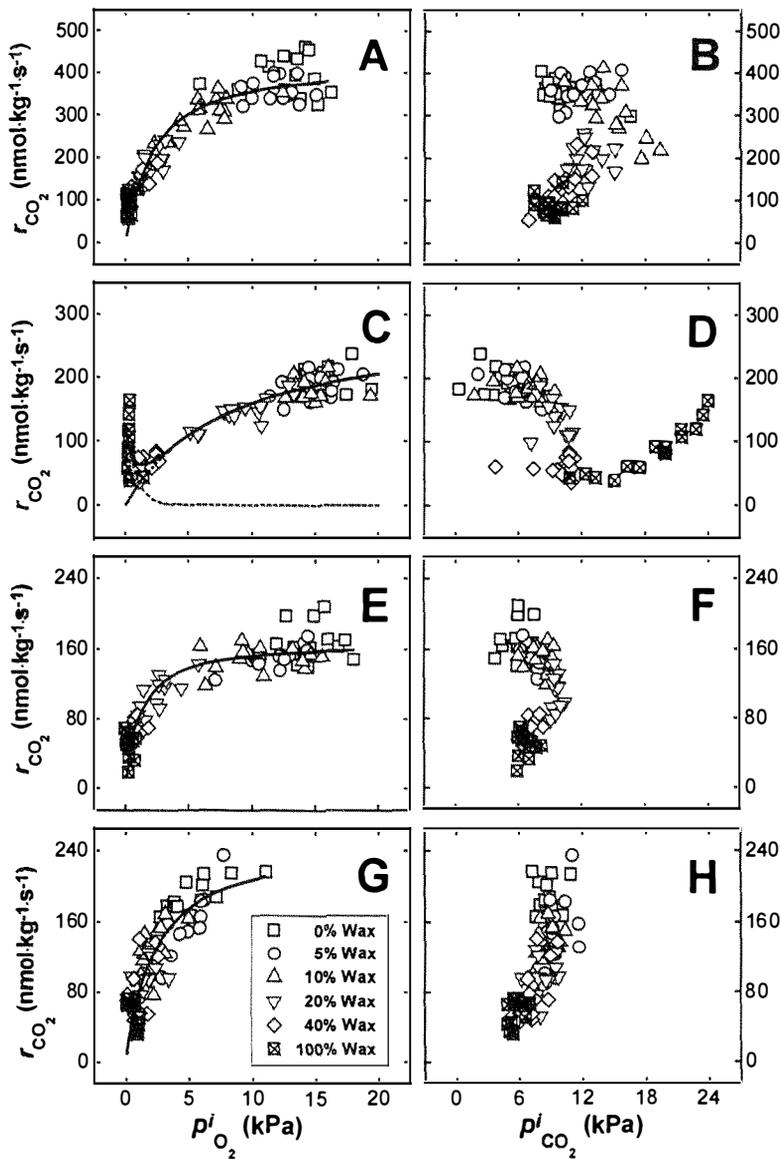


Figure 5.4 Scatter plots of internal partial pressure of O₂ (p'_{O_2}) or CO₂ (p'_{CO_2}) and r_{CO_2} at 20°C for ‘Bartlett’ (A and B), ‘Bosc’ (C and D), ‘Comice’ (E and F), and ‘Packham’s’ (G and H) pears treated at harvest with different coating concentrations. Solid lines (—) represent total respiration best fit for p'_{O_2} plots. For ‘Bosc’ respiration (C and D) the dotted (·····) and dashed (— —) lines are the best fits for the oxidative and fermentative components of total respiration, respectively.

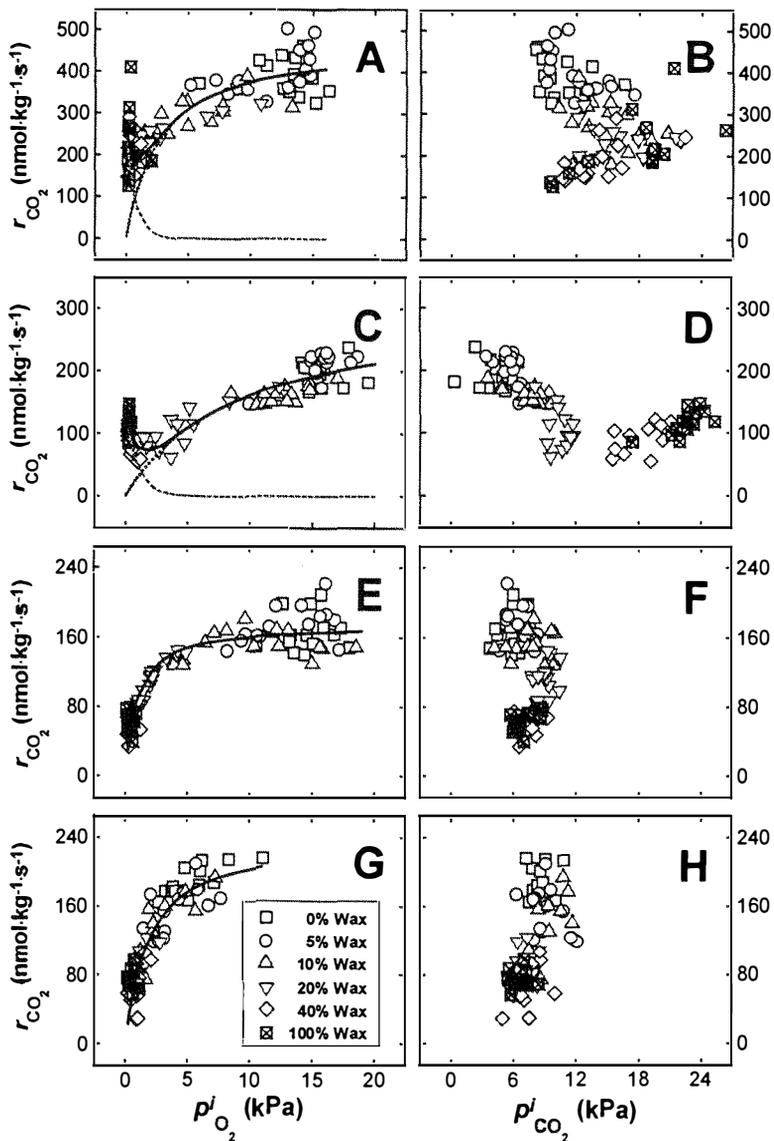


Figure 5.5 Scatter plots of internal partial pressure of O₂ ($p^i_{\text{O}_2}$) or CO₂ ($p^i_{\text{CO}_2}$) and r_{CO_2} at 20°C for ‘Bartlett’ (A and B), ‘Bosc’ (C and D), ‘Comice’ (E and F), and ‘Packham’s’ (G and H) pears treated after cold storage with different coating concentrations. Solid lines (—) represent total respiration best fit for $p^i_{\text{O}_2}$ plots. For ‘Bartlett’ (A and B) and ‘Bosc’ (C and D) respiration the dotted (·····) and dashed (---) lines are the best fits for the oxidative and fermentative components of total respiration, respectively.

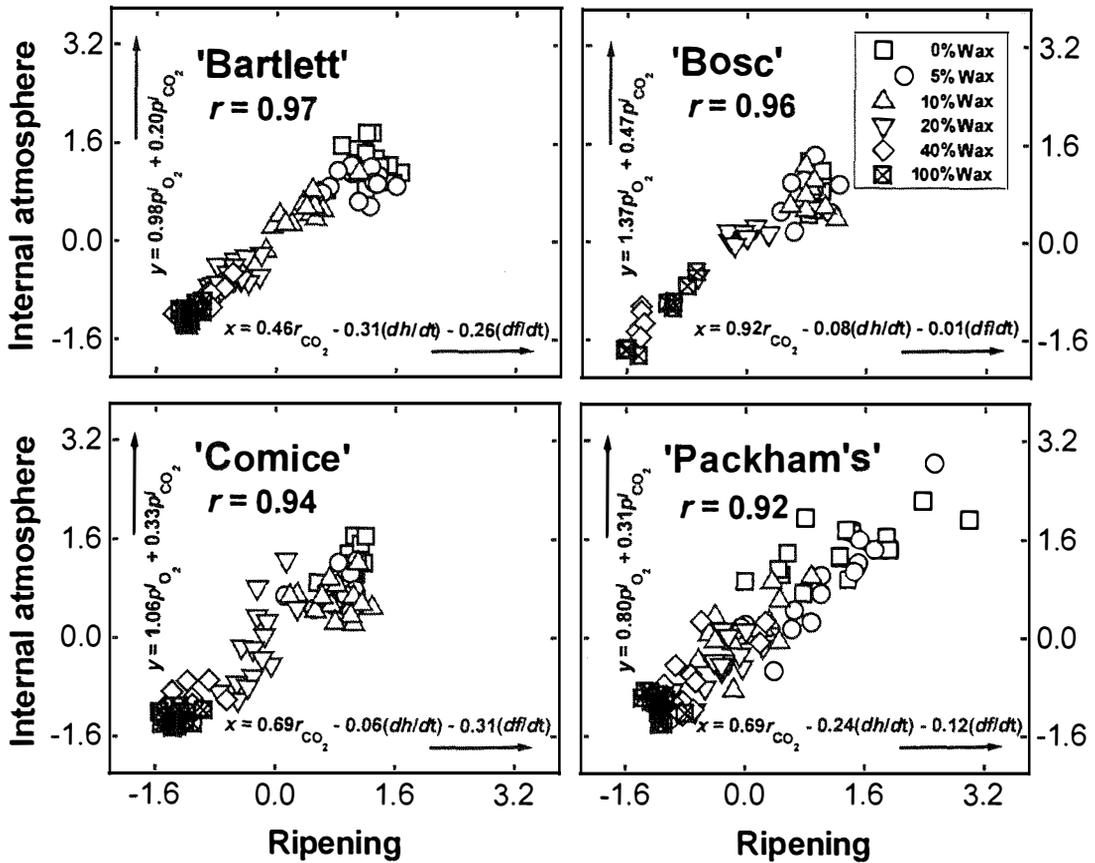


Figure 5.6 Plots of scores for the first pair of canonical variables of ripening attributes (represented by x axis and defined by linear combination of attributes r_{CO_2} , df/dt , dh/dt) and internal atmosphere composition (represented by y axis and defined by linear combination of attributes p'_{O_2} and p'_{CO_2}) of pear cultivars treated with different coating concentrations. Standardized canonical coefficients for ripening and internal atmosphere composition are represented by coefficients of each canonical variable (axis x and y). r = canonical correlation between the first pair of canonical variables.

Table 5.1 Estimated V_{max} (\pm SE) and K_m (\pm SE) of the Michaelis-Menten models $[dy/dt = (V_{max} \cdot p'_{O_2})/(K_m + p'_{O_2})]$ fitted from the plots between p'_{O_2} and df/dt (Fig. 5.2) and dh/dt (Fig. 5.3) for different pear cultivars. R^2 = determination coefficient.

Cultivar	df/dt			dh/dt		
	V_{max}	K_m	R^2 (%)	V_{max}	K_m	R^2 (%)
'Bartlett'	-2.19 ± 0.209	6.79 ± 1.525	83.23	-7.11 ± 0.671	10.80 ± 1.970	91.68
'Bosc'	-0.43 ± 0.044	6.10 ± 1.869	70.64	-2.76 ± 0.729	14.03 ± 7.309	68.49
'Comice'	-0.23 ± 0.010	1.23 ± 0.252	66.17	-2.83 ± 2.281	41.84 ± 44.135	66.45
'Packham's'	-0.69 ± 0.076	3.71 ± 0.798	66.64	-3.16 ± 1.583	22.71 ± 14.120	60.78

Table 5.2 Estimated V_{max} (\pm SE) and K_m (\pm SE) of the Michaelis-Menten models fitted for the oxidative r_{CO_2} [$r_{CO_2(ox)} = (V_{max} \cdot p'_{O_2})/(K_m + p'_{O_2})$], and constants a and b of the exponential models fitted for the fermentative r_{CO_2} [$r_{CO_2(fer)} = a \cdot e^{(b \cdot p'_{O_2})}$], from plots between total r_{CO_2} ($r_{CO_2(tot)}$) and p'_{O_2} (Figs. 5.4 and 5.5) for different pear cultivars. Fruit were coated at harvest or after cold storage. The constants a and b were estimated only for those treatments resulting in anaerobiosis. R^2 = determination coefficient for $r_{CO_2(tot)}$.

Cultivar	Coating	V_{max}	K_m	a	b	R^2 (%)
'Bartlett'	At harvest	431.00 ± 12.88	2.16 ± 0.24	-	-	89.30
	After storage	474.92 ± 24.37	2.66 ± 0.60	263.57 ± 20.38	1.45 ± 0.16	72.40
'Bosc'	At harvest	294.03 ± 21.36	8.55 ± 1.60	125.14 ± 12.36	1.36 ± 0.18	83.74
	After storage	308.18 ± 27.66	9.14 ± 2.02	137.91 ± 6.70	1.07 ± 0.12	82.52
'Comice'	At harvest	169.29 ± 3.70	1.13 ± 0.12	-	-	86.63
	After storage	175.13 ± 3.99	0.93 ± 0.10	-	-	82.78
'Packham's'	At harvest	252.90 ± 17.77	2.21 ± 0.36	-	-	69.11
	After storage	239.79 ± 10.86	1.80 ± 0.20	-	-	82.18

For all cultivars, aerobic r_{CO_2} and df/dt had much lower values for Michaelis-Menten constant (K_m ; 1.0 to 8.8 kPa for respiration and 1.2 to 6.8 kPa for softening) than dh/dt ($K_m > 10.8$ kPa; Tables 5.1 and 5.2). Substantial suppression of respiration and softening was only achieved with coating concentrations high enough to create very low $p_{\text{O}_2}^i$ (Figs. 5.2, 5.4 and 5.5). In contrast, any reduction of $p_{\text{O}_2}^i$ delayed colour change (Fig. 5.3). For a given $p_{\text{O}_2}^i$, aerobic r_{CO_2} had lower variability (Figs. 5.4 and 5.5) than df/dt (Fig. 5.2) and dh/dt (Fig. 5.3), especially for those cultivars with a long shelf life ('Bosc', 'Comice, and 'Packham's'). Small variability in dh/dt occurred at very low $p_{\text{O}_2}^i$ (Fig. 5.3), while df/dt also showed high variability at low $p_{\text{O}_2}^i$, due to its low K_m (Fig. 5.2).

When cultivars were coated at either harvest (pre-climacteric) or after cold storage (entering the climacteric), the different ripening stages were well described by respiration rates. After achieving the chilling requirement to ripen, fruit were in a much more advanced physiological stage (Fig. 5.7).

The respiratory responses to the modification of $p_{\text{O}_2}^i$ created by different coating concentrations (Figs. 5.4 and 5.5) and the LOL^i (Figs. 5.4, 5.5, and 5.8) were dependent on cultivar and ripening stage. The K_m estimated from the fitted models of aerobic r_{CO_2} , plotted against $p_{\text{O}_2}^i$, when averaged over times of coating application, were 2.4, 8.8, 1.0 and 2.0 kPa for 'Bartlett', 'Bosc', 'Comice' and 'Packham's', respectively (Table 5.2).

'Bartlett' coated at harvest did not show any signs of fermentation despite $p_{\text{O}_2}^i$ approaching 0 kPa in pears treated with undiluted coating. The total r_{CO_2} (Fig. 5.4A) and $p_{\text{CO}_2}^i$ (Fig. 5.8) were both reduced when $p_{\text{O}_2}^i$ approached 0 kPa. However, when the fruit were coated after cold storage, fermentation began when $p_{\text{O}_2}^i$ dropped below ~ 2.5 kPa (Figs. 5.5A and 5.8B). This mainly happened for fruit treated with coating concentrations $\geq 40\%$. The plots of r_{CO_2} (Fig. 5.5A) and $p_{\text{CO}_2}^i$ (Fig. 5.8B) against $p_{\text{O}_2}^i$ both showed a great variability between fruit at low $p_{\text{O}_2}^i$, with some fruit becoming anaerobic while others with a similar $p_{\text{O}_2}^i$ did not. 'Bartlett' fruit had a large variability in ripeness after one month cold storage before coating. When the ripeness of the fruit expressed

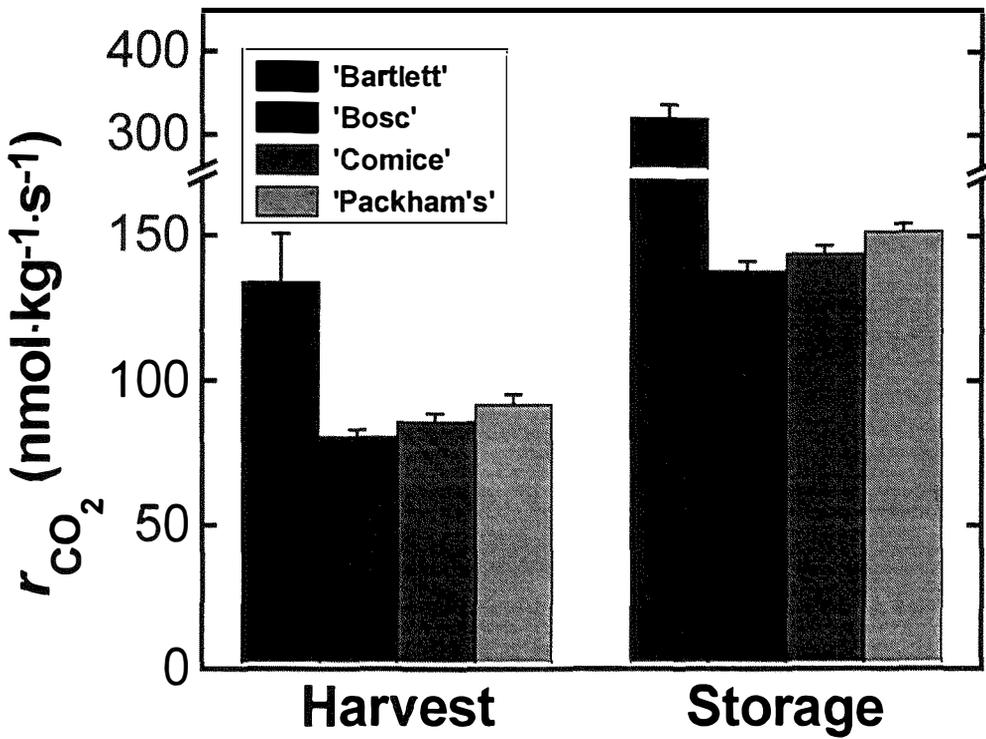


Figure 5.7 Respiration rates (r_{CO_2}) at 20°C of different pear cultivars immediately after harvest (pre-climacteric) and 24 h after removal from cold storage (entering the climacteric). Black vertical bars represent the standard error of the means (n = 15).

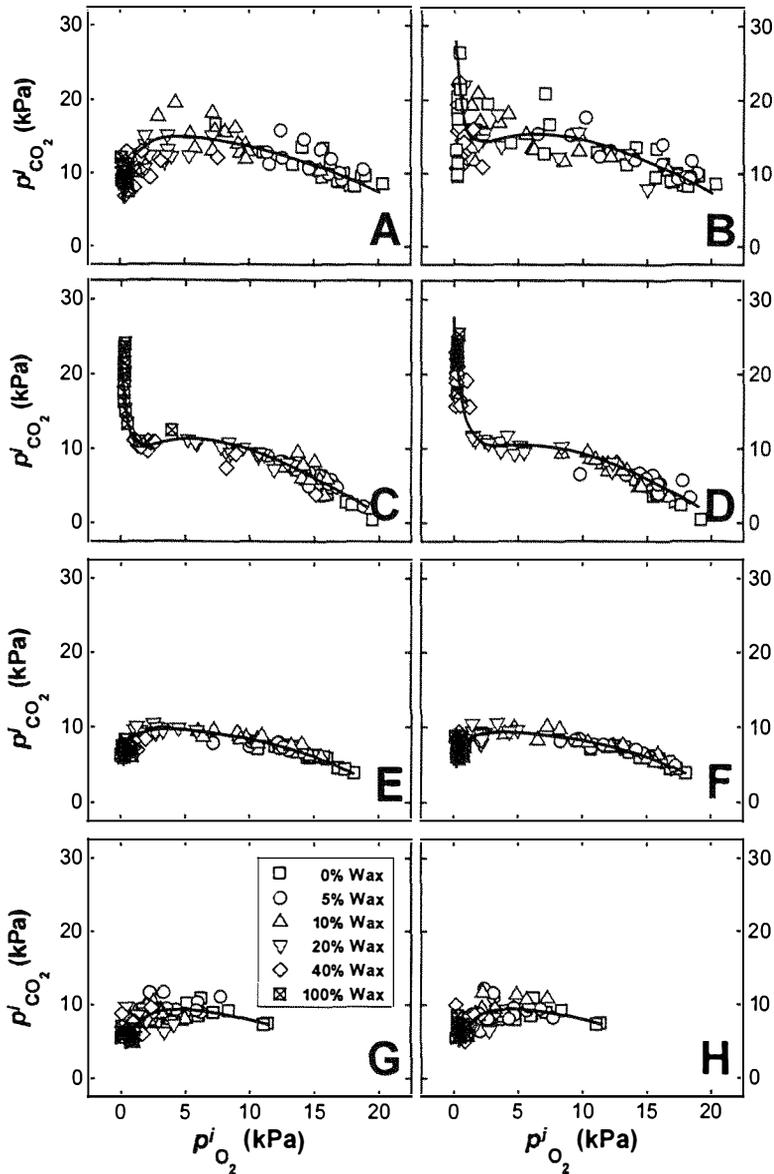


Figure 5.8 Scatter plots of internal partial pressure of O_2 ($p^i_{O_2}$) against internal partial pressure of CO_2 (p'_{CO_2}) for ‘Bartlett’ (A and B), ‘Bosc’ (C and D), ‘Comice’ (E and F), and ‘Packham’s’ (G and H) pears treated at harvest (A, C, E, and G) or after cold storage (B, D, F, and H) with different coating concentrations. Solid lines (—) represent the best fit achieved by using the mathematical model presented by Banks et al. (1997; equation 6, p. 267).

in terms of skin colour (h°) was included in the plot of p'_{O_2} versus p'_{CO_2} (Fig. 5.9) it can be seen that less ripe fruit did not become anaerobic, with a decrease in p'_{CO_2} , when p'_{O_2} approached to 0 kPa, while riper fruit became anaerobic at low p'_{O_2} , with an increase of p'_{CO_2} . Coating concentrations as low as 10% seemed to have induced anaerobiosis in very ripe fruit (Fig. 5.9). 'Bosc' pears started to ferment at p'_{O_2} below ~ 2.0 kPa when the fruit were coated at harvest with coating concentrations $\geq 40\%$ (Figs. 5.4C and 5.8C) or below ~ 3.0 kPa when the fruit were coated after cold storage with coating concentrations $\geq 20\%$ (Figs. 5.5C and 5.8D). For 'Comice' and 'Packham's', increasing the coating concentration dropped p'_{O_2} close to 0 kPa and provided progressively lower total r_{CO_2} (Figs. 5.4E, 5.4G, 5.5E and 5.5G) and p'_{CO_2} (Figs. 5.8E-5.8H), irrespective of ripening stage when the fruit were coated, indicating absence of anaerobic respiration.

'Comice' pears coated with coating concentrations $\leq 20\%$ showed small modification of internal atmosphere when in cold store, having p'_{O_2} values more than 19 kPa (Fig. 5.10A) and p'_{CO_2} less than 2 kPa (Fig. 5.10B). Fruit coated with concentrations of 40% and 100% had p'_{O_2} of about 15 and 11 kPa (Fig. 5.10A), and p'_{CO_2} of 4 and 5 kPa (Fig. 5.10B), respectively. When the fruit were removed from cold storage and left at 20°C, there was a much greater modification of p'_{O_2} than of p'_{CO_2} . Within 6 h, p'_{O_2} had almost reached to a new steady-state, while p'_{CO_2} showed an increase up to 24 h followed by a decrease, achieving steady-state after about 72 h. Increasing coating concentration substantially reduced p'_{O_2} , but there was little difference in p'_{O_2} between coating concentrations of 40% and 100%, while p'_{CO_2} increased in proportion with coating concentration.

Increasing coating concentration substantially suppressed softening during cold storage of 'Comice' pears (Fig. 5.11A) and df/dt of cold stored fruit followed an exponential model when plotted against p'_{CO_2} (Fig. 5.12) but not when plotted against p'_{O_2} (data not shown). Colour change was suppressed by coating concentrations of 40-100% but not by concentrations $\leq 20\%$ (Fig. 5.11B).

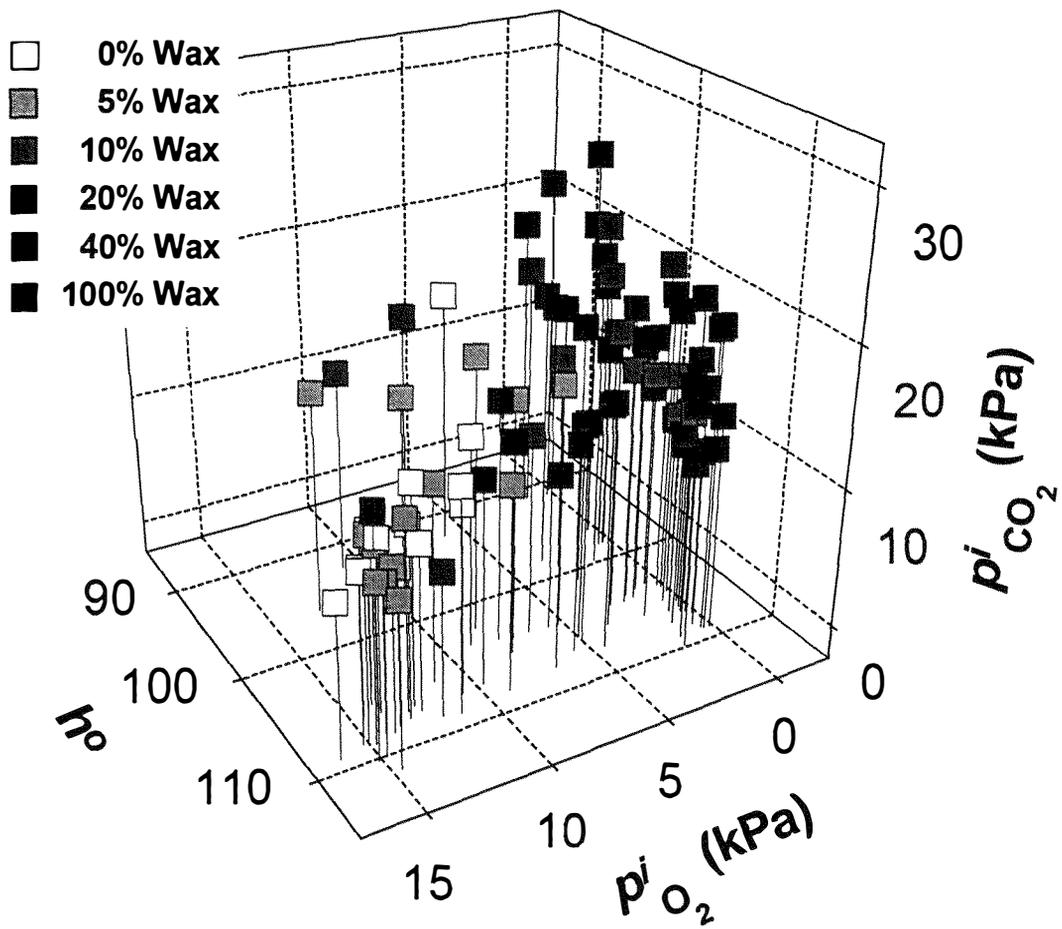


Figure 5.9 A three dimension scatter plot of internal partial pressure of O_2 ($p^i_{O_2}$), skin hue angle (h°) and internal partial pressure of CO_2 ($p^i_{CO_2}$) of 'Bartlett' pears treated after cold storage with different coating concentrations.

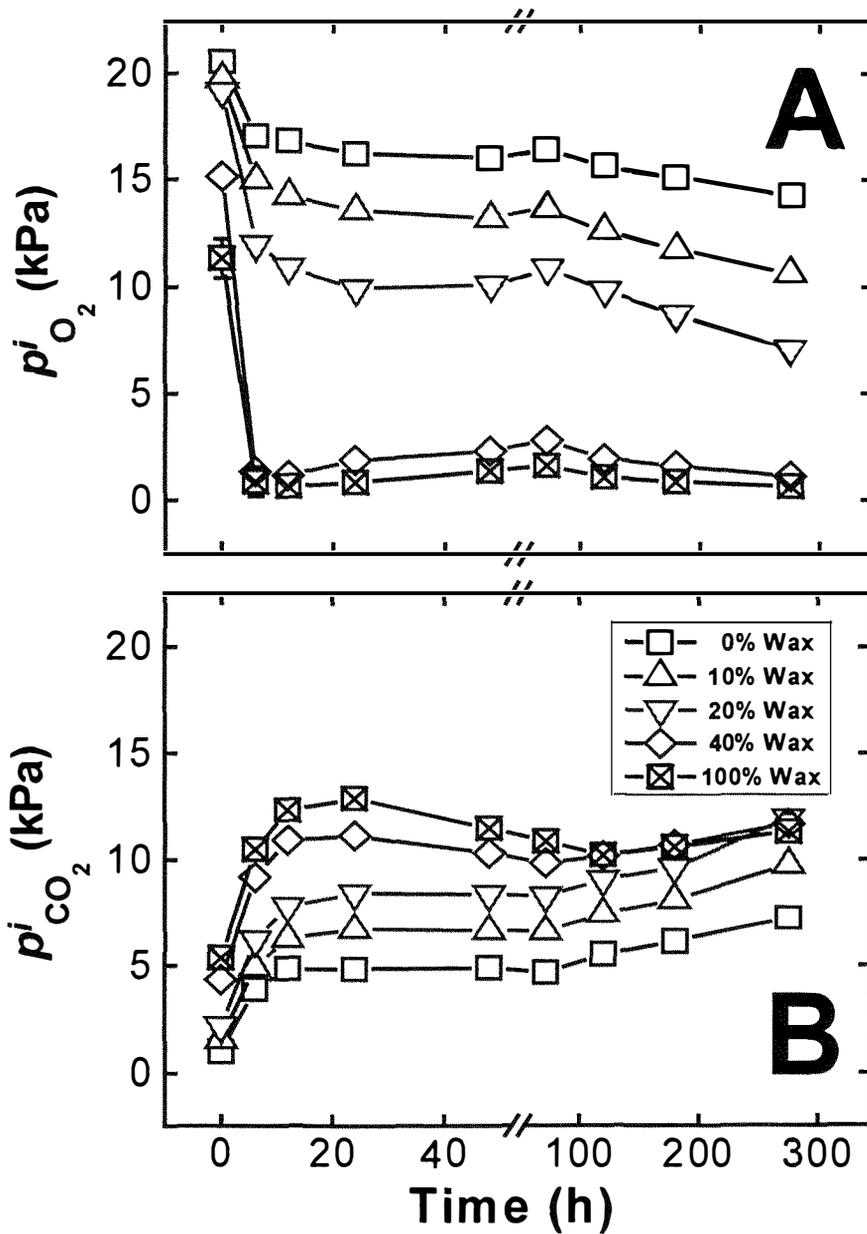


Figure 5.10 Internal partial pressure of O₂ (p'_{O_2} , **A**) and CO₂ (p'_{CO_2} , **B**) of 'Comice' pears at 0°C (first point in each graph) and during equilibration at 20°C and 60-70% RH (remaining points in each graph). Fruit were treated at harvest with different coating concentrations and left at 0 ± 0.5°C and 95-98% RH for two months before removal to 20°C and 60-70% RH. Standard errors of the means (n = 15) are smaller than symbols.

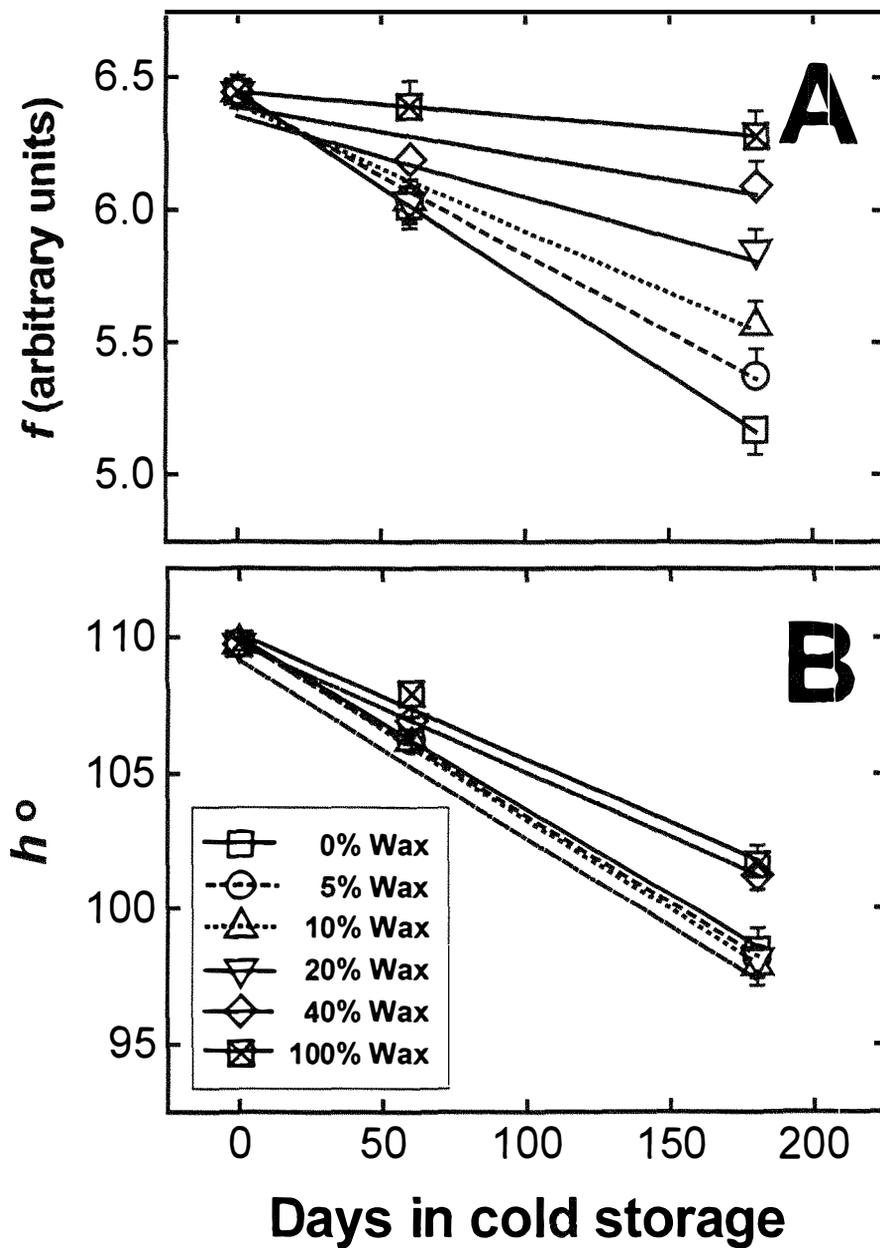


Figure 5.11 Changes in firmness (f , A) and skin hue angle (h° , B) of 'Comice' pears treated at harvest with different coating concentrations and stored at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH. Bars represent the standard errors of the means ($n = 15$). Lines represent the best fit.

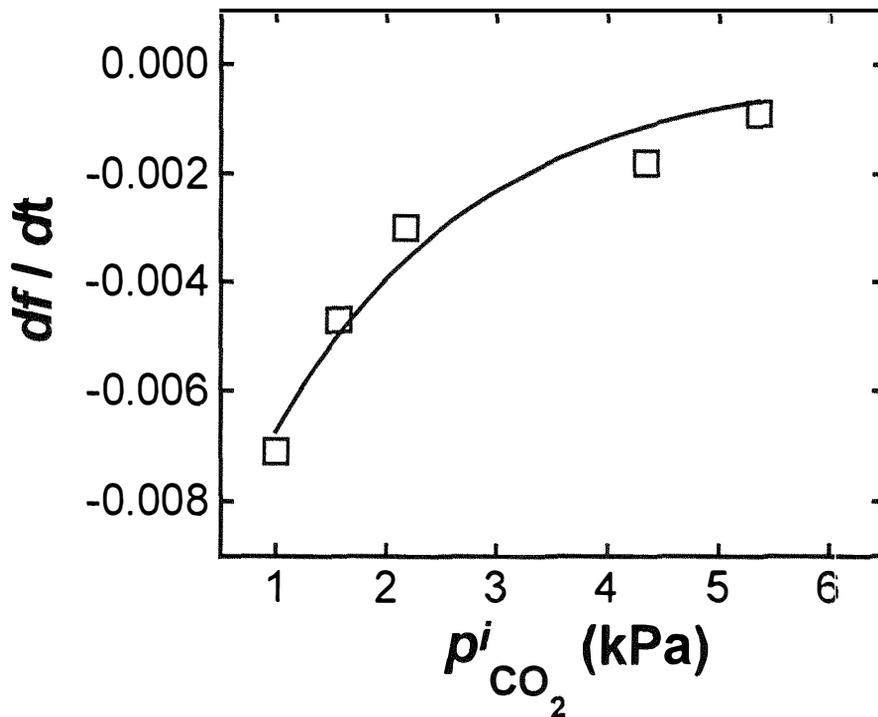


Figure 5.12 Plot of derivatives of firmness with respect to time at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH (df/dt) and internal partial pressure of CO_2 ($p^i_{\text{CO}_2}$) of ‘Comice’ pears treated at harvest with different coating concentrations. Line represents the best fit $\{y = -0.0115 (\pm 0.0019) \cdot e^{[-0.53 (\pm 0.10) x]}, R^2 = 95.55\%$.

5.5 Discussion

At ambient temperatures, for fruit in which $p^i_{O_2}$ remained above LOL^i , improving the character of cover of pears by increasing the coating concentration resulted in a larger modification of $p^i_{O_2}$ than of $p^i_{CO_2}$, consistent with reports of coating effects in other commodities (Banks et al., 1997; Ben-Yehoshua, 1966; Hagenmaier and Baker, 1993

and 1994; Kerbel et al., 1989; Magness and Diehl, 1924). This was the combined result of decreased respiration rate coupled with the selective permeability to these gases of surface coatings (Amarante et al., 1998b; Banks et al. 1993 and 1997). Amarante et al. (1998b) observed that for pears with non-lignified cells in the epidermis, increasing the coating concentration reduced the permeance of pores to gas exchange, with a greater effect on O_2 , since the pores are the main path for this gas, as opposed to CO_2 which is quite soluble in water and waxy materials of the cuticle. However, when p'_{O_2} is reduced below the LOL^i and the commodity starts fermenting, the differential effect of coating on permeance to the two gases would then have been offset by the increase in RQ , with a burst of p'_{CO_2} (as observed by the steep rise in p'_{CO_2} at very low p'_{O_2} values for 'Bosc' in Figs 5.8C and 5.8D). The plots between internal gas composition and r_{CO_2} , df/dt and dh/dt , and the results of canonical correlation analysis, support the notion that modification of p'_{O_2} rather than p'_{CO_2} was the principal means by which coating achieved its effects in delaying ripening of pears at ambient temperatures.

At low temperatures, coatings had their main effect on delaying softening rather than colour change, the opposite of the pattern observed at ambient temperatures. This difference appears to have been the result of a differential response of softening and skin colour change to gas composition at different temperatures. The degreening of the skin was highly dependent on p'_{O_2} at ambient temperatures; this also seems likely to be true at low temperatures. As it was only coating concentrations of 40-100% that substantially reduced p'_{O_2} at low temperatures, only these treatments had a small effect in delaying colour change during cold storage. Since rate of softening in 'Comice' was greatly suppressed only when p'_{O_2} was reduced below ~ 2.5 kPa at ambient temperatures (Fig. 5.2E), and coatings did not drop p'_{O_2} to such low levels during cold storage, it seems likely to have been the increase in p'_{CO_2} of fruit left in cold storage that played a major role in suppressing fruit softening (Fig. 5.12).

During cold storage of 'Comice', increasing coating concentration resulted in a increase of p'_{CO_2} while p'_{O_2} was depressed to no less than 10 kPa for fruit treated with

undiluted coating (time zero of Figs. 5.10A and 5.10B). Coated apples have been reported to have substantially higher p'_{CO_2} than non-coated fruit during cold storage (> 10 kPa for coated fruit and about 2 kPa for the controls; Magness and Diehl, 1924), or immediately after removal from cold storage (4 to 6 kPa for coated fruit and 1 to 2 kPa for the controls; Kerbel et al., 1989; Lau and Yastremsky, 1991), while p'_{O_2} was no less than 15-16 kPa in coated fruit (Kerbel et al., 1989; Lau and Yastremsky, 1991). Greater reductions of respiration rate are achieved by reducing p'_{O_2} below 4-5 kPa for apples (Dadzie et al., 1996; Yearsley et al. 1996). Similar results were observed in our study for pears, except for 'Bosc', that had a high K_m . These values are much lower than the p'_{O_2} of coated apples (Kerbel et al., 1989; Lau and Yastremsky, 1991; Magness and Diehl, 1924) and pears (Fig. 5.10A) in cold storage. At 20°C the solubility in water of CO₂ is more than 25 times higher than that of O₂, and this difference increases as temperature decreases as a result of a much higher increase of CO₂ than of O₂ solubility (Foust et al., 1980). This implies that for the same p'_{O_2} and p'_{CO_2} in the intercellular gas phase, there would be much higher concentrations of CO₂ than of O₂ dissolved in the cell sap of fruit stored at lower temperatures. Therefore, the increased p'_{CO_2} in the intercellular space at low temperature observed for coated fruit, combined with the greater solubility of CO₂ in the cell sap in such conditions, would have resulted in a substantial increase of CO₂ concentration in the liquid phase. This could have been the cause of the larger effect of p'_{CO_2} in delaying some aspects of ripening (softening) of coated commodities left at low temperature while, at high temperature, the larger reduction of p'_{O_2} would have become the dominant effect in delaying ripening.

Softening had lower K_m 's than skin colour for all pear cultivars left at ambient temperatures. Thus, small reductions in p'_{O_2} could substantively delay colour change but not softening, which was substantially reduced only at much lower p'_{O_2} . The higher sensitivity of colour change than softening to p'_{O_2} may have important implications on postharvest quality of coated commodities. The commodity may fail to change in colour while still being able to soften during shelf life when treated with coatings

(Amarante et al., 1998a; Smith and Stow, 1984) or stored in plastic films (Geeson et al., 1991a and 1991b). For pears (Amarante et al., 1998a; Meheriuk and Lau, 1988) and bananas (Blake, 1966; Ben-Yehoshua, 1966), coatings can cause uneven colour change characterised by skin blotchiness, with yellow areas interspersed with green tissue. This may be the result of uneven cover of the skin, with the coating failing to block some large pores. The skin and flesh tissues of pears and bananas can have large resistance to gas exchange, especially when the fruit ripens, as a result of flooding of intercellular spaces. This may create substantial gradients of p'_{O_2} between different areas under the skin. While the high p'_{O_2} in tissues near the uncovered skin would allow chlorophyll degradation, on covered areas nearby, the p'_{O_2} would be low enough to inhibit colour change.

Coated pears may have variable fruit quality in relation to firmness and colour change during shelf life. There was a naturally high variability for softening and colour change between fruit that had high and similar p'_{O_2} (Figs. 5.2 and 5.3). Coating the fruit with low to intermediate coating concentrations may result in a large variability in skin permeance to O_2 (Amarante et al., 1998b) and p'_{O_2} between fruit coated with the same coating concentration (Figs. 5.2-5.5 and Fig. 5.8). Colour change would be the most affected by this as a result of its high K_m for p'_{O_2} (Table 5.1 and Fig. 5.3), increasing the natural variability between fruit with the increase in p'_{O_2} variability between coated fruit. Treating the fruit with high coating concentrations dropped p'_{O_2} to such low levels that in some cases colour change was almost totally inhibited (Fig. 5.3). The variability of p'_{O_2} for fruit coated with low to intermediate coating concentrations (medium to high p'_{O_2} values) would not substantially suppress softening or increase the natural variability in softening between fruit, because of its low K_m for p'_{O_2} (Table 5.1). On the other hand, the variability in p'_{O_2} for fruit treated with high coating concentrations (low p'_{O_2} values) resulted in large variability in softening between fruit receiving the same coating treatment.

For cultivars having the risk of fermentation at low p'_{O_2} , this problem could be minimized by reducing the coating concentration to avoid excessive reduction of skin

permeance though, with such an approach, only small beneficial effects would be achieved in delaying ripening during cold storage and in suppressing respiration and softening during shelf life. For cultivars tolerant to hypoxia, high coating concentrations should be preferred to achieve most of the beneficial effects of coating in delaying ripening, reducing the incidence of senescence related disorders (Amarante et al., 1998a), reducing water loss (Amarante et al., 1998b) and friction discolouration of the skin (Amarante et al., 1998c), and to provide a more efficient cover of all pores to avoid the uneven skin colour change (Amarante et al., 1998a).

The fitted models for aerobic r_{CO_2} and p'_{O_2} (Table 5.2) indicated that for 'Bosc', as a result of its high K_m , there is potential to reduce r_{CO_2} by modest reductions in p'_{O_2} while, for the other cultivars with lower K_m , there was a substantial reduction of r_{CO_2} only by reducing p'_{O_2} below ~ 5 kPa. The results also indicated that cultivar and ripening stage of the fruit at the time of coating affected LOL^i . 'Comice' and 'Packham's' did not seem to become anaerobic, even with p'_{O_2} close to 0 kPa for fruit coated at different ripening stages with high coating concentrations. 'Bosc' was at risk of anaerobiosis at low very p'_{O_2} created by high coating concentrations, and there was an increase in the LOL^i when fruit were coated entering the climacteric (coated after cold storage). 'Bartlett' did not become anaerobic when treated with high coating concentrations at the pre-climacteric stage (coated at harvest) but started to ferment if treated when entering the climacteric (coated after cold storage), indicating increased LOL^i for 'Bartlett' fruit coated in a more advanced ripening stage. These results are in agreement with previous observations that cultivars differ in tolerance to hypoxia (Kader et al., 1989; Yearsley et al., 1997a) and that fruit in a more advanced ripening stage are generally more sensitive to hypoxic conditions (Boersig et al., 1988; Ke et al., 1993; Nanos et al., 1992). Boersig et al. (1988) found that pears in a more advanced ripening stage had a higher external anaerobic compensation point that the authors attributed to a decrease of the O_2 diffusion coefficient during ripening. This may result from clogging of the intercellular air spaces as a result of cellular leakage as the fruit age, that is likely to be the case with pears. However, given that internal

atmosphere composition formed the basis for characterising *LOL* in the current study, it seems likely that this change in sensitivity to hypoxia represents a genuine metabolic change in the fruit tissue. Nanos et al. (1992) reported that pears stored for two weeks at 0°C ripened normally, while those that had been stored for eight weeks at 0°C failed to recover normal ethylene and CO₂ production upon transfer to air after four days exposure to 0.25% O₂ at 20°C. These observations imply that pre-climacteric pears are both less stressed during hypoxia and have greater potential for post-hypoxia repair than pears of a more advanced physiological age. According to the authors, increased post-hypoxia respiratory and enzymatic activity and the elaboration of new alcohol dehydrogenase isoenzymes appeared to be part of the repair response. For peaches and pears exposed to 0.25% O₂ at 20°C for three to six days, more acetaldehyde and ethanol were accumulated in fruit in a more advanced ripening stage (Ke et al., 1993). These observations are consistent with the hypothesis of a decline in repair capacity during the later phases of the climacteric in the context of homeostasis and senescence as discussed by Romani (1987). It is possible that disorganization of mitochondrial activity, starting with the respiratory climacteric, may lead to loss of tight metabolic control and contribute to the increase of *LOL*ⁱ of ‘Bartlett’ and ‘Bosc’. In contrast, ‘Comice’ and ‘Packham’s’, two cultivars with long storage potential, may maintain a tight metabolic control of mitochondrial activity, being more tolerant to hypoxic conditions despite at a more advanced ripening stage after achieving the chilling requirement.

Overall, this paper has demonstrated the potential to use coatings to characterise ripening behaviour and *LOL*ⁱ based upon internal atmosphere composition. The markedly different behaviour of fruit from different cultivars to similar treatments and similar levels of internal atmosphere modification illustrate the complexity of interactions involved in control of the ripening process. It would be well worthwhile to explore possibilities to explain variations in storage behaviour, including disorder development, through such mechanisms.

5.6 Conclusion

Increasing coating concentration substantially delayed pear ripening at ambient temperature by reducing p'_{O_2} , with larger effects achieved in delaying change in colour than in reducing softening and respiration rate. The naturally high variability in skin colour change between fruit during the shelf life was exacerbated with more diluted coating formulations. At low temperature, coating seemed to delay softening by increasing p'_{CO_2} , while colour change seemed to be delayed by the slight reduction of p'_{O_2} .

'Comice' and 'Packham's' seemed to have a high tolerance to hypoxic conditions and may benefit from high coating concentrations to reduce water loss and delay ripening during cold storage and shelf life. 'Bartlett' and 'Bosc' tolerance reduced with advancing ripening, and the latter cultivar was the least tolerant of all cultivars. 'Bartlett' was tolerant to hypoxia if coated at harvest, while the same did not happen with 'Bosc'.

From these findings, it is clear that the optimisation of surface coatings should take into account differences between cultivars and ripening stage at which fruit are coated.

5.7 References

- Amarante, C., Banks, N.H. and Ganesh, S., 1998a. Ripening behaviour, postharvest quality and physiological disorders of coated pears. *Postharvest Biology and Technology* (in preparation).
- Amarante, C., Banks, N.H. and Ganesh, S., 1998b. Relationship between character of skin cover and permeance to gases of coated pears. *Postharvest Biology and Technology* (in preparation).
- Amarante, C., Banks, N.H. and Ganesh, S., 1998c. Effects of coating concentration, ripening stage, water status and fruit temperature on pear susceptibility to friction discoloration. *Postharvest Biology and Technology* (in preparation).
- Baldwin, E.A., 1994. Edible coatings for fresh fruits and vegetables: past, present, and future. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 25-64.
- Banks, N.H., 1983. Evaluation of methods for determining internal gases in banana fruit. *Journal of Experimental Botany*, 34: 871-879.
- Banks, N. H., Dadzie, B. K. and Cleland, D. J., 1993. Reducing gas exchange of fruits with surface coatings. *Postharvest Biology and Technology*, 3: 269-284.
- Banks, N. H., Cutting, J. G. M. and Nicholson, S. E., 1997. Approaches to optimising surface coatings for fruits. *New Zealand Journal of Crop and Horticultural Science*, 25: 261-272.
- Ben-Yehoshua, S., 1966. Some effects of plastic skin coating on banana fruit. *Tropical Agriculture*, 43: 219-232.
- Blake, J. R., 1966. Some effects of paraffin wax emulsions on bananas. *Queensland Journal of Agricultural and Animal Sciences*, 23: 49-56.
- Boersig, M. R., Kader, A. A. and Romani, R. J., 1988. Aerobic-anaerobic respiratory transition in pear fruit and cultured pear fruit cells. *Journal of the American Society for Horticultural Science*, 113: 869-873.
- Cameron, A. C., Beaudry, R. M., Banks, N. H. and Yelenich, M., 1994. Modified-atmosphere packaging of blueberry fruit: Modeling respiration and package oxygen concentrations at different temperatures. *Journal of the American Society for Horticultural Science*, 119: 534-539.
- Dadzie, B.K., Banks, N.H., Cleland, D.J. and Hewett, E.W., 1996. Changes in respiration and ethylene production of apples in response to internal and external oxygen partial pressures. *Postharvest Biology and Technology*, 9: 297-309.
- Foust, A.S., Wenzel, L.A., Clump, C.W., Maus, L. and Andersen, L.B., 1980. *Principles of unit operations*. 2nd edition. John Wiley, New York, 768 pp.

- Geeson, J. D., Genge, P. M., Smith, S. M. and Sharples, R. O., 1991a. The response of unripe Conference pears to modified atmosphere retail packaging. *International Journal of Food Science and Technology*, 26: 215-223.
- Geeson, J. D., Genge, P. M., Sharples, R. O. and Smith, S. M., 1991b. Limitations to modified atmosphere packing for extending the shelf-life of partly ripened Doyenné du Comice pears. *International Journal of Food Science and Technology*, 26: 225-231.
- Gran, C.D. and Beaundry, R.M., 1993. Determination of the low oxygen limit for several commercial apple cultivars by respiratory quotient breakpoint. *Postharvest Biology and Technology*, 3: 259-267.
- Hagenmaier, R.D. and Baker, R.A., 1993. Reduction in gas exchange of citrus fruit by wax coatings. *Journal of Agricultural and Food Chemistry*, 41: 283-287.
- Hagenmaier, R.D. and Baker, R.A., 1994. Internal gases, ethanol content and gloss of citrus fruit coated with polyethylene wax, carnauba wax, shellac or resin at different application levels. *Proceedings of the Florida State Horticultural Society*, 107: 261-265.
- Kader, A.A., 1989. Mode of action of oxygen and carbon dioxide on postharvest physiology of 'Bartlett' pears. *Acta Horticulturae*, 258: 161-167.
- Kader, A.A., Zagory, D. and Kerbel, E.L., 1989. Modified atmosphere packaging of fruits and vegetables. *Critical Reviews in Food Science and Nutrition*, 28: 1-30.
- Ke, D., and Kader, A. A., 1992. External and internal factors influence fruit tolerance to low-oxygen atmospheres. *Journal of the American Society for Horticultural Science*, 117: 913-918.
- Ke, D., Mateos, M. and Kader, A. A., 1993. Regulation of fermentative metabolism in fruits and vegetables by controlled atmospheres. *Proceedings from the Sixth International Controlled Atmosphere Research Conference, Cornell University, Ithaca, New York*. pp. 63-77.
- Kerbel, E. L., Mitchell, F. G., Kader, A. A. and Mayer, G., 1989. Effects of "Semperfresh" coating on postharvest life, internal atmosphere modification and quality maintenance of 'Granny Smith' apples. *Proceedings from the Fifth International Controlled Atmosphere Research Conference, Washington State University, Wenatchee*. pp. 247-254.
- Lau, O. L., and Yastremski, R., 1991. Retention of quality of 'Golden Delicious' apples by controlled- and modified-atmosphere storage. *HortScience*, 26: 564-566.
- Magness, J. R. and Diehl, H. C., 1924. Physiological studies on apples in storage. *Journal of Agricultural Research*, 27: 1-38.
- Meheriuk, M. and Lau, O. L., 1988. Effect of two polymeric coatings on fruit quality of 'Bartlett' and 'd'Anjou' pears. *Journal of the American Society for Horticultural Science*, 113: 222-226.

- Mellenthin, W.M., Chen, P.M. and Borgic, D.M., 1982. In-line application of porous wax coating materials to reduce friction discolouration of 'Bartlett' and 'd'Anjou' pears. *HortScience*, 17: 215-217.
- Nanos, G. D., Romani, R. J. and Kader, A. A., 1992. Metabolic and other responses of 'Bartlett' pear fruit and suspension-cultured 'Passa Crassane' pear fruit cells held in 0.25% O₂. *Journal of the American Society for Horticultural Science*, 117: 934-940.
- Peppelenbos, H. W., Tijskens, L. M. M., van't Leven, J. and Wilkinson, E. C., 1996. Modelling oxidative and fermentative carbon dioxide production of fruits and vegetables. *Postharvest Biology and Technology*, 9: 283-295.
- Richardson, D. G. and Gerasopoulos, D., 1993. Controlled atmosphere recommendations for pear fruits and storage chilling satisfaction requirements for ripening winter pears. *Acta Horticulturae*, 367: 452-454.
- Romani, R. J., 1987. Senescence and homeostasis in postharvest research. *HortScience*, 22: 865-868.
- SAS, 1990. SAS Institute INC. Cary, NC.
- Smith, S. M. and Stow, J. R., 1984. The potential of a sucrose ester coating material for improving the storage and shelf-life qualities of Cox's Orange Pippin apples. *Annals of Applied Biology*, 104: 383-391.
- Smith, S., Geeson, J. and Stow, J., 1987. Production of modified atmospheres in deciduous fruits by the use of films and coatings. *HortScience*, 22: 772-776.
- Yearsley, C.W., Banks, N.H., Ganesh, S. and Cleland, D.J., 1996. Determination of lower oxygen limits for apple fruit. *Postharvest Biology and Technology*, 8: 95-109.
- Yearsley, C. W., Banks, N. H. and Ganesh, S., 1997a. Temperature effects on the internal lower oxygen limits of apple fruit. *Postharvest Biology and Technology*, 11: 73-83.
- Yearsley, C. W., Banks, N. H. and Ganesh, S., 1997b. Effect of carbon dioxide on the internal lower oxygen limits of apple fruit. *Postharvest Biology and Technology*, 12: 1-13.

Effects of Coating Concentration, Ripening Stage, Water Status and Fruit Temperature on Pear Susceptibility to Friction Discolouration

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6.1 Abstract

Pear fruit (*Pyrus communis* L. cv 'Doyenne du Comice') were treated at harvest with different concentrations of a water-based carnauba wax emulsion and assessed for susceptibility to friction discolouration (FD) after different periods in cold storage. Susceptibility to FD was low at harvest and increased substantially with prolonged storage, with a larger increase occurring from one to two months storage than during the first month of storage. The relationship between coating concentration and FD followed a hyperbolic model, with large incremental reductions in FD being achieved by increasing coating concentration from 0% to 20% and from 0% to 40% for fruit damaged after one and two months storage, respectively. Increasing coating concentration reduced FD by providing a thicker coating layer that protected the skin from damage, and blocked the pores in the skin, reducing the internal O₂ partial pressure available for enzymatic browning. The lower internal O₂ level in coated fruit also delayed ripening, reducing fruit susceptibility to FD. Reducing fruit water loss preserved the integrity of skin and reduced susceptibility to FD. There was a quadratic relationship between fruit temperature and susceptibility to FD, with higher levels of FD being observed at temperatures lower or higher than 10-20°C. However, presence

of water condensation on cold fruit during friction damage incurred at ambient temperature, reduced the severity of skin browning. Higher coating concentrations were required to reduce FD of fruit left in cold storage for longer. The physical protection provided by skin coatings in combination with their effects in reducing the internal O₂ partial pressure and delaying ripening, presents a useful opportunity to reduce FD after cold storage, if adopted in conjunction with adequate temperature and humidity control during storage and post-storage handling of the fruit.

Keywords: Pear; *Pyrus communis* L.; friction discolouration; modified atmosphere; surface coating; wax; optimisation; browning; ripening stage; water status; temperature.

6.2 Introduction

Friction discolouration (FD) is one of the most serious postharvest problems in the pear industry (Mellenthin and Wang 1974; Wang and Mellenthin, 1973). This disorder is characterised by diffuse, brown skin discolouration, especially at high points on irregular fruit surfaces, following friction damage of the skin during the postharvest handling of the fruit (Meheriuk et al. 1994). The unsightly browning of the skin detracts from the appearance and consumer acceptance of the fruit (Raese, 1989). In New Zealand, packouts for pears vary from 35 to 75%, depending on cultivar, with fruit being rejected mainly as a result of friction damage (Mannering, 1996).

Most plant cells, especially in pear skin, undergo enzymatic browning when injury exposes the cell contents to O₂. In injured epidermal cells phenolic compounds (mainly *o*-dihydroxy phenols) are enzymatically oxidised by polyphenol oxidase (PPO; E.C 1.10.3.2, also called diphenol oxygen oxidoreductase or catechol oxidase) to form unstable quinone compounds (Mayer, 1987). The quinones rapidly condense and can combine with amino or sulfhydryl groups of proteins, forming relatively insoluble dark brown polymers (Macheix et al., 1990; Wang and Mellenthin 1973, 1974). In a normal

intact cell phenols are sequestered in the vacuole, whilst PPO is bound within chloroplast lamellae and grana (Mayer and Harel, 1979) or is soluble in the cytoplasm (Macheix et al., 1990). Mechanical damage of the cells causes loss of cellular compartmentalization bringing substrate and enzyme in contact, triggering the browning reaction (Macheix et al., 1990; Mayer and Harel, 1979).

Chlorogenic acid (5'-caffeoylquinic acid), (+)-catechin, and (-)-epicatechin are the most abundant phenolics (Ranadive and Haard, 1971; Amiot et al., 1995) and the main substrates of PPO in pears (Rivas and Whitaker, 1973; Walker, 1964). The skin of pears has a higher content of these phenols (Amiot et al., 1995) and a higher activity of PPO (Rivas and Whitaker, 1973) than the flesh and, therefore, a higher susceptibility to browning following mechanical damage. Amiot et al. (1995) reported a higher content of flavanols than of hydroxycinnamic ester in pears skin. This may indicate that the catechins, rather than chlorogenic acid, are the main substrates for PPO following mechanical damage of pear skin. Vámos-Vigyázó and Nádudvari-Márkus (1982) also observed that the enzymatic browning of pears was mainly related to fruit content of phenols other than chlorogenic acid.

Cultivar, fruit size, maturity and ripening stage are well known to affect pear susceptibility to FD. Cultivars having a higher phenolic content in the skin have higher susceptibility to the disorder (Amiot et al., 1995; Ranadive and Haard, 1971; Vámos-Vigyázó and Nádudvari-Márkus, 1982). Larger (Mellenthin and Wang, 1974) or more mature fruit are less susceptible (Kvåle, 1979 and 1988; Mellenthin and Wang, 1974) while riper fruit are more susceptible to FD (Amiot et al., 1995; Kvåle, 1988; Mellenthin and Wang, 1974; Smith, 1946; Wang and Mellenthin, 1973). The degree of browning depends on phenolics content and PPO activity. The ratio of enzyme activity and substrate content determines whether browning rates of a given fruit correlate with PPO activity or with phenols content (Vámos-Vigyázó, 1981). For pears, the changes in susceptibility to FD with maturity and degree of ripening seems to be related to phenol composition of the fruit, but not with PPO activity. Higher phenol content and higher susceptibility to friction discolouration were observed in fruit of lower maturity

(Kvåle, 1979; Mellenthin and Wang, 1974) or more advanced ripening stage (Amiot et al., 1995; Wang and Mellenthin, 1973). Less mature and riper pears were reported to have lower PPO activity (Mellenthin and Wang, 1974). Vámos-Vigyázó and Nádudvari-Márkus (1982) observed that differences in browning susceptibility between pear cultivars could be accounted for mainly by differences in phenol composition instead of PPO activity.

PPO is mainly insoluble, found bound to cellular membranes or conjugated to macromolecules in an inactive form (Mayer and Harel, 1979; Vámos-Vigyázó, 1981). The protein solubilization and activation occurs during ripening, aging, or under stress conditions (Mayer and Harel, 1979). In apple tissue culture there was an increase in the soluble form of the enzyme with aging or exposure to low ambient humidity (Volk et al., 1977). Mechanical injury and microorganism infection may also cause an increase in the soluble form of the enzyme in plant tissues (Mayer and Harel, 1979). Therefore, it is reasonable to assume that ripening and stress conditions (such as excessive water loss) can also increase pears susceptibility to FD by increasing the solubilization and the activation of PPO in the skin. This may also explain the lack of correlation between total extractable PPO activity or its total endogenous content and the susceptibility to browning of pears (Vámos-Vigyázó and Nádudvari-Márkus, 1982), as it is only the soluble fraction of the enzyme that seems to be mainly involved in browning (Mayer and Harel, 1979).

Antioxidants such as ascorbic acid and sulphur dioxide and the enzyme inhibitor 2-mercaptobenzothiazole reduce or prevent pear skin browning (Wang and Mellenthin 1974; Meheriuk et al. 1994). However, no chemicals have been registered for reducing FD of pears (Meheriuk et al. 1994).

To reduce FD on pears the fruit should be harvested at the correct maturity and graded and packed as soon as possible after harvesting. However, with increasing production of other pipfruit, especially apples, pears are no longer packed as soon as they are harvested, leading to longer storage periods in bins. Therefore, the adoption of postharvest handling and storage procedures to delay ripening and retain postharvest

quality may be beneficial in prolonging the storage period before packing. Fast cooling, reduced fruit water loss, storage at the correct temperature and CA/MA storage may be beneficial in this respect. According to Meheriuk et al. (1994), if pears are packed directly from cold storage, they should be packed cold and not warmed during packing to reduce scuffing and increase storage life. However, a conflicting observation was made by Kvåle (1979) who reported that grading pears immediately after removal from cold storage increased FD compared to delayed grading.

In banana (Banks and Joseph 1991) and apple (Johnson and Dover 1990), highly turgid fruits have been reported to be more susceptible to impact damage (bruising) than those at lower turgor. However, the effect of fruit water status to impact may be different to friction damage, and no such relationship has been demonstrated in pears.

Since the fruit surface does not discolour unless epidermal cells are mechanically injured, the application of coatings to pear fruit surface should reduce discolouration by reducing friction injury to epidermal cells. Moreover, surface coatings block pores in the skin reducing permeance to water vapour and gases (Amarante et al., 1998b; Ben-Yehoshua et al. 1985). This reduces water loss and internal O₂ partial pressure, delaying fruit ripening (Amarante et al., 1998c). Since susceptibility to FD increases with ripening (Amiot et al., 1995; Kvåle, 1988; Mellenthin and Wang, 1974; Smith, 1946; Wang and Mellenthin, 1973) and water loss (Mayer and Harel, 1979; Volk et al., 1977), coatings may offer some scope to reduce friction damage. Coatings may also reduce FD by lowering the fruit internal concentration of O₂, a co-substrate required for the enzymatic browning reaction. Application of polymeric coatings has delayed ripening (Amarante et al., 1998a and 1998c; Meheriuk and Lau 1988) and reduced FD (Mellenthin et al. 1982) in pears. However, although improving retention of quality, coatings may predispose some pear cultivars to internal disorders and poor ripening (Amarante et al., 1998a and 1998c; Meheriuk and Sholberg 1990).

This investigation characterises the effects of coating concentration, ripening stage, water loss and fruit temperature on susceptibility to FD of 'Doyenne du Comice', a pear cultivar highly susceptible to skin browning following mechanical damage.

6.3 Materials and methods

Pears (*Pyrus communis* L. cv. 'Doyenne du Comice') were harvested from Fruit Crops Unit orchard at Massey University at commercial maturity in 1996 and 1997, based on ENZA New Zealand (International) maturity index charts. For the coating experiments fruit were treated with a water-based carnauba wax emulsion (Capsicum/Zucchini Wax[®] Castle Chemicals, Australia) at different dilutions of the commercial formulation, as described by Amarante et al. (1998a), before storage at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH.

In the 1996 experiment, fruit were treated with coating concentrations of 0, 20, 40, 60, 80, and 100% (v/v) and stored in non-lined single layered boxes at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH. At harvest and after one and two months in cold storage, 25 fruit from each treatment were equilibrated for eight hours at 20°C and 60-70% RH and then given friction treatment by placing them on polyethylene brushes (Fig. 6.1) rotating at 110 rpm, for four minutes. They were subjectively assessed for friction discolouration 24 h later on a scale from 1 (= no visual discolouration) to 10 (= very badly discoloured; Fig. 6.2). To characterise the relationship between exposure time at ambient conditions after removal from the cold storage and friction damage susceptibility, groups of 25 fruit from each coating treatment were left in cold storage for two months and then submitted and assessed for FD as described before, after equilibration for 0, 8, 24 and 48 h at 20°C and 60-70% RH.

In the 1997 experiment, fruit were treated with coating concentrations of 0, 5, 10, 20, 40, and 100% (v/v), and stored in non-lined single layered boxes at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH for two and a half months. Groups of 22 fruit per treatment were weighed after coating and again after cold storage, 12 h after equilibration at 20°C and 60-70% RH, to assess total weight loss of each coating treatment. Respiration rate (r_{CO_2} , $\text{nmol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$), permeance to water vapour ($P'_{\text{H}_2\text{O}}$, $\text{nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$), firmness (f , arbitrary units) and skin hue angle (h°) were assessed as described by Amarante et al. (1998a and 1998b), after 24 h equilibration at 20°C and 60-70% RH. Fruit were then

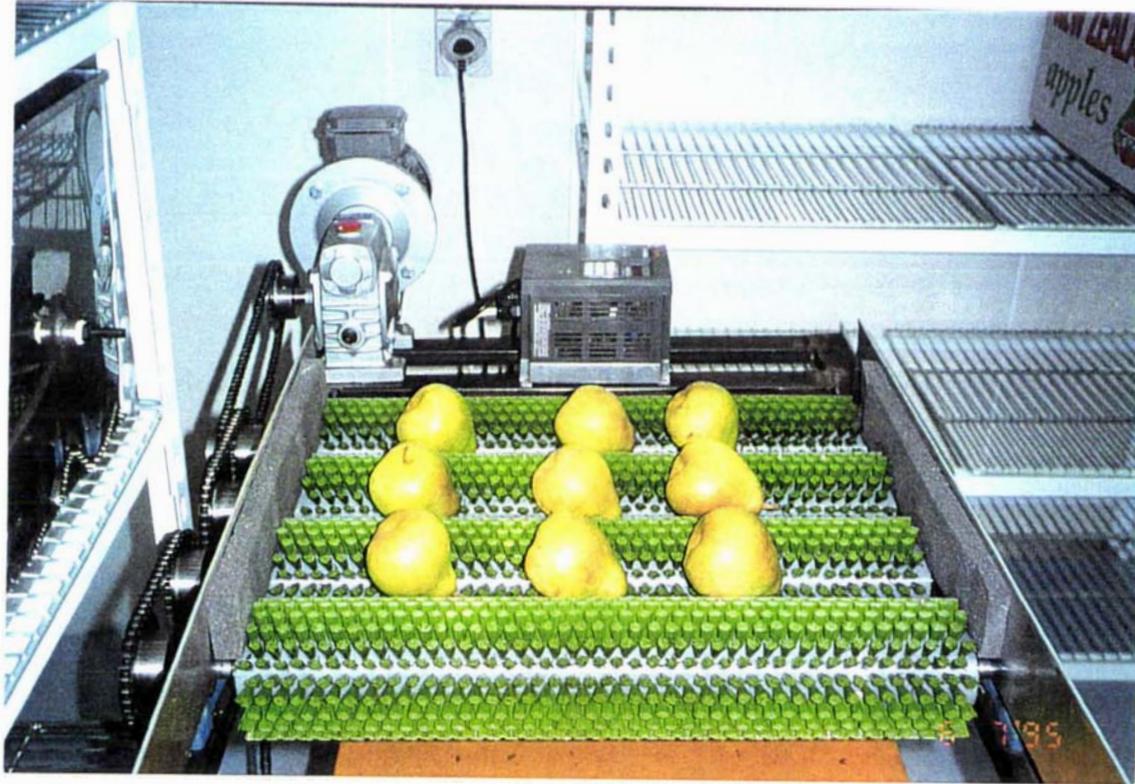


Figure 6.1 Polyethylene brushes used to cause friction damage on pears.



Figure 6.2 Scale for FD assessment on 'Comice' pears.

submitted to friction treatment. Skin FD was evaluated as described above, and also by measuring the change in lightness (DL) of the skin after the damage. The lightness at the equator of the non-blushed side of each fruit was determined with a chromameter (model CR-200; Minolta Corp., Japan) that had been calibrated to a standard green reflective plate (set CR-A47), as described by Amarante et al. (1998a and 1998b). Measurements of skin lightness before and 24 h after friction treatment were taken on the same area of skin and DL (due to FD) was corrected for change in lightness of the skin due to fruit ripening. After evaluating for FD, internal atmospheres were sampled destructively by direct removal and the values for partial pressures of O_2 (p'_{O_2} , kPa) and CO_2 (p'_{CO_2} , kPa) determined using an O_2 electrode (Citicell C/S type, City Technology Ltd., London, UK) in series with a miniature infra-red transducer (Analytical Development Company, Hoddesdon, UK), with O_2 -free N_2 as a carrier gas (flow rate $580 \text{ mm}^3 \cdot \text{s}^{-1}$).

The effect of water loss on susceptibility to FD was evaluated by storing non-coated fruit in plastic bags with eight holes (reduced water loss treatment) or in air (high water loss treatment) at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH for two months. Fruit were weighed at harvest and again 12 h after removal from cold storage for water loss estimation. After 24 h equilibration at 20°C and 60-70% RH, the fruit were assessed for r_{CO_2} and h^o and then friction treated, and assessed for intensity of damage 24 h later as described above. The experiment had a randomized block design with four replicates, each comprising 15 fruit.

The effect of fruit temperature on FD was assessed in 'Comice' pears after three months storage at $0 \pm 0.5^\circ\text{C}$ and 95-98% RH. Groups of 25 fruit were left at temperatures of 0, 10, 20, and 30°C for 8 h, by which time the core temperature had equilibrated with the ambient temperature (Fig. 6.3), before submitting the fruit to friction treatment. Fruit firmness was assessed non-destructively, as described above, after fruit temperature equilibration but before friction treatment was applied. The friction treatment was made at the equilibration temperature. Assessment of FD in terms of DL (as described above) was made 24 h later on fruit left at the same

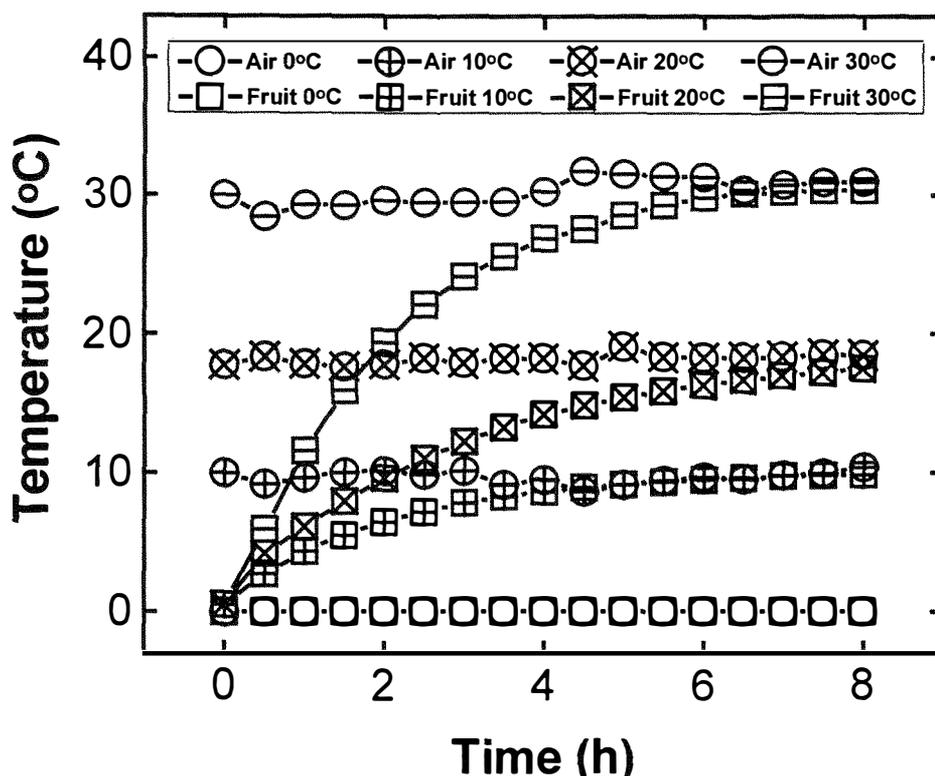


Figure 6.3 Equilibration of core fruit temperature of 'Comice' pears removed from cold storage ($0 \pm 0.5^\circ\text{C}$) and left at temperatures of 0°C , 10°C , 20°C , and 30°C and 60-70% RH.

temperature of friction treatment. After this assessment, fruit of all the treatments were left at 20°C and 60-70% RH for another 24 h and assessed again for *DL*.

Statistical analysis of the data was performed by using the SAS system (SAS, 1990). Analysis of variance (ANOVA) was performed by using the PROC GLM procedure; lines were fitted to mean data weighted by the inverse of the variance using the PROC REG or PROC NLIN procedures. The significance of changes in susceptibility to FD with fruit temperature and with time at 20°C after removal from cold storage of pears treated at harvest with different coating concentrations was investigated by using orthogonal polynomial contrasts.

6.4 Results

Substantial reduction of FD was achieved by increasing coating concentration and reducing the period of cold storage before the friction treatment (Figs. 6.4 and 6.5). The fitted hyperbolic models for the relationship between coating concentration and FD showed that the largest reduction in FD occurred when increasing the coating concentration from 0% to 20% for fruit damaged at harvest or after one month storage, with smaller improvements achieved with further increases in coating concentration. For fruit damaged after two months in cold storage, there was a substantial increase in susceptibility to FD, and a coating concentration of 40% was required to provide a more substantial reduction of FD, with further increases in coating concentration having a comparatively small beneficial effect. There was a highly significant difference in FD between times in cold storage ($P < 0.0001$), with a smaller change in susceptibility to FD from harvest to one month storage than from one month to two months storage (Figs. 6.4 and 6.5).

Delays after removal from cold storage substantially increased the susceptibility to FD of fruit treated with concentrations of 0% and 20%, while fruit treated with concentrations $\geq 40\%$ did not significantly increase in susceptibility with time (Fig. 6.6). Orthogonal polynomial contrasts showed a significant linear effect of time for coating concentrations of 0% and 20% ($P < 0.05$), but not for concentrations $\geq 40\%$. Although FD increased with time for fruit treated with coating concentration of 20%, FD intensity was much lower and also the slope of the increase with time was smaller than that of controls (Fig. 6.6).

There was a linear relationship between DL and ripening stage of the fruit before friction damage. There was a strong relationship of DL with respiration; similar but progressively weaker relationships were found with f and then h^o (Fig. 6.7). The relationship between DL and $P'_{\text{H}_2\text{O}}$ and weight loss followed a modified Michaelis-Menten equation, with K_m values of $3.0 \text{ nmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$ and 0.45%, respectively (Fig. 6.8).

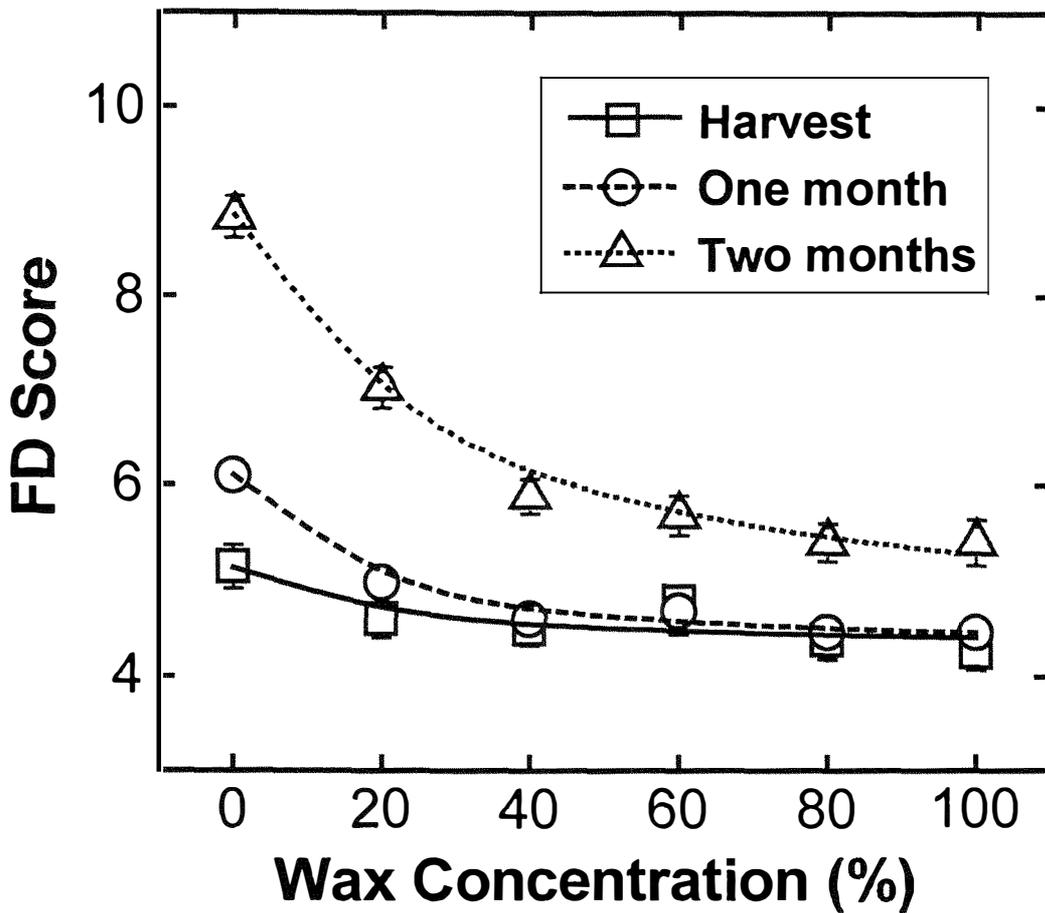


Figure 6.4 Effects of coating concentration and duration of cold storage on FD of ‘Comice’ pears. Bars represent standard errors of the means ($n = 25$). Lines represent the best fit for fruit friction damaged at harvest [—; $y = \{0.8 (\pm 0.4) \cdot [1 - [x / [x + 17.0 (\pm 27.0)]]\}] + 4.3 (\pm 0.30)$; $R^2 = 74.54\%$] and after cold storage for one month [-----; $y = \{1.8 (\pm 0.1) \cdot [1 - [x / [x + 12.0 (\pm 3.9)]]\}] + 4.3 (\pm 0.10)$; $R^2 = 98.86\%$] and two months [.....; $y = \{4.58 (\pm 0.4) \cdot [1 - [x / [x + 24.0 (\pm 7.0)]]\}] + 4.4 (\pm 0.34)$; $R^2 = 99.01\%$].

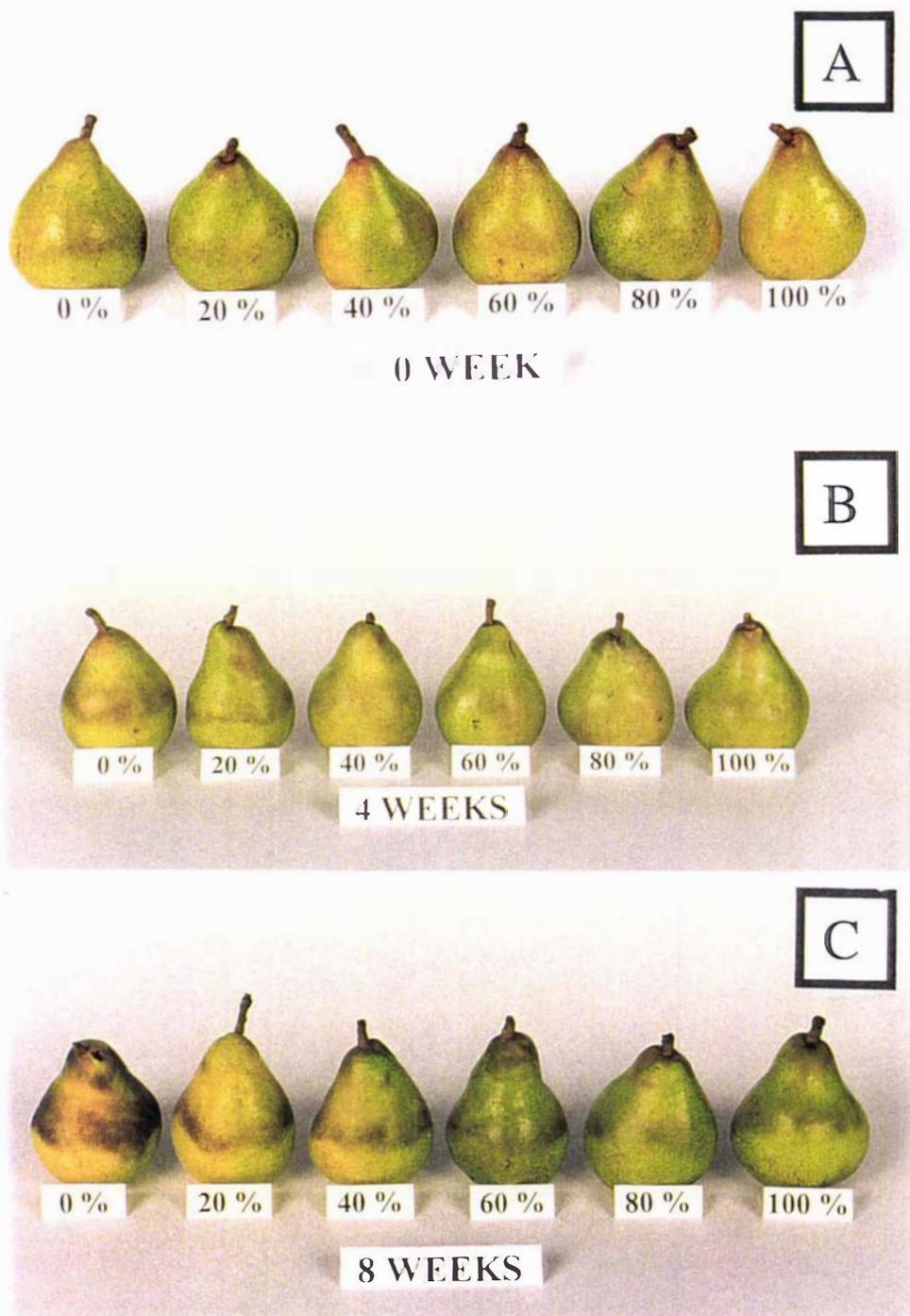


Figure 6.5 Intensity of FD on pears treated with different coating concentrations and submitted to friction damage at harvest (A), and after one (B) or two (C) months in cold storage at $0 \pm 0.5^{\circ}\text{C}$ and 95-98% RH. Fruit were equilibrated at 20°C and 60-70% RH for 24 h before friction damage.

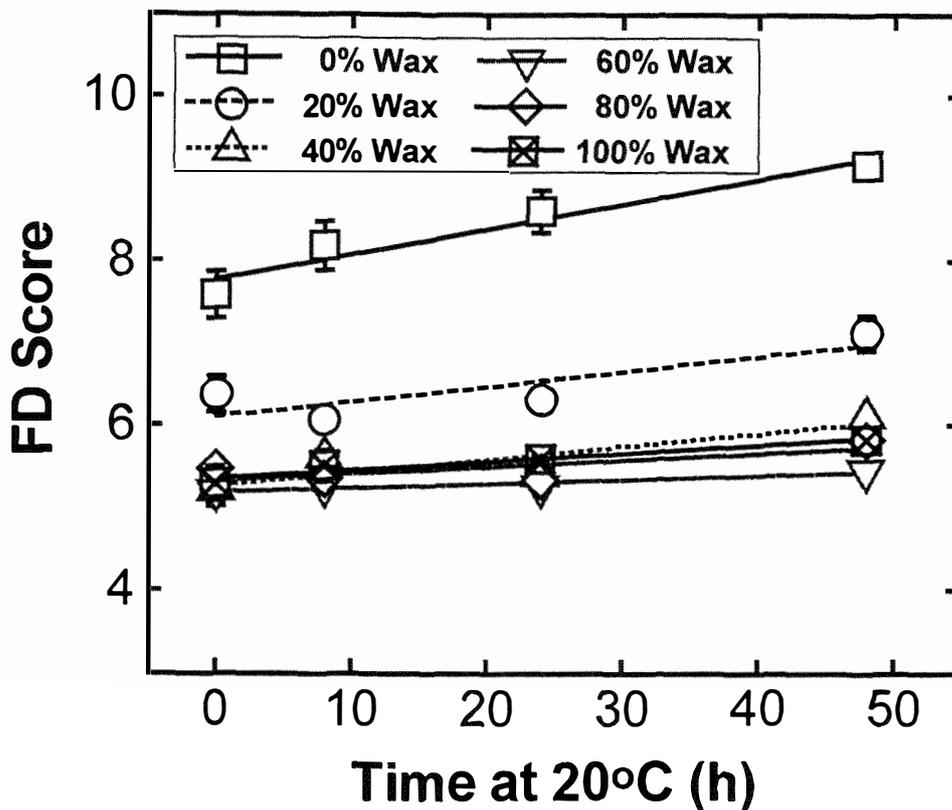


Figure 6.6 Effect of equilibration time at 20°C and 60-70% RH (after removal from cold storage) before friction damage on FD of 'Comice' pears treated with different coating concentrations at harvest. Bars represent standard errors of the means ($n = 25$). Lines represent the best fit for fruit treated with coating concentrations of 0% [$y = 7.80 (\pm 0.10) + 0.031 (\pm 0.005) x$; $R^2 = 94.11\%$], 20% [$y = 6.10 (\pm 0.20) + 0.018 (\pm 0.008) x$; $R^2 = 71.57\%$], 40% [$y = 5.20 (\pm 0.18) + 0.016 (\pm 0.007) x$; $R^2 = 72.97\%$], 60% [$y = 5.17 (\pm 0.03) + 0.005 (\pm 0.001) x$; $R^2 = 88.90\%$], 80% [$y = 5.30 (\pm 0.10) + 0.008 (\pm 0.005) x$; $R^2 = 55.48\%$], and 100% [$y = 5.34 (\pm 0.05) + 0.010 (\pm 0.002) x$; $R^2 = 93.39\%$]. Linear orthogonal polynomial contrasts for time at 20°C significant only for coating concentrations of 0% and 20% ($P < 0.05$).

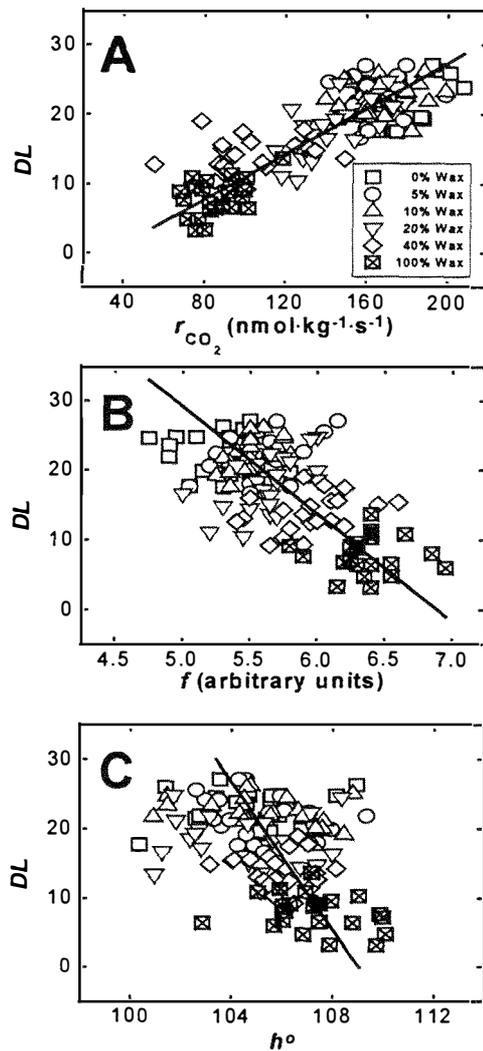


Figure 6.7 Relationship between respiration rate (r_{CO_2} , **A**), fruit firmness (f , **B**) and skin colour (h° , **C**) of the fruit before friction damage and FD (browning of the skin expressed in terms of DL) of ‘Comice’ pears. Fruit were equilibrated at 20°C and 60-70% RH for 24 h before ripening assessment and friction damage. Lines were fitted to mean data weighted by the inverse of the variance for r_{CO_2} , [$y = -5.0 (\pm 1.9) + 0.16 (\pm 0.01) x$; $R^2 = 97.40\%$; $P < 0.001$], f [$y = 106.0 (\pm 13.0) - 15.00 (\pm 2.00) x$; $R^2 = 92.37\%$; $P < 0.01$], and h° [$y = 578.0 (\pm 153.0) - 5.3 (\pm 1.40) x$; $R^2 = 77.06\%$; $P < 0.05$].

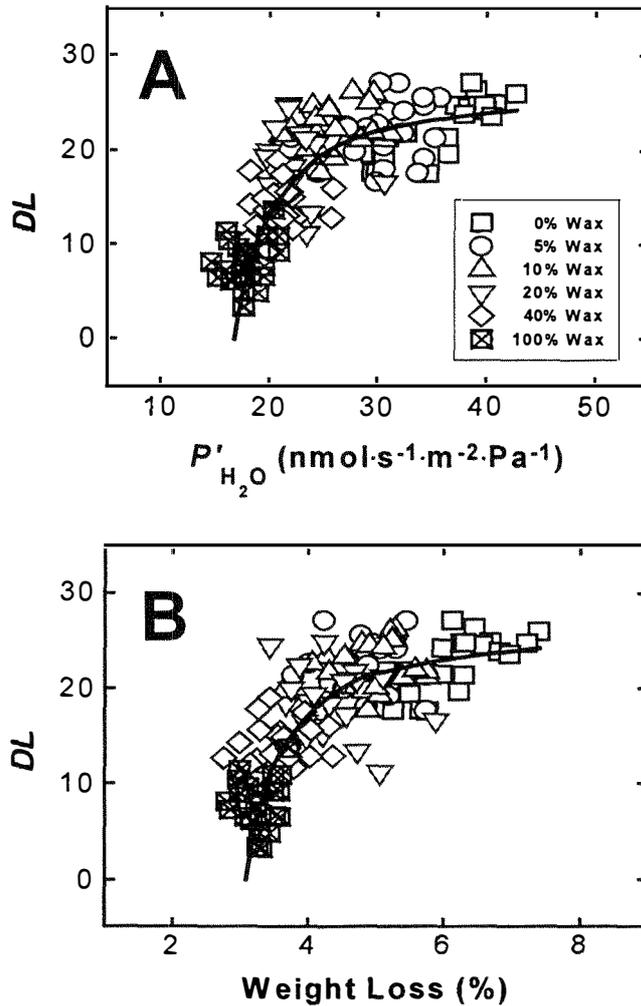


Figure 6.8 Relationship between permeance to water loss (P'_{H_2O} , **A**) and weight loss (% of the initial value, **B**) before friction damage and FD (browning of the skin expressed in terms of DL) of 'Comice' pears. Fruit were equilibrated at 20°C and 60-70% RH for 24 h before friction damage. Lines were fitted to mean data weighted by the inverse of the variance using a modified Michaelis-Menten model for P'_{H_2O} [$y = \{27.0 (\pm 3.1) \cdot (x - 16.8 (\pm 0.7))\} / \{3.0 (\pm 1.6) + (x - 16.8 (\pm 0.7))\}$; $R^2 = 95.15\%$] and weight loss [$y = \{26.8 (\pm 2.2) \cdot (x - 3.08 (\pm 0.08))\} / \{0.45 (\pm 0.19) + (x - 3.08 (\pm 0.08))\}$; $R^2 = 98.02\%$].

The relationship between DL and p'_{O_2} after friction damage followed a Michaelis-Menten equation (Fig. 6.9A); the same was not observed for p'_{CO_2} (Fig. 6.9B). The K_m for the plot with p'_{O_2} was 0.5 kPa, with more substantial reductions of DL achieved with p'_{O_2} below ~ 4 kPa, mainly corresponding to coating concentrations $\geq 40\%$.

Reducing water loss during cold storage by packing the fruit in plastic bags had a highly significant effect ($P < 0.0001$) in reducing fruit susceptibility to FD (Figs. 6.10 and 6.11). Weight losses were $0.82 \pm 0.03 \%$ and $4.80 \pm 0.07 \%$ of the initial weight for fruit packed or not in plastic bags, respectively. There was no significant difference between the two treatments in terms of respiration rate ($127.10 \pm 2.65 \text{ nmol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$ and $134.71 \pm 4.84 \text{ nmol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$ for low and high weight loss treatments, respectively) and skin colour (h° of 99.35 ± 1.34 and 99.16 ± 2.10 for low and high weight loss treatments, respectively) after 24 h equilibration at 20°C before friction treatment.

There was a quadratic relationship between fruit temperature and FD (Fig. 6.12). There was no significant difference in DL between temperatures from 0°C to 20°C , when the fruit were left at the same temperature of damage treatment for 24 h. However, when fruit from all treatments were left at 20°C for another 24 h and assessed again for FD, there was a substantial increase in browning of the damaged skin for fruit submitted to friction treatment at 0°C , and a small increase for fruit damaged at 10°C (Figs. 6.12 and 6.13). Fruit firmness, before friction treatment, decreased linearly as fruit temperature increased (Fig. 6.14).

6.5 Discussion

Surface coatings substantially reduced FD. With longer storage there was a substantial increase in susceptibility to FD, especially after one month storage, and, therefore, higher coating concentrations were required to reduce FD. The increase in susceptibility to FD with prolonged cold storage might have been the result of advanced ripening of the fruit, since coatings have a small effect in modifying the fruit internal atmosphere and delaying ripening at low temperatures (Amarante et al.,

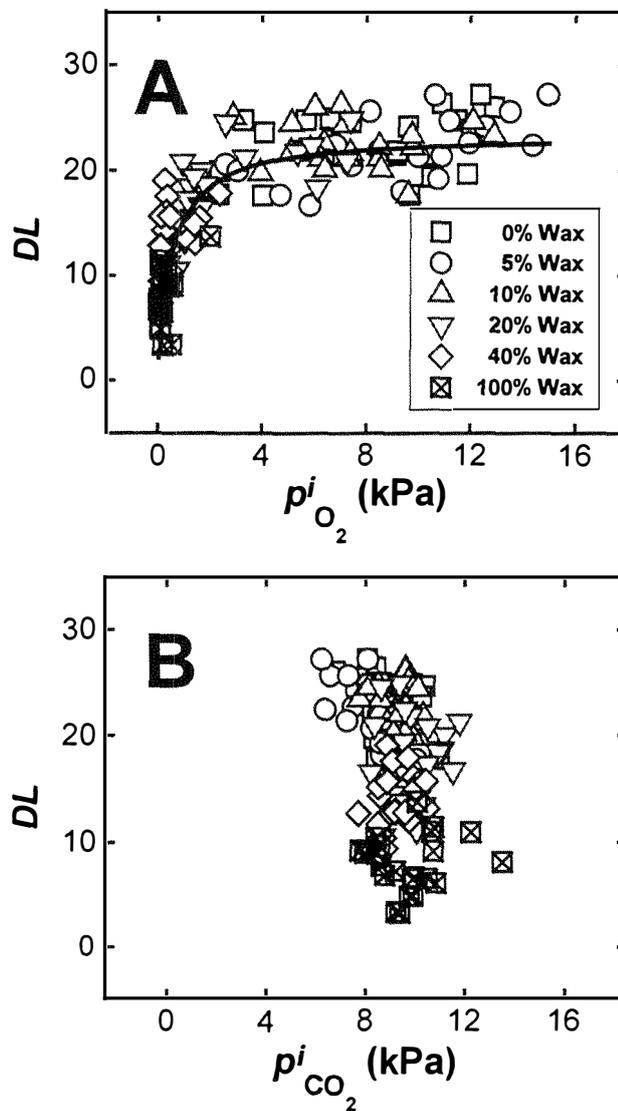


Figure 6.9 Relationship between internal partial pressure of O₂ ($p^i_{O_2}$, **A**) and CO₂ ($p^i_{CO_2}$, **B**) of the fruit after friction damage and FD (browning of the skin expressed in terms of DL) of ‘Comice’ pears. Fruit were equilibrated at 20°C and 60-70% RH for 24 h before friction damage and 24 h later assessed for FD and fruit internal atmosphere. Line for the relationship between DL and $p^i_{O_2}$ was fitted to mean data weighted by the inverse of the variance using a Michaelis-Menten model $[y = \{23.4 (\pm 0.74) \cdot x\} / \{0.50 (\pm 0.08) + x\}; R^2 = 97.33\%]$.

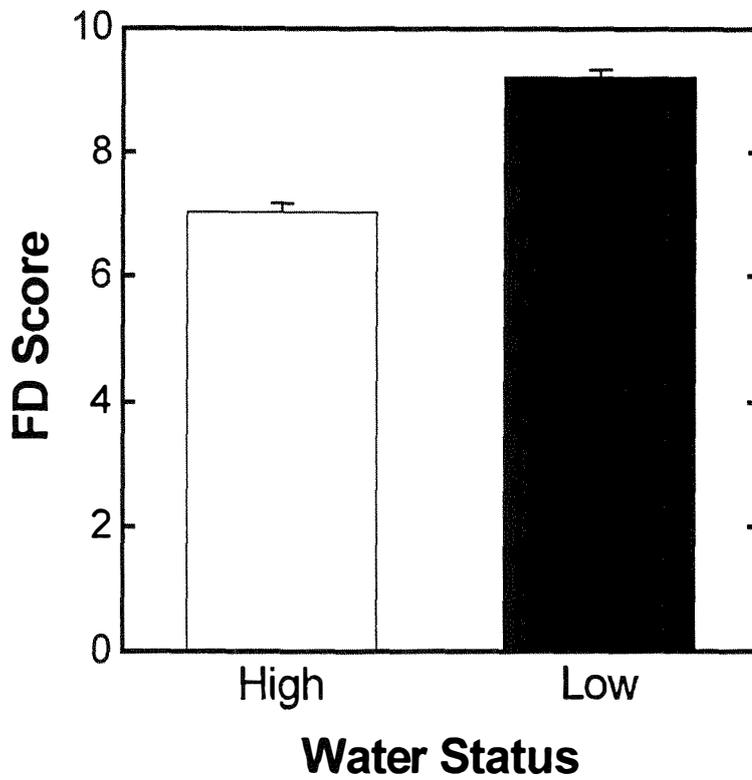


Figure 6.10 Effect of fruit water status prior to friction damage on FD of ‘Comice’ pears. Black bars represent standard errors of the means (n = 4).



Figure 6.11 Difference in FD between fruit having high or low water status before friction damage.

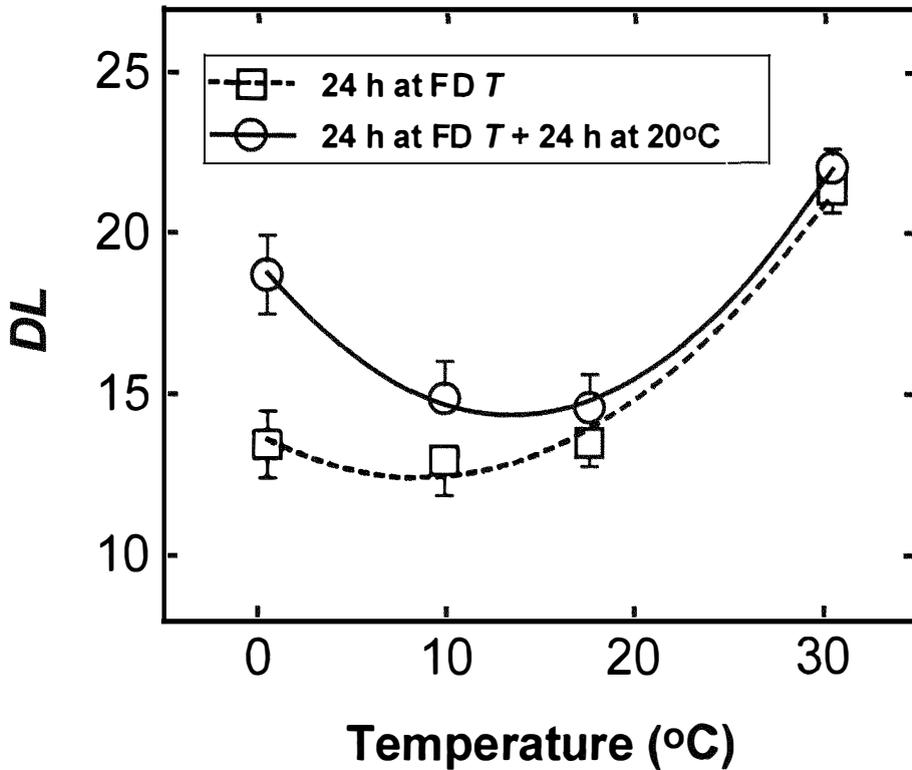


Figure 6.12 Effect of fruit temperature prior to friction damage on FD of 'Comice' pears. Pears were assessed for FD after being left for 24 h at the same temperature of friction damage [----; $y = 13.7 (\pm 0.7) - 0.30 (\pm 0.10)x + 0.018 (\pm 0.003)x^2$; $R^2=99.01\%$] and again after being left for another 24 h at 20°C and 60-70% RH [—; $y = 19.1 (\pm 0.3) - 0.72 (\pm 0.05)x + 0.027 (\pm 0.001)x^2$; $R^2=99.75\%$]. Bars represent standard errors of the means ($n = 25$). Lines represent the best fit. Quadratic orthogonal polynomial contrasts for fruit temperature highly significant for the two data sets ($P < 0.0001$).

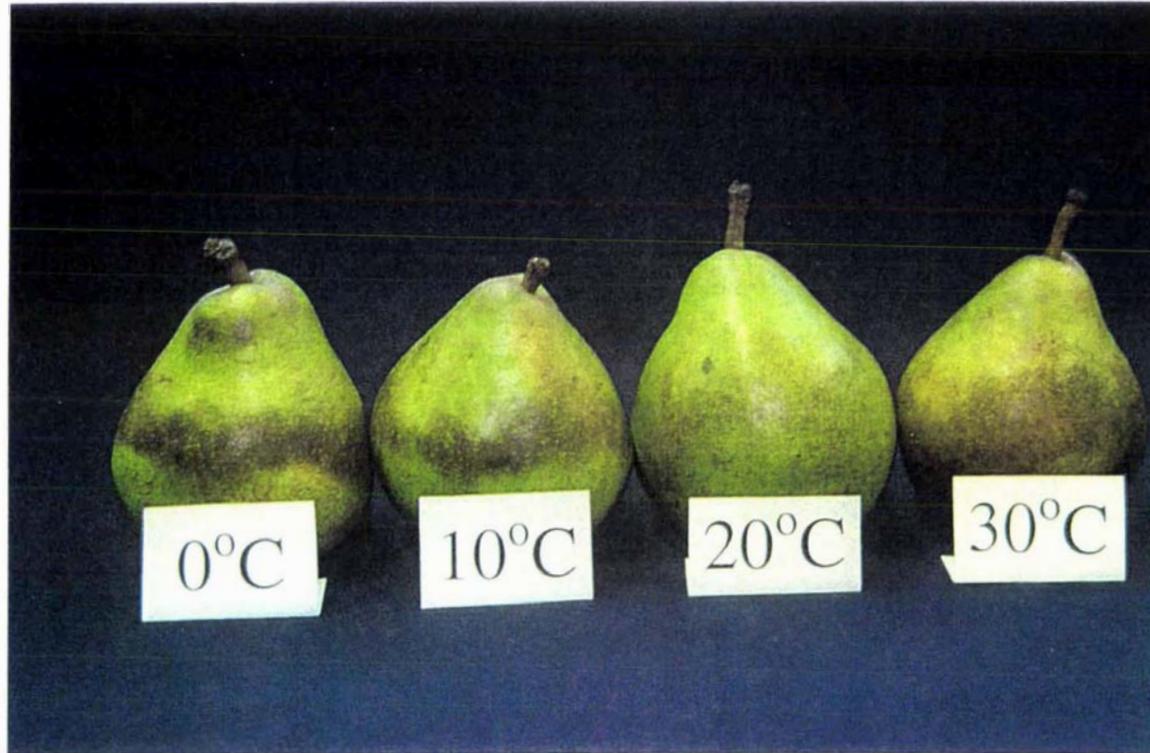


Figure 6.13 Differences in FD between fruit equilibrated at different temperatures before friction damage. The photo was taken after 24 h at 20°C (48 h after friction damage).

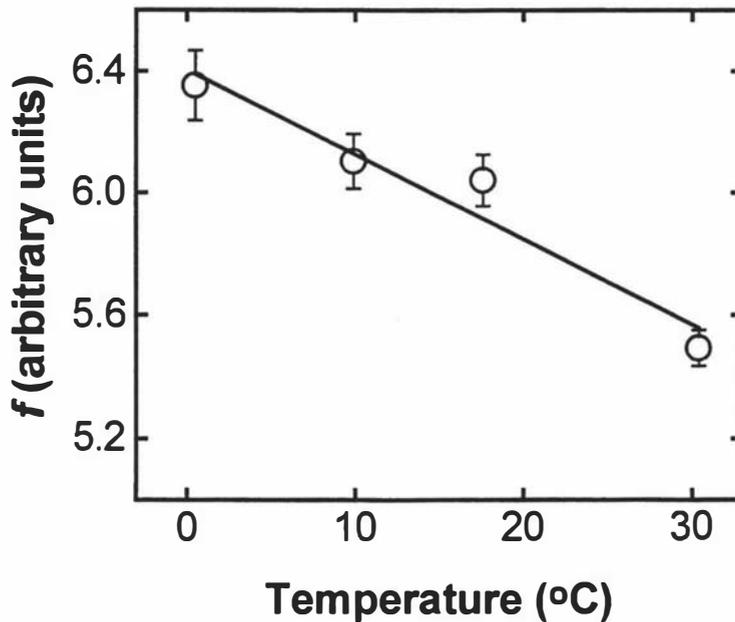


Figure 6.14 Fruit firmness of ‘Comice’ pears after 8 h equilibration at different temperatures. Bars represent standard errors of the means ($n = 25$). Line represents the best fit [— ; $y = 6.40 (\pm 0.09) - 0.028 (\pm 0.005) x$; $R^2 = 94.42\%$; $P < 0.05$].

1998c). Longer exposure to ambient temperatures after removal from cold storage linearly increased the susceptibility to FD of non-coated fruit and, to a lesser extent, of fruit coated with a coating concentration of 20%. This possibly reflects changes in susceptibility to FD with ripening, with high coating concentrations reducing p'_0 and preventing ripening, thus avoiding increase of FD with time at ambient temperature. Increasing coating concentrations may also result in a thicker wax layer on the skin, which helps in providing a better protection of the skin against friction damage.

Packing the fruit in perforated plastic bags did not modify the gas composition of the atmosphere around the fruit and there was no effect in delaying fruit ripening.

However, the increased RH inside the bags reduced weight loss of the fruit during cold storage and this substantially reduced susceptibility to FD (Figs. 6.10 and 6.11). Increasing coating concentration reduced $P'_{\text{H}_2\text{O}}$ and percentage weight loss, and this could have also contributed to reduce FD. However, the plots of $P'_{\text{H}_2\text{O}}$ and fruit weight loss against DL showed that more substantial reduction in FD occurred with larger reductions in $P'_{\text{H}_2\text{O}}$ and fruit weight loss. There were small reductions in DL for fruit treated with coating concentrations $\leq 10\%$, with more substantial results being achieved with coating concentrations $\geq 40\%$. However, more substantial reductions in $P'_{\text{H}_2\text{O}}$ and fruit weight loss occurred with small increases in coating concentration (from 0% to 20%; Fig. 6.8).

These results show that increasing coating concentration reduced FD not so much by reducing fruit water loss, but mainly by improving blockage of pores, reducing p'_{O_2} , and by creating a thicker layer on the skin, which provided a better protection against the friction damage caused by the brushes. After being submitted to FD, only fruit treated with coating concentrations $\geq 40\%$ had substantially lower p'_{O_2} than the other treatments (Fig. 6.9A). This seems to show that only those fruit treated with high coating concentrations retained blocked pores and an intact cuticle after brushing, and the reduced p'_{O_2} may have substantially contributed to prevent the enzymatic browning (which requires O_2) of some damaged skin cells. Increasing the coating concentration did not significantly change p'_{CO_2} after friction damage (Fig. 6.9B), as a result of differential permeability to O_2 and CO_2 and suppression of respiration rate of coated fruit (Amarante et al., 1998b and 1998c). Therefore, CO_2 apparently had no effect in controlling FD.

The relationship between p'_{O_2} and DL (Fig. 6.9A) as well as between p'_{O_2} and the ripening attributes of respiration, f and h^p were reasonably described by Michaelis-Menten equations (Amarante et al., 1998c). Therefore, the plots of DL against these ripening attributes gave a linear relationship. This indicates that FD was in some way related to p'_{O_2} , more than the ripening attributes. Rather, the ripening attributes, in common with FD susceptibility, were dependent upon p'_{O_2} . Increasing the coating

concentration reduces $p_{O_2}^i$, which in turn suppresses respiration, f and h^o (Amarante et al., 1998c). Rates of respiration before friction treatment was applied were strongly related to FD. Ripening expressed in terms of f and h^o did not show the same strong relationship with DL as a result of small inhibition of fruit ripening by coatings during cold storage, the short equilibration time after storage (only 24 h) and the large variability in these responses in coated pears (Amarante et al., 1998c).

The Michaelis-Menten relationship between FD and $p_{O_2}^i$ may be the result of reduced PPO activity with reduced $p_{O_2}^i$ (Rivas and Whitaker, 1973; Lerner and Mayer, 1976) or, alternatively, may reflect the reduction in damage of cells in the skin provided by the coating layer. The relative contribution of these two factors on skin browning of coated pears can not be determined from our data.

Rising fruit temperature at the temperature of friction treatment reduced fruit firmness, but this was not directly related to DL . Assessing FD 24 h after the damage, when the fruit remained at the same temperature, showed an increase in FD only for temperatures higher than 20°C. However, when the same fruit were exposed to 20°C for another 24 h and assessed again for FD, there was an increase in FD for fruit damaged when cold. This seems to indicate that the low fruit temperature increased FD of the skin, and leaving the fruit at this low temperature only delayed the development of the enzymatic browning. However, when the fruit were exposed to ambient conditions, they rapidly became brown. Because the temperature for equilibration and friction damage application were the same, there was no effect of condensation, which seems to have a substantial effect in reducing FD. For fruit removed from cold storage and treated with friction at 20°C, the water vapour condensation on the skin may have helped in reducing FD, in comparison to fruit damaged after eight or more hours of equilibration at 20°C (Fig. 6.6). The lower level of FD for coated fruit damaged when their temperature was ~ 0°C (time zero at 20°C; Fig. 6.6), may also be a combined effect of the low temperature reducing PPO activity and a gradual reduction of $p_{O_2}^i$ (as a result of increase in fruit respiration rate) reducing the enzymatic browning during fruit equilibration at ambient temperature. The water

condensation in the damaged skin mainly of fruit treated with coating concentrations of 0% and 20% also may have contributed to reduce the enzymatic browning reaction. Leaving the fruit for longer at 20°C may have resulted in drying of the condensed water, which may have increased the friction damage (as a result of there being less water to lubricate the skin during the brushing). It may also resulted in more intense enzyme browning immediately after the FD in the absence of water in the damaged tissue of the skin.

Smith (1946) did not observe an increase in FD susceptibility of pears warmed up from -0.5°C to 2-3°C before friction damage. Kvåle (1979) reported higher levels of skin discolouration for pears graded immediately after removal from cold storage (fruit temperature of 0°C) as compared to fruit warmed up for two days at 10-15°C. It is possible that the lower ambient temperature in Kvåle's study (10-15°C) resulted in much less condensation on the surface of fruit graded cold, providing less protection against FD. As the fruit were graded on a commercial grader, it is possible that a substantial proportion of total damage on the skin was caused by impact damage (bruising) against hard edges of the grader, instead of friction damage. The fruit were also equilibrated at ambient temperature for two days, so they may have lost more water. As a result, the combination of lower turgor (Banks and Joseph 1991; Johnson and Dover 1990) and higher temperature of the fruit left at ambient temperature (Sekse and Opedal, 1993) may have rendered these fruit less susceptible to impact damage than cold fruit, resulting in less skin discolouration. The high turgor and low temperature of the fruit may render the cells less elastic and more prone to breakage under impact damage. On the other hand, water loss may render the fruit more prone to brushing friction damage by causing disorganisation of the cellular membrane system as a result of cellular dehydration of the skin, increasing the level of soluble active PPO (Mayer and Harel, 1979; Volk et al., 1977). With loss of water, the skin tends to shrink forming a rougher surface, and this can increase the friction between the cells in the skin and the stiff brushes, resulting in a higher level of cellular damage and FD. This may also explain the reduction of FD by surface coatings. The coating layer could

reduce water loss (and reduce shrinkage) and smooth the skin surface, reducing the friction damage of the cells. Amarante et al. (1998b) have shown that high coating concentrations can fill in the cracks and pores of the cuticle, providing a smoother skin finish.

Since fruit susceptibility to FD increased with advanced ripening and weight loss, the main strategy to reduce the problem would be to pack the fruit at harvest or as soon as possible after harvesting. If the fruit is going to be packed after cold storage, the adoption of postharvest handling procedures to suppress ripening and reduce water loss should be considered. Fast cooling, storage at the correct temperature (ideally at -0.5°C), covering the bulk bins with plastic films to reduce water loss and, when possible, storage under CA conditions, could be used to substantially prolong the period of storage without excessive increase in the risk of FD occurring at grading. Coatings offer some protection against water loss during storage, but have a limited potential in suppressing ripening at low temperatures, offering little scope to delay the increase in FD susceptibility during cold storage. However, by creating a protection layer on the skin, reducing p'_{O_2} , and suppressing ripening at ambient temperatures, coatings offer an attractive option to reduce FD after cold storage.

6.6 Conclusion

Reduction of FD in pears is likely to be achieved by postharvest treatment with wax coating, reducing water loss, and grading and packing the fruit as soon as possible after harvesting, while the fruit are cold. Fruit in a more advanced ripening stage required higher coating concentrations to reduce FD. Increasing the coating concentration provided a thicker wax layer which gives a better protection of the epidermis against FD and also block the pores of the skin, reducing p'_{O_2} , which seems to contribute to reduce the enzymatic browning of damaged cell in the epidermis. Cold fruit seem to be more susceptible to FD, but water condensation after removal from the cold storage may help in reducing FD during and after mechanical damage.

6.7 References

- Amarante, C., Banks, N.H. and Ganesh, S., 1998a. Ripening behaviour, postharvest quality and physiological disorders of coated pears. *Postharvest Biology and Technology* (in preparation).
- Amarante, C., Banks, N.H. and Ganesh, S., 1998b. Relationship between character of skin cover and permeance to gases of coated pears. *Postharvest Biology and Technology* (in preparation).
- Amarante, C., Banks, N.H. and Ganesh, S., 1998c. Characterising ripening behaviour and the lower oxygen limit in relation to the internal atmosphere of coated pears. *Postharvest Biology and Technology* (in preparation).
- Amiot, M.J., Tacchini, M., Aubert, S.Y. and Oleszek, W., 1995. Influence of cultivar, maturity stage, and storage conditions on phenolic composition and enzymatic browning of pear fruits. *Journal of Agricultural and Food Chemistry*, 43: 1132-1137.
- Banks, N.H. and Joseph, M., 1991. Factors affecting resistance of banana fruit to compression and impact bruising. *Journal of the Science of Food and Agriculture*, 56: 315-323.
- Ben-Yehoshua, S., Burg, S. P. and Young, R., 1985. Resistance of citrus fruit to mass transport of water vapor and other gases. *Plant Physiology*, 79: 1048-1053.
- Johnson, D.S. and Dover, C.J., 1990. Factors affecting the bruise susceptibility of 'Bramley's Seedling' apples. In: *Proceedings of International Conference on Agricultural Mechanization, 27-30 March, Zaragoza, Spain. Vol. 2. Workshop on Impact Damage of Fruits and Vegetables*, pp. 87-94.
- Kvåle, A., 1979. Friction discolouration of two pear cultivars in relation to date of harvest and phenolic compounds in the fruit. *Acta Agriculturae Scandinavica*, 29: 29-32.
- Kvåle, A., 1988. Skin discolouration of four pear cultivars in relation to maturity, degree of ripening and duration of storage. *Norwegian Journal of Agricultural Research*, 2: 139-142.
- Lerner, H.R. and Mayer, A.M., 1976. Reaction mechanism of grape catechol oxidase – a kinetic study. *Phytochemistry*, 15: 57-60.
- Macheix, J.-J., Fleuriet, A., Billot, J., 1990. *Fruit Phenolics*. CRC Press, Boca Raton, Florida, 378 pp.
- Mannering, R., 1996. Pears pick up after determined effort. *The Orchardist*, 69: 18-19.
- Mayer, A.M. and Harel, E., 1979. Polyphenol oxidases in plants. *Phytochemistry*, 18: 193-215.
- Mayer, A.M., 1987. Polyphenol oxidases in plants – recent progress. *Phytochemistry*, 26: 11-20.
- Meheriuk, M. and Lau, O. L., 1988. Effect of two polymeric coatings on fruit quality of 'Bartlett' and 'd'Anjou' pears. *Journal of the American Society for Horticultural Science*, 113: 222-226.
- Meheriuk, M. and Sholberg, P., 1990. Postharvest treatments of pears. *Postharvest News and Information*, 1: 441-446.

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- Meheriuk, M., Prange, R.K., Lidster, P.D. and Porritt, S.W., 1994. Postharvest disorders of apples and pears. Agriculture Canada, Publication 1737/E, 67 pp.
- Mellenthin, W.M., Chen, P.M. and Borgic, D.M., 1982. In-line application of porous wax coating materials to reduce friction discolouration of 'Bartlett' and 'd'Anjou' pears. *HortScience*, 17: 215-217.
- Mellenthin, W.M. and Wang, C.Y., 1974. Friction discoloration of 'd'Anjou' pears in relation to fruit size, maturity, storage and polyphenoloxidase activities. *HortScience*, 9: 592-593.
- Raese, J.T., 1989. Physiological disorders and maladies of pear fruit. *Horticultural Reviews*, 11: 357-411.
- Ranadive, A.S. and Haard, N.F., 1971. Changes in polyphenolics on ripening of selected pear varieties. *Journal of the Science of Food and Agriculture*, 22: 86-89.
- Rivas, N.J. and Whitaker, J.R., 1973. Purification and some properties of two polyphenol oxydases from Bartlett pears. *Plant Physiology*, 52: 501-507.
- SAS, 1990. SAS Institute INC. Cary, NC.
- Sekse, L. and Opedal, M.L., 1993. Effects of temperature on bruising damage in 'Gravenstein' apples. *Acta Horticulturae*, 326: 299-303.
- Smith, E., 1946. Handling injuries on pears following cold storage. *Proceedings of the American Society for Horticultural Science*, 47: 79-83.
- Vámos-Vigyázó, L., 1981. Polyphenol oxidase and peroxidase in fruits and vegetables. *CRC Critical Reviews in Food Science and Nutrition*, 15: 49-127.
- Vámos-Vigyázó, L. and Nádudvari-Márkus, V., 1982. Enzymatic browning, polyphenol content, polyphenol oxidase and peroxidase activities in pear cultivars. *Acta Alimentaria*, 11: 157-168.
- Volk, R., Harel, E., Mayer, A.M. and Gan-Zvi, E., 1977. Catechol oxidase in tissue culture of apple fruit. *Journal of Experimental Botany*, 28: 820-830.
- Walker, J.R.L., 1964. The polyphenoloxidase of pear fruit. *Australian Journal of Biological Science*, 17: 575.
- Wang, C.Y. and Mellenthin, W.M., 1973. Relationship of friction discoloration to phenolic compounds in 'd'Anjou' pears. *HortScience*, 8: 321-323.
- Wang, C.Y. and Mellenthin, W.M., 1974. Inhibition of friction discoloration on 'd'Anjou' pears by 2-mercaptobenzothiazole. *HortScience*, 9: 196.

7.1 Project overview

The majority of surface coatings literature has been mainly empirical, describing changes in quality of coated horticultural commodities, without providing a mechanistic model for the mode of action of such treatments in delaying ripening. The research carried out in this area has not attempted to characterise the relationship between character of cover of the coated commodity and changes in skin permeance to water vapour and gases. The main focus has been in evaluating the barrier properties of coating films to water vapour and gases (Elson et al., 1985; Gennadios et al., 1994; Hagenmaier and Shaw, 1990, 1991a, 1991b, 1992; Hagenmaier and Baker 1994a and 1996; Mannheim and Soffer, 1996; Martín-Polo et al., 1992; McHugh and Krochta, 1994). Although this may provide important information for the selection of commercial coatings for fresh fruits and vegetables, the performance of the coating material under the test conditions may be far from providing the best results in practical terms. Commodities may respond differently to the same coating treatment, as a result of differences in: coating/commodity interaction (the nature of commodity skin; Claypool and King, 1941), commodity characteristics (respiration rate, area/mass ratio, *LOL*ⁱ, ripening stage, initial quality, susceptibility to physiological disorders, mineral composition, inherent postharvest biochemistry; Boersig et al., 1988; Ke et al., 1993; Ke and Kader, 1992; Nanos et al., 1992; Yearsley et al. 1997a and 1997b) and environmental conditions (temperature and RH; Banks et al., 1997a; Kester and Fennema, 1986) in which the coated produce will be stored. The environmental conditions may have a large impact on permeance attributes of the surface coating and on plant tissue physicochemical and biochemical properties (Chapter 2).

The main contribution of this work has been to characterise the relationships between character of cover of a hydrophobic commercial coating and finish of the skin, changes in skin permeance, modification of internal atmosphere, ripening

behaviour, sensory attributes and physiological disorders of different pear cultivars. The impact of ripening stage at which fruit were coated on *LOLⁱ* has also usefully added to knowledge on the postharvest physiology of coated pears. The following discussion covers these issues, all of which are important in the optimisation of surface coatings on pears. A diagrammatic model is presented, highlighting the interaction of physical and physiological factors affecting the performance of a surface coating in preserving the postharvest quality of coated pears (Fig. 7.1).

7.2 Physical and physiological basis for the beneficial effects of surface coatings in preserving postharvest quality of pears

Surface coatings may improve the postharvest quality of pears as a result of physical interaction between the coating film and the commodity skin, changing skin permeance and, therefore, reducing water loss, modifying fruit internal atmosphere and affecting physiological ripening processes in the fruit (Fig. 7.1).

7.2.1 Changes in skin permeance to water vapour and gases

7.2.1.1 Coating formulation

The physical and chemical properties of the coating films not only affect their barrier properties to water vapour and gases (Hagenmaier and Shaw, 1992; Hagenmaier and Baker, 1993 and 1994b; Kester and Fennema, 1989; Martín-Polo et al., 1992) but, most importantly, determines the extent of pore blockage in the skin and reduction of water loss and gas exchange by the coated commodity (Fig. 7.1; Banks et al., 1993a and 1997b; Hagenmaier and Baker, 1993). Hydrophilic films such as polysaccharide and shellac are poor barriers to water loss and, as a result of their

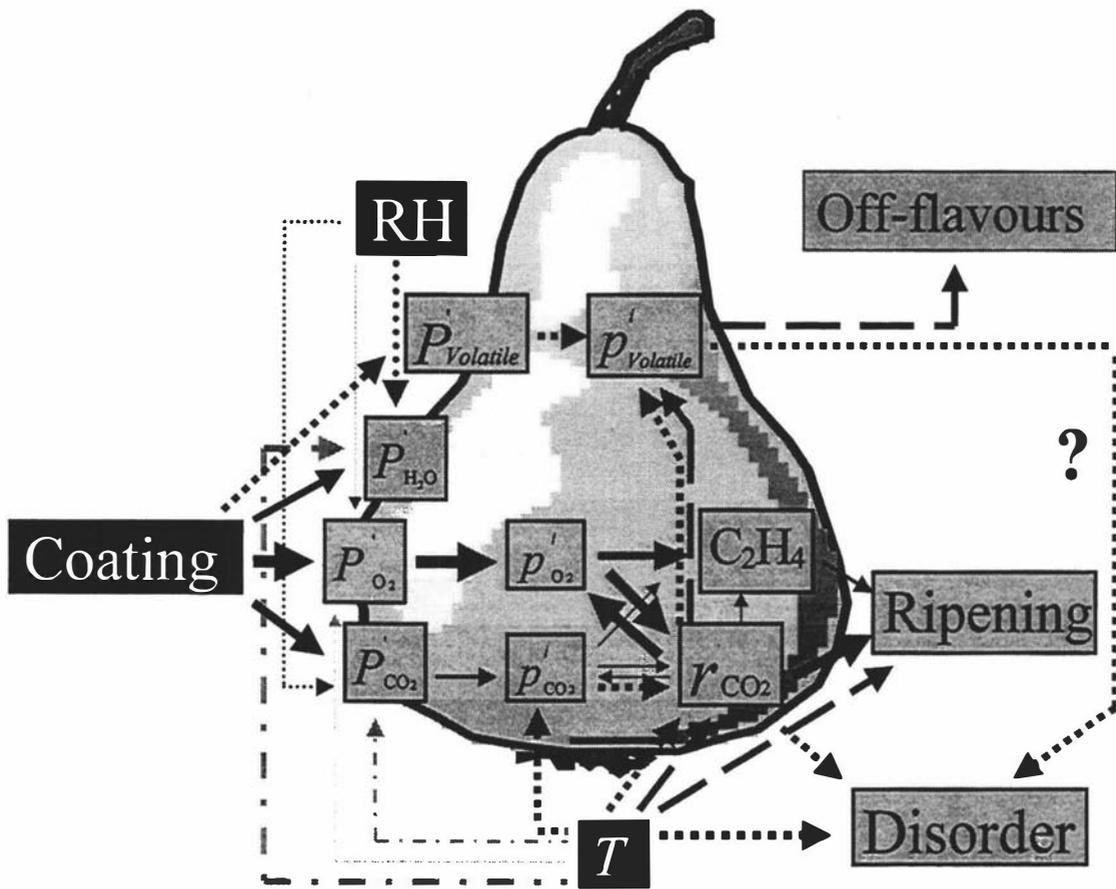


Fig. 7.1 Schematic diagram for the effects of surface coatings and environmental conditions on gas exchange and postharvest physiology of coated commodities. Arrow thickness is proportional to the magnitude of physical, compositional or physiological effect. Arrows represent: the effects of coatings on skin permeance, modification of internal atmosphere and ripening (—>); effects of relative humidity (RH;>) and temperature (T ; - - ->) on permeance attributes; effects of T rise on ripening and fermentation (- - ->); and physical and/or physiological factors which may contribute to the manifestation of physiological disorders during cold storage of coated pears (----->). P'_j = permeance to gas j ; p'_j = internal partial pressure of gas j ; r_{CO_2} = rate of respiratory CO_2 production.

high polarity, have low permeability to O₂ (Hagenmaier and Shaw, 1992). Therefore, commodities treated with such coatings may be rendered anaerobic and produce off-flavours (Banks et al., 1997b; Hagenmaier and Baker, 1993 and 1994b). Shellac formulations are mainly preferred for their effects in imparting gloss to the skin (Hagenmaier and Baker, 1994b) and they provide some limited barrier to water loss (Baldwin et al., 1995; Hagenmaier and Shaw, 1992). However, these emulsion formulations with low surface tension are very effective in blocking pores in the skin, over-restricting gas exchange (Hagenmaier and Baker, 1993). They also have low permeance to CO₂ (Hagenmaier and Baker, 1993; Hagenmaier and Shaw, 1991a and 1992; Trout et al., 1953), that may contribute to induce fermentation and cause internal disorders related to high CO₂/low O₂. Polysaccharide-based coatings do not impart enough gloss and, therefore, lipids, waxes and shellac have been added to these coating formulations to improve the skin finish and reduce water loss of coated commodities (Kamper and Fennema, 1984a and 1984b; Drake et al., 1987; Hagenmaier and Shaw, 1990). However, these composite formulations do not effectively provide either sheen or water barrier (Baldwin et al., 1997; Hagenmaier and Baker, 1996). Waxes offer the best performance in reducing water loss as a result of their more hydrophobic properties and by presenting a partially crystalline nature, with the hydrocarbon chains packed in an orthorhombic orientation (Donhowe and Fennema, 1993; Kester and Fennema, 1989). The addition of shellac components to waxes improves the gloss but substantially increases the permeance to water vapour and reduces permeance to permanent gases, increasing the risk of fermentation (Cuquerella et al., 1981; Hagenmaier and Baker, 1993 and 1994b). Waxes have low permeance to gases (Donhowe and Fennema, 1993). However, because of the globular nature of wax-based commercial coatings, forming micro and macro-emulsions, they offer low risk of completely blocking the pores in the skin, avoiding over-restriction of gas exchange and fermentation (Hagenmaier and Baker, 1993). In this respect, the size of globules of the wax formulation would be expected to affect the level of change in skin permeance of the coated commodity, with smaller globule size providing greater

blockage of pores and larger reductions in skin permeance (Baldwin et al., 1997). Natural waxes such as carnauba and candelilla waxes will probably be considered more acceptable in the next few years as the main ingredients of commercial surface coatings (Baldwin, 1994; Hernandez, 1994). The main advantages pointed out above for waxes were the prime reason for the selection of a carnauba-based commercial coating in the present study.

7.2.1.2 Coating deposit

The literature shows that increasing the coating deposit reduces the commodity skin permeance to water vapour and gases (Hagenmaier and Baker, 1994b), reducing weight loss (Ben-Yehoshua, 1966 and 1967; Farooqi and Hall, 1973; Hagenmaier and Baker, 1994a and 1994b) and delaying ripening (Ben-Yehoshua, 1966 and 1967; Farooqi and Hall, 1973; Magness and Diehl, 1924; Fig. 7.1). However, no attempt has previously been made to characterise these relationships. This is especially important considering differences in skin nature between commodities and cultivars of the same commodity, as well as differences in postharvest physiology.

This study shows the potential of reduced concentrations of a commercial carnauba coating in reducing the permeance of smooth skinned pear cultivars. Diluting the coating formulation did not increase the surface tension, but reduced the concentration of total solids deposited on the skin (Chapter 4). For cultivars with non-lignified cells in the skin ('Bartlett', 'Comice' and 'Packham's'), larger reductions in skin permeance to water vapour (P'_{H_2O}), O_2 (P'_{O_2}) and CO_2 (P'_{CO_2}) were observed at low levels of coating deposit (Chapter 4). This seems to be the result of diluted coating formulations achieving the most substantial incremental change in covering of pores in the skin. There was a marked distinction in the extent of modification of permeance to gases and water vapour with increases in coating deposit. As a result of differences in solubility coefficients between O_2 , CO_2 and H_2O in water and waxes ($S_{H_2O} \gg S_{CO_2} > S_{O_2}$; Banks et al., 1993a; Foust et al., 1980), improving the blockage of pores in the skin

comparatively resulted in $P'_{O_2} < P'_{CO_2} \ll P'_{H_2O}$ (Chapter 4). This explains the more substantial reduction of P'_{O_2} and P'_{CO_2} with improvements in pore blockage, rather than P'_{H_2O} (Chapter 4; Fig. 7.2). Covering these imperfections of the skin with a thin coating layer achieved most of the potential reductions in water loss, but there was still an extensive diffusion of water through the cuticle and the coating film. However, covering the pores in the skin had a more dramatic effect in reducing P'_{O_2} and P'_{CO_2} , especially P'_{O_2} , since O_2 has a lower solubility in water and wax components of the coating matrix than CO_2 (Figs. 7.1 and 7.2). The results presented in Chapter 4 show that more extensive blockage of lenticels was achieved with coating concentrations $\geq 20\%$, while most of the potential reduction of P'_{H_2O} , P'_{O_2} and P'_{CO_2} were achieved with coating concentrations $\leq 20\%$. This seems to indicate that a substantial proportion of total gas exchange may occur through the cracks in the cuticle, in addition to the lenticels (Fig. 7.2). Therefore, small increases in the amount of coating deposit seem to reduce P'_{H_2O} , P'_{O_2} and P'_{CO_2} by improving the blockage of cracks, and secondly by improving the blockage of lenticels in the skin. Further improvements in blockage of lenticels (by treating the fruit with coating concentrations $\geq 20\%$) resulted in further small reductions in P'_{O_2} and P'_{CO_2} . Coating concentrations $\geq 20\%$ reduced P'_{H_2O} still further, although to a smaller proportional extent, presumably by increasing the thickness of the coating layer.

'Bosc' pears with lignified cells in the skin have an epidermal layer with high P'_{H_2O} and low P'_{O_2} and P'_{CO_2} (Fig. 7.3). For this cultivar, increasing the coating concentration provided little scope to improve the cover of the lignified cells of the skin and, therefore, the reduction of P'_{H_2O} was small (Fig. 7.3). However, increasing the coating concentration gradually improved the cover of the large lenticels in the skin, reducing both P'_{O_2} and P'_{CO_2} close to zero (Fig. 7.3). The reduction of permeance to both gases near to zero resulted in a large depletion of internal O_2 and may have also contributed to the extensive accumulation of internal CO_2 , with both gases having a synergistic effect in inducing fermentation and internal physiological disorders in this cultivar.

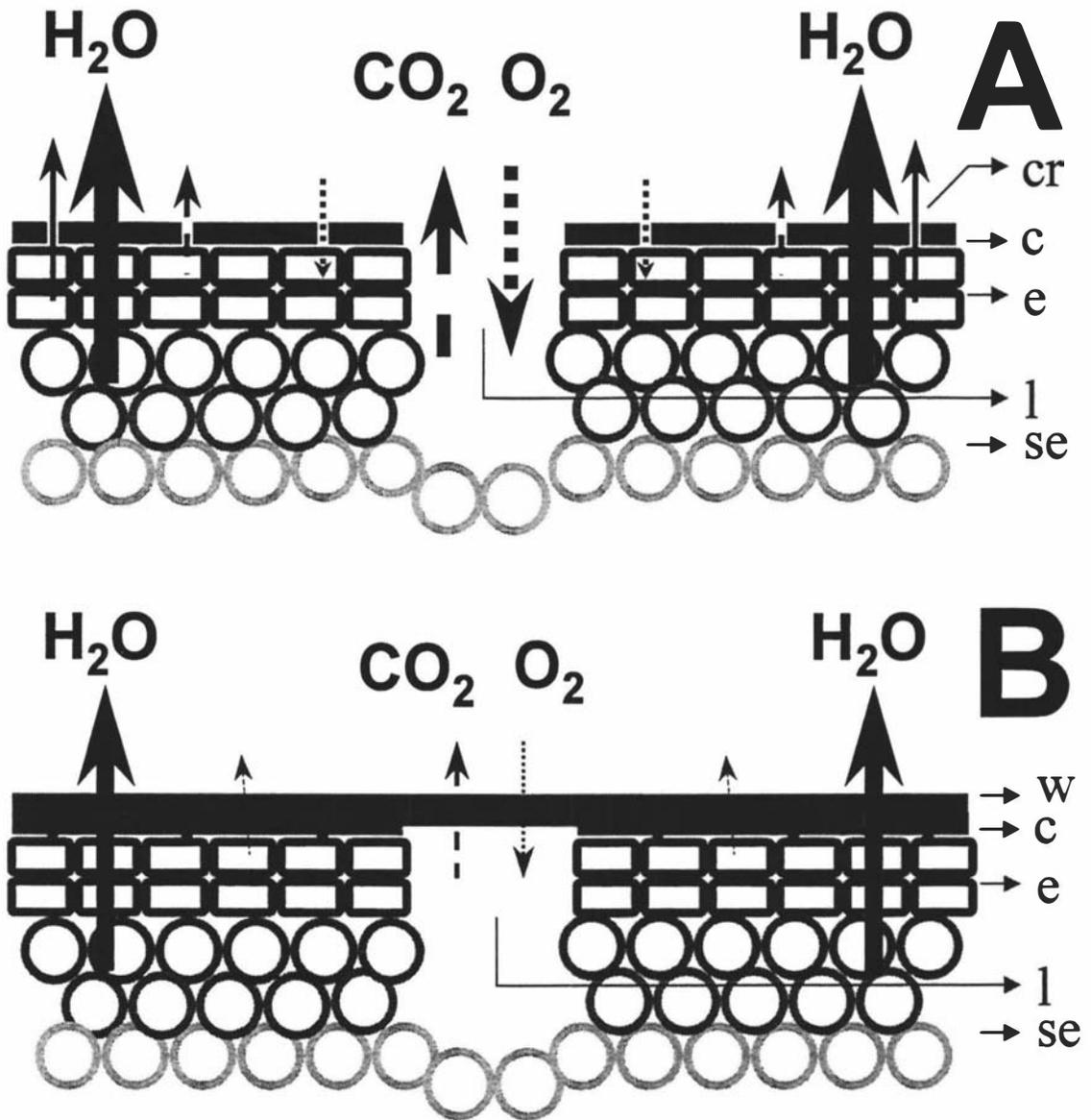


Fig. 7.2 Hypothetical model for the differences in skin permeance to O₂ (↓), CO₂ (↑) and water vapour (↑) in a non-coated (A) and a coated (B) pear without lignified cells in the skin. Arrow size is proportional to the differences in permeance values between gases and between coated and non-coated fruit (cr = crack in the cuticle; c = cuticle; e = epidermis; l = lenticel; se = sub-epidermis; w = wax coating layer).

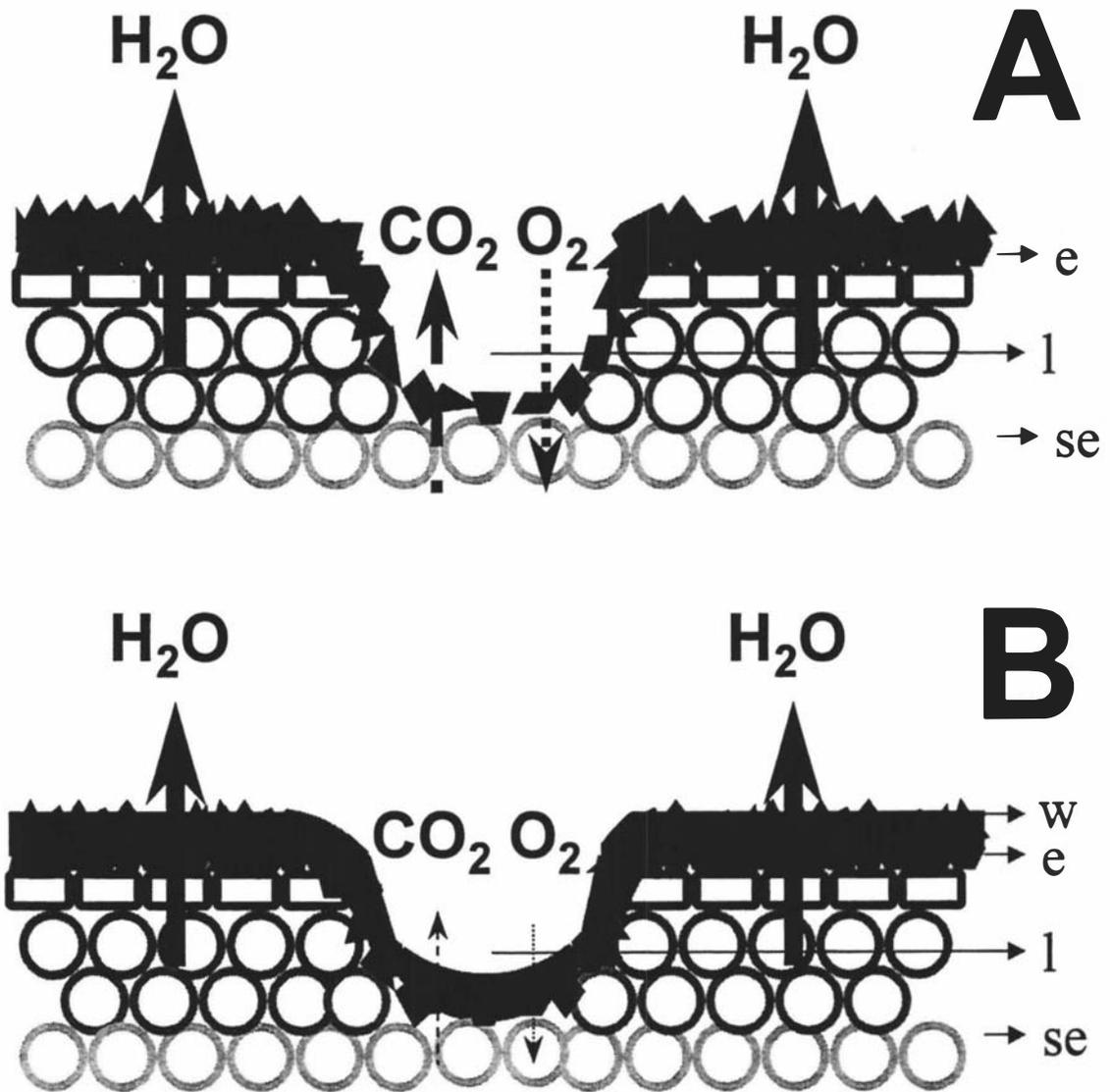


Fig. 7.3 Hypothetical model for the differences in skin permeance to O_2 (\downarrow), CO_2 (\uparrow) and water vapour (\uparrow) in a non-coated (A) and a coated (B) pear with lignified cells in the skin. Arrow size is proportional to the differences in permeance values between gases and between coated and non-coated fruit (e = epidermis; l = lenticel; se = sub-epidermis; w = wax coating layer).

7.2.2 Changes in internal atmosphere

Both low O₂ and/or high CO₂ have been extensively studied in terms of their effects on suppressing respiration rate and delaying ripening of horticultural products (Kader, 1989; Kader et al., 1989). In the literature dealing with surface coatings the relative contribution of O₂ and CO₂ in delaying ripening during cold storage and shelf life of coated commodities is largely unclear (Magness and Diehl, 1924; Smith and Stow, 1984; Smith et al., 1987). In the present study with surface coatings on pears, the results show that the relative contribution of low O₂ and high CO₂ depends on the temperature at which fruit are kept and the physiological ripening process. At ambient temperatures, coatings suppressed respiration rate and delayed softening and colour change by reducing $p_{O_2}^i$. This was the result of high respiration rates at ambient temperatures. The increase in $p_{CO_2}^i$ was less than the depression of $p_{O_2}^i$, as a result of both suppression of aerobic respiration at low $p_{O_2}^i$ coupled with the higher permeance of coating to CO₂ relative to O₂ (Banks et al., 1997b). The large increase of $p_{CO_2}^i$ in 'Bosc' when treated with high coating concentration was presumably the result of blockage of lenticels, the main path for both O₂ and CO₂ exchange, in association with fermentation induced by the combined effect of low O₂/high CO₂.

During long term cold storage coatings also substantially delayed ripening. Although, the effect was not as strong as that observed at ambient temperatures. This seemed to be the result of small changes in $p_{O_2}^i$ during cold storage of coated pears, which is known to have the most substantial effects in suppressing respiration and delaying ripening in CA storage (Cameron et al., 1994; Dadzie et al., 1996; Gran and Beaudry, 1993; Peppelenbos et al., 1996; Yearsley et al. 1996). More significant effects of coating concentration were observed in delaying softening than colour change. At low temperatures there was a substantial decrease of $p_{O_2}^i$, but not large enough (no less than 10 kPa) to greatly delay ripening. Only chlorophyll degradation seemed to be delayed by the more substantial reduction of $p_{O_2}^i$ in cold stored fruit treated with high coating concentrations ($\geq 40\%$). On the other hand, the most

significant delay in softening of coated pears was achieved by the increase of $p_{\text{CO}_2}^i$ and CO_2 solubility in the cell sap at low temperatures.

7.2.3 Respiratory metabolism

The majority of literature concerning optimisation of CA/MA storage has focused on the effects of low O_2 concentration, since a smaller and also less consistent effect of high CO_2 has been reported on respiratory metabolism of fruits and vegetables (Boersig et al., 1988; Dadzie et al., 1996; Gran and Beaudry, 1993; Peppelenbos et al., 1996; Yearsley et al., 1997b). The main focus has been in characterising the relationship between O_2 concentration and respiration, to reveal the shape of this relationship and to identify the lower O_2 limit of the commodity (LOL^i ; Boersig et al., 1988; Dadzie et al., 1996; Gran and Beaudry, 1993; Peppelenbos et al., 1996). The results presented in Chapter 5 showed that this approach applies for the LOL^i estimation of coated pears. For fruit exposed to high temperatures the aerobic respiration rate followed a Michaelis-Menten relationship with $p_{\text{O}_2}^i$, but not with $p_{\text{CO}_2}^i$, which was not largely modified by coating treatments. This relationship may help in characterising differences between different commodities, and cultivars of the same commodity, in achieving the beneficial effects of respiratory suppression by the plant tissue with $p_{\text{O}_2}^i$ reductions. Such information makes this approach more attractive in relation to the approaches presented by Banks et al. (1997b; plots between $p_{\text{CO}_2}^i$ and $p_{\text{O}_2}^i$), and by Yearsley et al. (1996; plots between respiratory quotient [RQ] and anaerobic volatiles internal concentration and $p_{\text{O}_2}^i$), which are more suitable for estimation of commodity LOL^i . However, all these approaches estimate the LOL^i , providing a mechanistic basis for models used to predict the lowest and safe $p_{\text{O}_2}^i$ to achieve the best beneficial effects of CA/MA storage, including surface coatings, as presented in Chapter 5.

7.2.4 Ethylene biosynthesis and action

The effect of coatings on C_2H_4 metabolism in pears was not the main scope of this study. However, from the results of this work it can be speculated that during cold storage, as a result of small modification of internal atmosphere in coated fruit, there was a limited effect of coatings in inhibiting the non-autocatalytic C_2H_4 biosynthesis (System I). The main effect of coatings may be expected after removal from cold storage, during shelf life. Under such conditions increasing the coating concentration resulted in substantial reduction of p'_{O_2} , which may have largely suppressed autocatalytic C_2H_4 biosynthesis (System II, Fig. 7.1), contributing to delay fruit ripening. The reduction of System II C_2H_4 biosynthesis by low p'_{O_2} may be the result of low cellular energy level (as a result of reduction of aerobic respiration) reducing *de novo* synthesis of C_2H_4 biosynthesis enzymes, as well as the direct effect of low O_2 inhibiting C_2H_4 action and ACC-O activity (Chapter 2). This issue deserves investigation in future research work with surface coatings.

7.2.5 Ripening behaviour

As for respiration, changes in firmness and skin colour of coated pears during shelf life were reasonably well defined by Michaelis-Menten equations when plotted against p'_{O_2} , but not against p'_{CO_2} (Chapter 5). With respect to p'_{O_2} , the K_m values for softening were lower than those for skin colour change for all pear cultivars. The more substantial inhibition of colour change than softening reflects differences in O_2 requirement for these two ripening processes. The change in colour from green to yellow is the result of oxidative degradation of chlorophyll's (green pigments), leaving the more stable carotenoids (yellow/orange pigments) in the skin (Salisbury and Ross, 1992). The enzymatic system for chlorophyll oxidation seems to have a very low affinity for O_2 , with small reductions of p'_{O_2} created by coatings drastically inhibiting the process. Softening, on the other hand, seems to require much lower p'_{O_2} to be suppressed. The K_m values for plots of aerobic respiration and firmness against p'_{O_2} ,

were similar, indicating that by reducing the respiratory energetic metabolism, coatings may have suppressed *de novo* synthesis of cell wall degrading enzymes, delaying softening at ambient temperatures. Only 'Bartlett' had a much higher K_m for softening than for aerobic respiration. This may be the result of substantial modification of internal atmosphere during cold storage, when the fruit were treated with moderate coating concentrations, as a result of cultivar high respiration rate. These coating treatments may have delayed ripening during cold storage, which may have resulted in a residual effect in retarding softening after removal to ambient temperatures.

During cold storage there were comparatively smaller modifications of coated pears' internal atmospheres than at ambient temperatures. Under such circumstances, there was a more significant effect of high CO₂ instead of low O₂ in delaying softening at low temperature, while for colour change low O₂ was still the most important. High CO₂ may have delayed softening by its effects in inhibiting several respiratory enzymes and ethylene biosynthesis and action during long term storage (Chapter 2). The effect of high CO₂ in delaying softening may be expected to increase in relative importance, when compared to the effect of low O₂, with reduction of storage temperature (which will reduce respiration rate, increasing CO₂/O₂ ratio for these gases partial pressure in the gas phase and solubility in the cell sap) especially in cultivars having high respiration rates.

7.2.6 Physiological disorders

Optimum CA/MA composition would be that at which rates of deterioration, including development of disorders, are reduced to a minimum (Banks et al., 1993b). Therefore, all work with optimisation of surface coatings should not only consider the assessment of coating effects in delaying ripening and improving some aspects of commodity quality, but also the risk of physiological disorders which may be predisposed by the coating treatment. Coatings can cause physiological disorders when

the commodity is exposed to extremes of temperature, either low or high. In cold stored apples surface coatings can aggravate the incidence of superficial scald in early harvested fruit (Hitz and Haut, 1938; Kerbel et al., 1989), and if the coating is too restrictive to gas exchange it may cause skin injury, which may be related to the accumulation of anaerobic volatiles (Farooqi and Hall, 1973; Lau and Meheriuk, 1994). Coatings can increase the incidence of internal disorders (flesh browning) in apple cultivars susceptible to the damage, which is caused by low temperature in combination with atmospheres containing high CO₂/low O₂ (Smith and Stow, 1984). Watkins et al. (1995) have recently shown that superficial scald in apples can also be an expression of chilling injury. According to Meheriuk et al. (1994), the inductive factors for internal browning and low-temperature breakdown are similar enough to suggest that both disorders are manifestation of a common metabolic disturbance. This may explain the increase in incidence of these disorders caused by coatings and low temperature in apple cultivars susceptible to them. The combination of a stressful low temperature with the creation of an internal atmosphere conducive to the disorders by the surface coating (very low O₂ and/or very high CO₂) may have a synergistic effect in increasing the physiological damage in susceptible tissues (Wang, 1990). Since coatings do not seem to drop $p_{O_2}^i$ in apples and pears below ~ 10 kPa during cold storage (Chapter 5; Kerbel et al., 1989; Lau and Yastremsky, 1991), hypoxia does not seem to be the main inductive factor for internal and superficial browning disorders. At low temperatures, however, there is a substantial increase in $p_{CO_2}^i$, and because CO₂ solubility in water increases with reduction of temperature (Foust et al., 1980), this may result in very high content of CO₂ dissolved in the cell sap. Therefore, the accumulation of this gas under low temperature conditions could be a significant factor for the incidence of internal and superficial browning disorders in coated commodities (Fig. 7.1). Apples exposed to high CO₂ accumulate acetaldehyde, ethanol, and acetic, malic, fumaric, citric, and succinic acids (Meheriuk et al., 1994). This may be the result of high CO₂ increasing or reducing the activity of several glycolytic and Krebs cycle enzymes, by means of "fine" (activation or inhibition of existing enzymes

activity) or “molecular” (activation or inhibition of enzymes *de novo* synthesis) control (Chapter 2). After long term cold storage the participation of both control mechanisms may lead to the accumulation of toxic metabolites and the manifestation of physiological disorders (Toivonen, 1997).

The results presented in Chapter 3 show that cultivars susceptible to internal disorders (‘Bartlett’ and ‘Bosc’) developed the disorder if coated before but not if coated after cold storage. The high respiration rate of ‘Bartlett’ may have resulted in a higher accumulation of CO₂ during cold storage in fruit treated with high coating concentrations, resulting in a higher incidence of internal disorder. ‘Bosc’ had a much lower respiration rate but also developed the disorder in cold storage when coated with high coating concentrations. This cultivar seems to have a very low epidermal permeance to gases, and the main gas exchange occurs through the lenticels (Chapter 4). High coating concentrations may have blocked the lenticels, resulting in a large build up of internal CO₂, resulting in internal damage. ‘Comice’ and ‘Packham’s’ have low respiration rates, and because P'_{CO_2} is still higher than P'_{O_2} in coated fruit, this may have avoided the build up of internal CO₂ to a damaging level. These differences in susceptibility to internal disorders may also be the result of metabolic differences between cultivars, apart from differences in internal accumulation of CO₂.

Surface coatings can increase the internal concentration of anaerobic volatiles such as ethanol, acetaldehyde and ethyl acetate (Baldwin et al., 1995; Hagenmaier and Baker, 1993; Hagenmaier and Baker, 1994b; Nisperos-Carriedo et al., 1990), and their accumulation may contribute to development of internal disorders (Fig. 7.1; Toivonen, 1997). However, it is not clear if the accumulation of these volatiles results from increasing anaerobic respiration (as a result of low p'_{O_2} and/or high p'_{CO_2} ; Hagenmaier and Baker, 1994b) or from reduction in skin permeance to these compounds by the surface coating (Fig. 7.1; Baldwin et al., 1995). The increases in the concentrations of these anaerobic volatiles have been shown to be a natural event during ripening and senescence of fruits (Ke et al., 1994; Nanos et al., 1992), and reducing skin permeance by coating may contribute to their accumulation and exacerbate the incidence of

internal disorders. Coatings with lower permeance to gases, such as shellac, may be expected to cause larger depletion of O₂ and build-up of CO₂. In addition, they may also increase the accumulation of anaerobic volatiles by reducing their escape through the skin (Baldwin et al., 1995), increasing the risk of fermentation and/or internal disorders (Chapter 2). Wax- and polysaccharide-based coatings are more permeable and, therefore, present less risk (Chapter 2). This issue deserves further investigation.

7.2.7 Sensory attributes

The accumulation of anaerobic volatiles may be detrimental in cold stored coated fruits, possibly contributing to the development of internal disorders and off-flavours after long term storage (Magness and Diehl, 1924; Toivonen, 1997; Trout et al., 1953). However, this accumulation of anaerobic volatiles may improve the quality of coated fruit destined for fresh market or for juice processing, if the fruit is kept at ambient temperatures after coating (Baldwin et al., 1995; Lakshminarayana et al., 1974; Nisperos-Carriedo et al., 1990). Even in this case, if the fruit starts to ferment and accumulate large amounts of anaerobic volatiles, off-flavours may develop (Hagenmaier and Baker, 1993 and 1994b). In the current study, for fruit coated at harvest before cold storage, only 'Bosc' coated with undiluted coating fermented, and these were the only fruit in which panellists detected off-flavours. Therefore, care should be taken to avoid coating treatments which may drop $p_{O_2}^i$ below the LOL^i and cause fermentation and development of off-flavours.

7.2.8 Skin finish

Surface coatings can improve skin gloss, a feature which is largely dependent on coating formulation (Hagenmaier and Baker, 1994b) and character of cover of the skin (Chapters 3 and 4). The improvement of skin gloss is the result of coating filling in cracks in the cuticle, resulting in a higher light reflectance and improvement of skin

finish (Glenn et al., 1990). Cultivars having less cracks and a naturally high skin reflectance to light have a high potential to benefit from improvements in gloss when coated, with better results achieved by increasing coating concentration, which improves the cover of cracks and pores in the cuticle (Chapters 3 and 4).

Apart from improving gloss and the attractiveness to the consumer, coatings have a high potential to reduce friction discolouration (FD) and wastage of pears during postharvest handling and marketing. FD is the main problem for the pear industry (Mellenthin and Wang 1974; Wang and Mellenthin, 1973). While pre-harvest FD is difficult to control and is responsible for the largest proportion of total fruit being rejected during the pack-out (total rejects between 35 to 75% in New Zealand; Mannering, 1996), there is still some scope for reducing postharvest FD, if some postharvest handling techniques are adopted in conjunction with surface coating treatments (Chapter 6; Mellenthin et al., 1982). There is no published information about losses of pears during the marketing chain, but it seems likely that the wastage as a result of postharvest FD is as high as that observed at pre-harvest. The handling system adopted by the retailers is not adequate (such as the selling of pears loose in large boxes), and a large proportion of fruits might be lost in the supermarkets as a result of FD. The results presented on Chapter 6 show that coatings reduce FD by providing a protection layer on the skin, which also reduce fruit susceptibility to FD by reducing weight loss and reducing fruit p'_{O_2} during shelf life. The reduction in p'_{O_2} delays ripening and may reduce the oxidative enzymatic browning reaction, reducing susceptibility to and intensity of FD.

7.3 Physiological and environmental factors affecting postharvest quality of coated pears

7.3.1 Cultivar

The optimisation of surface coatings for pears is affected by differences between cultivars in skin permeance to gases, ripening response to the modification of p'_{O_2} , and character of skin cover by the coating film. As discussed above, cultivars with smooth skin ('Bartlett', 'Comice' and 'Packham's') developed the large reductions in permeance to water vapour and gases with low coating deposits on the skin. For cultivars having high skin permeance to gases ('Bartlett' and 'Comice'), treating the fruit with intermediate coating concentrations may result in variable coverage of pores in the skin, variable changes in P'_{O_2} , variable p'_{O_2} , and, therefore, variable ripening behaviour. For cultivars with lignified cells in the skin ('Bosc'), improving the coating deposit on the skin resulted in small reductions of permeance to water vapour and blockage of lenticels caused over restriction of gas exchange rendering the fruit anaerobic.

Cultivars differ in terms of the relationship between respiration rate and p'_{O_2} . 'Bosc' had the lowest K_m for aerobic respiration, showing more beneficial effects of reduced p'_{O_2} than the other three cultivars ('Bartlett', 'Comice' and 'Packham's'). This cultivar also had the highest risk of becoming anaerobic under hypoxic conditions. The shape of this relationship between respiration and p'_{O_2} , when characterised for different cultivars of a given commodity, contributes to the optimisation of gas composition for CA/MA storage in general, as well as to the optimisation of surface coatings.

7.3.2 Ripening stage

Fruit tissues in a more advanced ripening stage are less tolerant to hypoxic conditions (Boersig et al., 1988; Ke et al., 1993; Nanos et al., 1992), possibly as a result of higher resistance of flesh tissue to gas diffusion (Boersig et al., 1988) and

lower repair capacity during and after hypoxic conditions (Nanos et al., 1992). These studies only characterised tissue metabolic changes (Ke et al., 1993; Nanos et al., 1992) and *LOL* (Boersig et al., 1988) in relation to the external partial pressure of O_2 ($p_{O_2}^e$), rather than to $p_{O_2}^i$. This makes it difficult to separate the effects of ripening on changes in resistance of flesh tissue to gas diffusion and on physiological changes in tolerance to hypoxia. Yearsley (1996) did not observe consistent and significant shifts of LOL^i (characterised for $p_{O_2}^i$) in apples with advances in ripening stage. In the present study with pears, there was a clear indication of increase in LOL^i with advance in ripening for pears cultivars less tolerant to hypoxia ('Bartlett' and 'Bosc'). Given that internal atmosphere composition formed the basis for characterising *LOL* in the current study, it seems likely that this change in sensitivity to hypoxia represents a genuine metabolic change in the fruit tissue, instead of changes in gas diffusion with fruit ripening. Also, we have observed that assessing internal atmosphere by sampling from both on external chamber and from the core cavity showed that differences of $p_{O_2}^i$ between these two locations were less than 1 kPa in non-coated 'Comice' pears after two weeks shelf life at 20°C. Fruit coated after cold storage were in a more advanced physiological stage (entering the climacteric), but high coating concentrations may have suppressed ripening during shelf life and prevented extensive flooding of intercellular spaces and the decrease of diffusivity of gases within the flesh. This may have prevented large gradients of partial pressures between the atmospheres in the core and under the skin. It reinforces the notion that increases in LOL^i with ripening was the result of decreases in tissue tolerance to hypoxia. In Yearsley's (1996) work with apples, the absence of any change of LOL^i with ripening may be the result of applying cold storage periods (from 11 to 14 weeks) not long enough to result in significant differences in metabolic activity to affect tolerance to hypoxia. In the work with pears, fruit were left in cold storage for at least the period required to achieve the chilling requirement to ripen. This, in addition to more substantial changes in biochemical and physiological properties of pears than of apples with ripening, may explain the

differences between the results presented in Chapter 5 and those observed by Yearsley (1996).

The results presented in Chapter 5 show that the characterization of LOL^i as a function of ripening stage may provide a more robust mechanistic model for the optimisation of surface coatings for pears.

7.3.3 Temperature

From Fick's First Law of Diffusion (Chapters 2 and 4):

$$p_{O_2}^i = p_{O_2}^e - \left(\frac{r_{O_2}^T}{P_{O_2}^T \cdot A} \right) \quad [7.1]$$

where:

- $r_{O_2}^T$ = rate of O_2 uptake (aerobic respiration) for the commodity at temperature T ($\text{mol}\cdot\text{s}^{-1}$);
- $P_{O_2}^T$ = commodity skin permeance to O_2 at temperature T ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$);
- A = commodity surface area (m^2).

An increase in temperature would be expected to have a stronger effect in increasing $r_{O_2}^T$ than elevating $P_{O_2}^T$ (Banks et al., 1997a). Thus, for a given level of $p_{O_2}^e$, $p_{O_2}^i$ would be expected to be lower at high temperatures by an amount that would depend upon absolute values of $P_{O_2}^T$, $r_{O_2}^T$, and A . Yearsley et al. (1997a) has shown that for apples, LOL^i was not greatly influenced by temperatures not exceeding 28°C . However, LOL^i in pears seemed to depend on ripening stage (Chapter 5). If the fruit's ripening stage, LOL^i and $r_{O_2}^T$ are known, $P_{O_2}^T$ could be optimised to achieve a $p_{O_2}^i$ above the LOL^i , by tailoring the coating treatment for a specific environmental condition to which the commodity will be exposed. For this, the power law relationships between $r_{O_2}^T$ and temperature, and also the relationship between $P_{O_2}^T$ and temperature for commodities treated with different coating deposits, would need to be characterised.

Raising the temperature would be expected to have a smaller effect on increasing P'_{O_2} than P'_{CO_2} (since CO_2 moves more readily through the cuticle than O_2), and a much lower effect than on P'_{H_2O} (which moves much more readily through the cuticle; Fig. 7.1). Although the relationship between P'_{O_2} and temperature would be expected to be small for non-coated fruit, since the main path for this gas is through pores in the skin (Cameron et al., 1994), the role of the coating layer to its exchange should not be disregarded when pore blockage is enhanced by improving the coating deposit on the skin. In this situation the cuticle and coating layer might contribute significantly to O_2 exchange, with a substantial effect of temperature on final levels of P'_{O_2} . Estimation of temperature effect on r'_{O_2} and P'_{O_2} of commodities treated with different levels of coating deposit may improve the mechanistic model to optimise the use of surface coatings in different environmental temperature conditions.

7.3.4 Relative humidity

Increasing RH will be expected to increase skin permeance to water vapour and gases in their order of solubility coefficients in water: $P'_{H_2O} \gg P'_{CO_2} > P'_{O_2}$ (Fig. 7.1; Foust et al, 1980; Gontard et al., 1996). The elevation in sorbed moisture has also a plasticizing effect that tends to increase the diffusion constant for water vapour and gases (Kester and Fennema, 1986). Since permeance is determined by both the diffusion constant and the solubility coefficient (Chapter 2), permeance to water vapour and gases is enhanced at high RH. This effect will be largely dependent on coating polarity, with films that have a larger proportion of polar components adsorbing more water molecules in the coating matrix, resulting in a larger increase in permeance to water vapour and gases with the increase of RH (Gontard et al., 1996; Kester and Fennema, 1986). Although we may expect a lower effect of RH on permeance for hydrophobic coatings (such as waxes), this should not be disregarded. Natural waxes differ in their content of polar components (Donhowe and Fennema, 1993), and wax-based commercial coating formulations are made with the addition of

several polar components used to improve some of their physical and mechanical properties (such as plasticizers, emulsifiers, lubricants, binders, de-foaming agents, or formulation aids; Baldwin et al., 1997). Therefore, we may expect a substantial effect of RH on permeance properties of commodities treated with these “hydrophobic” coating films. It would be useful to characterise the changes in permeance of a commodity treated with different coating deposits in relation to the combined effects of temperature and RH. Increasing RH and temperature is expected to increase permeance to gases by increasing water content in the film and the diffusion constant (Kester and Fennema, 1986), even though there is a small decrease in the solubility coefficient of gases in the watery film matrix with the increase in temperature (Foust et al, 1980).

From the above, it is clear that when ever possible, precise control of temperature and RH should be sought when studying the effects of surface coatings on gas exchange and ripening attributes of coated commodities. This information should be included to characterise skin permeance to gases under specific conditions of RH and temperature to which the coated commodity will be exposed during the postharvest phase.

7.4 Draw-backs of skin coatings

7.4.1 Temperature abuse

Temperature rise is expected to have a larger effect in increasing respiration rate than P_{O_2}' (Banks et al., 1997a). This may result in p_{O_2}' dropping below the LOL^i , rendering the product anaerobic when the commodity is exposed to high temperatures. For this reason, coating treatments should be optimised for the highest temperature the commodity may eventually be exposed to throughout the marketing chain, resulting in less beneficial effect of the treatment in suppressing ripening at lower temperatures. This is the main limitation of surface coatings for fruits destined for fresh marketing,

since long term exposure to high temperature abuse can cause development of off-flavours. For fruit destined for processing, as well as for fresh market, if excessive accumulation of anaerobic volatiles is avoided to prevent development of off-flavours, this may in fact improve the final product flavour (Baldwin et al., 1995; Lakshminarayana et al., 1974; Nisperos-Carriedo et al., 1990). For pears, if postharvest handlers along the fresh fruit marketing chain are able to keep the temperature no higher than 20°C, coatings can offer an excellent opportunity to preserve fruit postharvest quality.

7.4.2 Ripening uniformity

There is a naturally high variability in ripening rate between fruit of the same batch. As a result of the Michaelis-Menten relationship between ripening attributes and p'_{O_2} , progressively larger effects in delaying ripening are achieved with lower p'_{O_2} . Improving the coating deposit on the skin provides more substantial reduction of p'_{O_2} , increasing still further the high natural ripening variability, resulting in a variable product postharvest quality (Chapters 3 and 5).

7.4.3 Variable response for different ripening attributes

In pears, softening has a lower K_m for p'_{O_2} than skin colour change (Fig. 7.4; Chapter 5). The higher sensitivity of colour change than softening for p'_{O_2} may result in coated pears that are still able to soften while skin colour change is greatly inhibited when p'_{O_2} reduction is moderate (Fig. 7.4; Chapters 3 and 5). The storage of pears in modified atmosphere packages might have the same effect, with softening proceeding faster than chlorophyll loss, so that the appearance of the fruit fail to match its internal condition (Geeson et al., 1991a; Geeson et al., 1991b). Further reductions of p'_{O_2} would substantially delay softening while still inhibiting colour change. At these low p'_{O_2} levels, small variability in p'_{O_2} would result in large variability of fruit firmness, but not

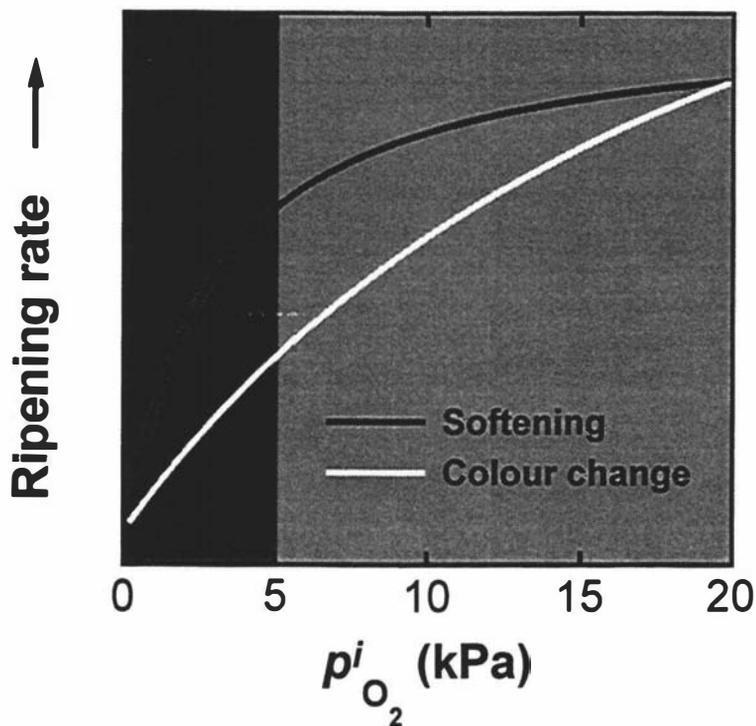


Figure 7.4 Changes in firmness and skin colour of coated pears in relation to internal O_2 partial pressure (p'_{O_2}). In the light gray part, reduction of p'_{O_2} would result in more substantial inhibition of changes in colour than firmness. In the dark gray part, reduction of p'_{O_2} would result in more substantial inhibition of firmness than changes in colour.

of colour change, since at low p'_{O_2} the colour change is almost totally inhibited. Figure 7.4 shows that at any p'_{O_2} level, variable ripening quality would result from variable p'_{O_2} between coated fruit: pears would have large variability in colour at high to moderately low p'_{O_2} , while the variability in firmness would dominate at moderately low to very low p'_{O_2} .

Since pears with a bright yellow skin have been rated ideal by the consumers in a study made in Canada (Kappel et al., 1995), the excessive inhibition of colour change may represent a significant commercial draw-back of surface coatings for pears.

However, if changes in consumer attitude could be achieved, then the marketing of a well flavoured coated pear with a green skin may become feasible. This certainly would be less of a problem for new pear cultivars having blushed skin and launched in the market recently. For such pear cultivars coatings could be used to reduce weight loss, delay ripening and improve skin finish without the “degreening inhibition” problems.

7.5 Use of surface coatings to characterise ripening behaviour, LOL^i and physiological disorders with respect to internal gas composition for CA/MA optimisation of horticultural commodities

In the present study, coatings have been shown to have a practical application in creating different levels of internal atmosphere modification at ambient temperatures. The larger modification of $p_{O_2}^i$ than of $p_{CO_2}^i$, achieved by coatings at these temperatures resulted in the ripening behaviour of coated pears following a Michaelis-Menten model when plotted against $p_{O_2}^i$, while $p_{CO_2}^i$ had virtually no explanatory power for these variables. If for other coated commodities $p_{O_2}^i$ is also the main determinant of ripening behaviour, plots against $p_{O_2}^i$ can be used to optimise and predict changes in different ripening attributes for a given CA/MA storage condition. In addition, modeling ripening in relation to internal O_2 composition reduces the variability between fruits in comparison to studies made in relation to external O_2 concentration. For a given external O_2 concentration there will be large variation in internal O_2 composition between fruits of the same batch, as a result of their differences in P_{O_2}' and respiration rate (Banks et al., 1993b). As the O_2 concentration to which tissues respond most directly is that in the cell sap, which is at steady-state with $p_{O_2}^i$ (Dadzie et al., 1996; Yearsley et al., 1996), this approach would provide a more robust mechanistic model to characterise the commodity ripening behaviour (Banks et al., 1993b).

In addition to the characterization of ripening behaviour in relation to $p_{\text{O}_2}^i$, coatings can also be used to estimate the commodity LOL^i . LOL^i seems to be relatively independent of temperatures no higher than about 30°C (Yearsley et al., 1997a), and of $p_{\text{CO}_2}^e$, no higher than 8 kPa at ambient temperatures (Yearsley et al., 1997b). Therefore, the LOL^i estimated at ambient temperatures for fruit coated at different ripening stages might help in the optimisation of CA/MA storage in a variety of environmental conditions.

A similar approach can be used to model internal gas composition in relation to the incidence of internal physiological disorders. In addition to O_2 and CO_2 internal atmosphere compositions, the assessment of the concentration of some volatiles, which have been reported to have casual relationships with some internal disorders, should be monitored. Plots between physiological disorders and the internal concentration of these volatiles, $p_{\text{CO}_2}^i$ and $p_{\text{O}_2}^i$ at different temperatures could help in characterising the conditions conducive for the disorders, and thereby helping to develop strategies to avoid the disorder.

7.6 Applications of multivariate analysis techniques in postharvest research

Data analysis in postharvest research has mainly focused on performing analysis of variance (ANOVA) on each attribute of the experimental unit (eg. fruit) to study the effects of a group of treatments. However, the information provided by this sort of analysis disregards the fact that the system being studied involves many inter-correlated variables. This approach ignores relationships between attributes and their multivariate structure, and erroneously promotes a univariate view of the system under examination (Cruz-Castillo et al., 1994). This not only represents lost opportunities, but also an inefficient use of resources during execution of the research. Multivariate statistical techniques take into account the inter-relationships among the multiple measurements of the individuals being investigated (Cliff, 1987; Jobson, 1992). In the

present study, two multivariate techniques have been explored for data analysis and interpretation: canonical discriminant analysis (CDA) and canonical correlation analysis (CCA).

CDA determines how best to discriminate groups of treatments, given quantitative measurements of several attributes on the individuals, and provides information about the relative discriminatory power of each attribute (Cruz-Castillo et al., 1994). In Chapter 3, CDA was performed to discriminate between treatments with coating concentration, given the assessment of three ripening attributes: respiration, softening and skin colour change rates. Although the ANOVA showed a highly significant effect of coating concentration for each ripening attribute considered separately, it did not provide information about the joint contribution of all attributes for between treatment variation. The CDA results showed a higher power of respiration, followed by firmness and skin colour in discriminating between treatments. This was the result of small between group and/or large within group variability for firmness and skin colour, especially the latter attribute, when all the variables were considered jointly to separate coating treatments. These results provide practical information about the ripening of coated pears: treated fruit have variable quality in terms of softening and skin colour change, especially the later attribute, that may have detrimental effects on product marketability. A simple ANOVA followed by multiple-comparison test would not reveal this fact.

In Chapter 4, CDA was performed to discriminate between coating concentration treatments, in terms of P'_{H_2O} , P'_{O_2} and P'_{CO_2} . Again, ANOVA results indicated a highly significant difference between coating treatments for each permeance attribute considered separately. The CDA results showed that the power of permeance attributes contributing jointly to separate coating treatments was largely dependent on relative contribution of pores and cuticle to gas exchange for each cultivar. 'Bosc', with lignified cell in the skin, had an epidermis with high P'_{H_2O} and low P'_{CO_2} . Increasing the amount of coating deposited on the skin resulted in small incremental reductions of P'_{H_2O} (possibly resulting in small between treatment variation) and substantial but

variable changes in P'_{CO_2} (possibly resulting in large within treatment variation). Therefore, for this cultivar, the separation of coating treatments could be accounted for almost exclusively by changes in P'_{O_2} , achieved by improving the blockage of pores with the increases in coating concentration. For cultivars with a high skin permeance to gases ('Bartlett' and 'Comice'), as a result of a high contribution of pores to gas exchange, improving the coating deposit resulted in a substantial reduction of skin permeance to gases, but with more variable reduction of P'_{O_2} than P'_{CO_2} , probably as a result of variable blockage of pores between fruits treated with intermediate coating concentrations. For these cultivars, improving the coating deposit also substantially reduced P'_{H_2O} and, therefore, P'_{H_2O} and P'_{CO_2} contributed most to separate between treatments. For Packham's', with low skin permeance to gases, increasing the coating deposit improved the blockage of partially blocked pores, resulting in larger between and/or smaller within treatment variation for P'_{O_2} than for P'_{CO_2} (which still moves in significant quantities through the coated cuticle). For this cultivar, improving the coating deposit also substantially reduced P'_{H_2O} and, therefore, P'_{H_2O} and P'_{O_2} contributed most to separate between treatments. This information helps in interpreting the results of the effects of coating deposit in changing the skin permeance to different gases. It also shows that coatings may have different impacts on each permeance attribute, depending on skin nature of pear cultivars, which may have implications in terms of reduction of water loss and internal atmosphere modification, affecting postharvest quality of the coated commodity. For cultivars with variable changes in P'_{O_2} when treated with intermediate coating concentrations, this can result in variable p'_{O_2} , which can exacerbate the naturally high variability in softening and skin colour changes (mainly in colour) that occurs between fruit.

The characterization of discriminatory power of each attribute in a CDA can be improved by calculating the parallel discriminant ratio coefficient (DRC) for each attribute, defined as the product between SCC (standardized canonical coefficients) and r (correlation between the canonical discriminant functions [CDFs] and the original attributes), as suggested by Tomas (1992). This can also alleviate the

confusion between the interpretation of SCC and r values during the interpretation of CDA (Cruz-Castillo et al., 1994). When a limited number of CDFs (one or two) explains most of the total variation, their canonical scores may undergo ANOVA followed by an independent multiple comparison test to discriminate between treatments (Cruz-Castillo et al., 1994). This approach was used in Chapters 3 and 4, where more than 89% of total variation was explained by the first CDF, and ANOVA was used to rank and discriminate between coating concentrations.

CCA is used to study the relationships between two groups of attributes and to determine those attributes in each group which explain the main source of 'similarity' between the two groups of original attributes (Cliff, 1987). CCA finds linear combinations of the two groups of attributes (called canonical variables) that are highly correlated, and the coefficients of each canonical variable indicates the relative power of each attribute in each canonical correlation (Jobson, 1992). It should be noted here that CCA is a generalization of multiple regression analysis (Cliff, 1987). In multiple regression analysis, a single attribute "Y" is related to two or more attributes "X's", and represents the maximum correlation between "Y" and a linear combination of "X's". In CCA instead, several "Y" attributes are simultaneously related to several "X" attributes.

In Chapter 5, CCA was used to assess the degree of association between internal gas composition (p'_{O_2} and p'_{CO_2}) and ripening attributes (respiration and changes in firmness and skin colour), and also to identify the gas more strongly associated with the ripening behaviour of coated pears. Apart from graphical characterization of the relationships between ripening attributes and internal gas composition presented in Chapter 5, CCA allows a mathematical description of them. In conjunction with CCA, the SAS system (SAS, 1990) can also perform a canonical redundancy analysis. This provides the proportions of total variance of original attributes in one group explained by the canonical variables of the opposite group, being an indicator of how good a canonical variable is as predictor of the opposite group of variables (Cliff, 1987; Jobson, 1992). In addition, this analysis provides information on squared multiple

correlation's between canonical variables in one group and each original attribute in the opposite group. This indicates how good a canonical variable of one group (such as p'_{O_2} , since this gas has been shown in Chapter 5 to have the strongest association with ripening behaviour of coated pears) can be to predict a specific attribute of the opposite group (respiration, firmness or skin colour). The canonical redundancy analysis may have practical applications for the optimisation of CA/MA storage, when the main objective may be to characterise the relationship between atmosphere gas composition (such as combinations of O_2 , CO_2 , ethylene concentrations) and retention of several aspects of the commodity quality (such as firmness, skin colour, flavour, off-flavours and disorders).

7.7 Future directions

Future publications with surface coatings should clearly state the chemical composition and method of emulsion preparation of the commercial coating formulation. There are so many different coating formulations on the market now, that it is almost impossible to compare them using trade names within the literature. In several published scientific papers only the trade name of the coating used is referred. Other papers reported using a "wax coating" and declined to provide details of the wax base. Both these types of omissions render the papers virtually useless for making any worthwhile comparisons. It is also suggested that the application rate should be standardized and expressed in terms of surface coating dry matter/commodity skin area or coating thickness, to provide a useful standard base for comparison. Another interesting aspect that may be worth investigating is how coatings interact with the different skin characteristics of commodities other than pears.

Most of the reported assessments of film permeability characteristics are conducted at temperatures between 25°C and 30°C, under conditions of 0% RH for O_2 and RH gradient close to 100% for water vapor. While this is worthwhile for comparing various attributes of films, it fails to replicate the conditions on the coated commodity.

It is suggested that the information gained could be enhanced by using 98%/60% RH gradient in the chambers for gases and water vapour permeability assessment, and at standard temperatures of 0°C (mimicking cold storage temperatures) and 20°C (mimicking shelf life temperature conditions).

The level of modification of internal atmosphere is mainly determined by character of cover of the skin by the coating and respiration rate of the commodity. Therefore, direct measurement of commodity permeance to gas exchange under controlled environmental conditions should be preferred for selection and optimisation of surface coatings. As the permeability of coating films is so variable at different temperatures and RH's it is important to report the environmental conditions experienced by the coated commodities during postharvest assessments. Besides water vapour, O₂, and CO₂ permeance estimation, the permeance of surface coatings to toxic volatiles (such as acetaldehyde and ethanol) should be investigated. This may help in the selection of edible coatings presenting low risk of inducing off-flavours and internal disorders.

Estimation of temperature effect on r'_o and of temperature and RH effects on P'_o of commodities treated with different levels of coating deposit might improve the optimisation of surface coatings for different environmental conditions. Characterising the LOL^i as a function of ripening stage could help in establishing the optimum amount of coating that can be applied to each type of commodity to ensure optimum retention of postharvest quality. These pieces of information will be fundamental to produce a more robust mechanistic model for optimising the use of surface coatings for different commodities and environmental storage conditions. To characterise postharvest quality for different coated commodities, information will be required about the relationship between the extent of internal atmosphere modification and changes in distinct physiological ripening processes, such as respiration, softening and skin colour change. The optimisation of surface coatings should also consider the assessment of sensory attributes and incidence of physiological disorders after long-term cold storage and also after a shelf life period.

Finally, coating optimisation experiments conducted within the laboratory should be also trialed in commercial packhouse conditions to ensure recommendations are relevant to the industry. Perhaps collaborative work with engineers designing waxing plants and the chemists formulating the coatings could help industry to optimise applying coatings to various commodities. Further research into the factors causing, and solutions for minimizing variability between and within lines of fruit would be useful. At present in order to reduce the risk of a few fruit turning anaerobic the coating level needs to be much less than optimum for the majority of the fruit.

7.8 Conclusions

The optimisation of surface coatings for pears should consider differences between cultivars, ripening stage and treatment period. For cultivars that have a risk of developing internal disorders caused by excessive internal accumulation of CO_2 at low temperatures when treated with high coating concentrations, as a result of high respiration rate ('Bartlett') or low P'_{CO_2} of coated skin ('Bosc'), coating treatments should be restricted only for fruit which will not subsequently be exposed to low temperature. The tolerance to hypoxic conditions, expressed in terms of LOL^i , was dependent on cultivar and fruit ripening stage. 'Bartlett' and 'Bosc' were less tolerant to hypoxia created by high coating concentrations, and tolerance reduced with ripening advancement. 'Comice' and 'Packham's' were highly tolerant to hypoxia and the fruit did not ferment despite $p'_{\text{O}_2} \cong 0$ kPa, even for fruit entering the climacteric. For all pear cultivars, the substantial suppression of ripening during shelf life was achieved by reducing p'_{O_2} instead of increasing p'_{CO_2} . However, the variable cover of skin pores in cultivars having high permeance to gases might result in variable P'_{O_2} and variable p'_{O_2} when the fruit are treated with intermediate coating concentrations. This might increase the naturally high ripening variability of pears by increasing the variability in p'_{O_2} between fruit treated with the same coating concentration. In pears, softening had a lower K_m for p'_{O_2} than skin colour. Therefore, coated pears might have variable

postharvest quality mainly in terms of colour change, and the fruit may still soften while being unable to change in colour. This might fail to produce a fruit of sufficiently uniform quality to be of commercial benefit.

The low postharvest quality of coated pears in terms of variable ripening might be compensated for by the effects of coatings in improving the gloss and reducing water loss, skin friction discolouration, senescent scald, senescent breakdown and total wastage of pear cultivars with non-lignified cells in the skin. For these cultivars ('Bartlett', 'Comice' and 'Packham's'), more substantial reduction in P'_{H_2O} was achieved by treating the fruit with low wax concentrations. If a similar response of P'_{H_2O} to low concentration wax coating can be achieved with other fruits, this treatment could represent a technology with a high potential to reduce water loss, without adversely affecting internal atmosphere composition and causing anaerobiosis in commodities less tolerant to hypoxic conditions. For 'Comice', improving the coating deposit resulted in more substantial modification of internal atmosphere during cold storage, slightly improving ripening delay. These treatments also substantially reduced wastage by diminishing the incidence of senescence related disorders (breakdown and scald) after long term storage and skin friction discolouration during shelf life. Since coatings have more limited effect in delaying ripening in cold storage than during shelf life, an alternative approach could be to optimise coating concentrations to treat the fruit on removal from CA storage in order to delay deterioration during marketing.

The use of coatings to delay ripening might represent an attractive technology for less developed countries, which are limited in refrigeration facilities to preserve the product quality from harvest to distribution to the final consumers. This can substantially reduce wastage if care is taken to avoid temperature abuse or treatments with coating formulations that can over-restrict gas exchange and result in fermentation. Coating may have a large potential for use in commodities with coloured skin (having high anthocyanin and carotene contents in the epidermal cells), for which the problems with variable degreening caused by coatings would not be such a great concern. The concern about the impacts of coatings on human health is not a major

problem for fresh commodities which have the skin removed before consumption. This issue should also be considered in terms of cultural differences. While in some countries it is common practice to peel fruits such as apples and pears before consumption, this is not the case for others. In the first group coatings have a larger commercial potential, without the major concern of human ingestion of these so called “edible coatings”. This will be still less a concern if the development of new coating formulations focus on the selection of dietary food approved ingredients.

7.9 References

- Baldwin, E.A., 1994. Edible coatings for fresh fruits and vegetables: past, present, and future. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 25-64.
- Baldwin, E. A., Nisperos-Carriedo, M., Shaw, P. E. and Burns, J. K., 1995. Effect of coatings and prolonged storage conditions on fresh orange flavor volatiles, degrees Brix, and ascorbic acid levels. *Journal of Agricultural and Food Chemistry*, 43: 1321-1331.
- Baldwin, E. A., Nisperos, M. O., Hagenmaier, R. D. and Baker, R. A., 1997. Use of lipids in coatings for food products. *FoodTechnology*, 51: 56-62, 64.
- Banks, N. H., Dadzie, B. K. and Cleland, D. J., 1993a. Reducing gas exchange of fruits with surface coatings. *Postharvest Biology and Technology*, 3: 269-284.
- Banks, N. H., Cleland, D. J., Yearsley, C.W., and Kingsley, A.M., 1993b. Internal atmosphere composition – a key concept in responses of fruits and vegetables to modified atmospheres. *Proceedings of the Australasian Postharvest Conference*. The University of Queensland, Gatton College, Lawes, Queensland, Australia. pp. 137-143.
- Banks, N. H., Cheng, Q., Nicholson, S. E., Kingsley, A. M., and Jeffery, P. B., 1997a. Variation with temperature in effects of surface coatings on gas exchange of apples.
- Banks, N. H., Cutting, J. G. M. and Nicholson, S. E., 1997b. Approaches to optimising surface coatings for fruits. *New Zealand Journal of Crop and Horticultural Science*, 25: 261-272.
- Ben-Yehoshua, S., 1966. Some effects of plastic skin coating on banana fruit. *Tropical Agriculture*, 43: 219-232.
- Ben-Yehoshua, S., 1967. Some physiological effects of various skin coatings on orange fruit. *Israel Journal of Agricultural Research*, 17: 17-27.
- Boersig, M. R., Kader, A. A. and Romani, R. J., 1988. Aerobic-anaerobic respiratory transition in pear fruit and cultured pear fruit cells. *Journal of the American Society for Horticultural Science*, 113: 869-873.
- Cameron, A. C., Beaudry, R. M., Banks, N. H. and Yelenich, M., 1994. Modified-atmosphere packaging of blueberry fruit: Modeling respiration and package oxygen concentrations at different temperatures. *Journal of the American Society for Horticultural Science*, 119: 534-539.
- Claypool, L. L. and King, J. R., 1941. Fruit waxing in relation to character of cover. *Proceedings of the American Society for Horticultural Science*, 38: 261-265.
- Cliff, N., 1987. *Analyzing Multivariate Data*. Harcourt Brace Jovanovich, Inc., Orlando, Florida, 494 pp.

- Cruz-Castillo, J.G., Ganeshanandam, S., MacKay, B.R., Lawes, G.S., Lawoko, C.R.O., Woolley, D.J., 1994. Applications of canonical discriminant analysis in horticultural research. *HortScience*, 29: 1115-1119.
- Cuquerella, J., Martinez-Javega, J. M. and Jimenez-Cuesta, M., 1981. Some physiological effects of different wax treatments on Spanish citrus fruit during cold storage. *Proceedings of the International Society of Citriculture*, 2: 734-737.
- Dadzie, B.K., Banks, N.H., Cleland, D.J. and Hewett, E.W., 1996. Changes in respiration and ethylene production of apples in response to internal and external oxygen partial pressures. *Postharvest Biology and Technology*, 9: 297-309.
- Donhowe, I. G. and Fennema, O., 1993. Water vapor and oxygen permeability of wax films. *Journal of the American Oil Chemists' Society*, 70: 867-873.
- Drake, S. R., Fellman, J. K. and Nelson, J. W., 1987. Postharvest use of sucrose polyester for extending the shelf-life of stored 'Golden Delicious' apples. *Journal of Food Science*, 52: 1283-1285.
- Elson, C.M., Hayes, E.R. and Lidster, P.D., 1985. Development of the differentially permeable fruit coating "Nutri-Save" for the modified atmosphere storage of fruit. In: S.M. Blankership (Editor), *Proceedings from the Fourth National Controlled Atmosphere Research Conference*. Horticultural Report North Carolina State University, Raleigh, pp. 248-262.
- Farooqi, W.A. and Hall, E.G., 1973. Effect of wax coatings containing diphenylamine on apples and pears during storage and ripening. *Australian Journal of Experimental Agriculture and Animal Husbandry*, 13: 200-204.
- Foust, A.S., Wenzel, L.A., Clump, C.W., Maus, L. and Andersen, L.B., 1980. *Principles of unit operations*. 2nd edition. John Wiley, New York, 768 pp.
- Geeson, J. D., Genge, P. M., Smith, S. M. and Sharples, R. O., 1991a. The response of unripe Conference pears to modified atmosphere retail packaging. *International Journal of Food Science and Technology*, 26: 215-223.
- Geeson, J. D., Genge, P. M., Sharples, R. O. and Smith, S. M., 1991b. Limitations to modified atmosphere packing for extending the shelf-life of partly ripened Doyenné du Comice pears. *International Journal of Food Science and Technology*, 26: 225-231.
- Gennadios, A., McHugh, T. H., Weller, C. L. and Krochta, J. M., 1994. Edible coatings and films based on proteins. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 201-277.
- Glenn, G.M., Rom, C.R., Rasmussen, H.P. and Poovaiah, B.W., 1990. Influence of cuticular structure on the appearance of artificially waxed 'Delicious' apple fruit. *Scientia Horticulturae*, 42: 289-297.

- Gontard, N., Thibault, R., Cuq, B. and Guilbert, S., 1996. Influence of relative humidity and film composition on oxygen and carbon dioxide permeabilities of edible films. *Journal of Agricultural and Food Chemistry*, 44: 1064-1069.
- Gran, C.D. and Beaundry, R.M., 1993. Determination of the low oxygen limit for several commercial apple cultivars by respiratory quotient breakpoint. *Postharvest Biology and Technology*, 3: 259-267.
- Hagenmaier, R.D. and Baker, R.A., 1993. Reduction in gas exchange of citrus fruit by wax coatings. *Journal of Agricultural and Food Chemistry*, 41: 283-287.
- Hagenmaier, R.D. and Baker, R.A., 1994a. Wax microemulsions and emulsions as citrus coatings. *Journal of Agricultural and Food Chemistry*, 42: 899-902.
- Hagenmaier, R.D. and Baker, R.A., 1994b. Internal gases, ethanol content and gloss of citrus fruit coated with polyethylene wax, carnauba wax, shellac or resin at different application levels. *Proceedings of the Florida State Horticultural Society*, 107: 261-265.
- Hagenmaier, R.D. and Baker, R.A., 1996. Edible coatings from candelilla wax microemulsions. *Journal of Food Science*, 61: 562-565.
- Hagenmaier, R. D. and Shaw, P. E., 1990. Moisture permeability of edible films made with fatty acid and (hydroxypropyl)methylcellulose. *Journal of Agricultural and Food Chemistry*, 38: 1799-1803.
- Hagenmaier, R. D. and Shaw, P. E., 1991a. Permeability of shellac coatings to gases and water vapour. *Journal of Agricultural and Food Chemistry*, 39: 825-829.
- Hagenmaier, R. D. and Shaw, P. E., 1991b. Permeability of coatings made with emulsified polyethylene wax. *Journal of Agricultural and Food Chemistry*, 39: 1705-1708.
- Hagenmaier, R. D. and Shaw, P. E., 1992. Gas permeability of fruit coating waxes. *Journal of the American Society for Horticultural Science*, 117: 105-109.
- Hernandez, E. 1994. Edible coatings from lipids and resins. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 279-303.
- Hitz, C. W. and Haut, I. C., 1938. Effect of certain waxing treatments at time of harvest upon the subsequent storage quality of Grimes Golden and Golden Delicious apples. *Proceedings of the American Society for Horticultural Science*, 36: 440-447.
- Jobson, J.D., 1992. *Applied Multivariate Data Analysis. Volume II: Categorical and Multivariate Methods*. Springer-Verlag, New York, USA, 731 pp.
- Kader, A.A., 1989. Mode of action of oxygen and carbon dioxide on postharvest physiology of 'Bartlett' pears. *Acta Horticulturae*, 258: 161-167.

- Kader, A.A., Zagory, D. and Kerbel, E.L., 1989. Modified atmosphere packaging of fruits and vegetables. *Critical Reviews in Food Science and Nutrition*, 28: 1-30.
- Kamper, S. L. and Fennema, O., 1984a. Water vapour permeability of edible bilayer films. *Journal of Food Science* 49: 1478-1481, 1485.
- Kamper, S. L., and Fennema, O., 1984b. Water vapor permeability of an edible, fatty acid, bilayer film. *Journal of Food Science* 49: 1482-1485.
- Kappel, F., Fisher-Fleming, R. and Hogue, E.J., 1995. Ideal pear sensory attributes and fruit characteristics. *HortScience*, 30: 988-993.
- Ke, D. and Kader, A. A., 1992. External and internal factors influence fruit tolerance to low-oxygen atmospheres. *Journal of the American Society for Horticultural Science*, 117: 913-918.
- Ke, D., Mateos, M. and Kader, A. A., 1993. Regulation of fermentative metabolism in fruits and vegetables by controlled atmospheres. *Proceedings from the Sixth International Controlled Atmosphere Research Conference, Cornell University, Ithaca, New York*. pp. 63-77.
- Ke, D., Yahia, E., Mateos, M. and Kader, A. A., 1994. Ethanolic fermentation of 'Bartlett' pears as influenced by ripening stage and atmospheric composition. *Journal of the American Society for Horticultural Science*, 119: 976-982.
- Kerbel, E. L., Mitchell, F. G., Kader, A. A. and Mayer, G., 1989. Effects of "Semperfresh" coating on postharvest life, internal atmosphere modification and quality maintenance of 'Granny Smith' apples. *Proceedings from the Fifth International Controlled Atmosphere Research Conference, Washington State University, Wenatchee*. pp. 247-254.
- Kester, J. J. and Fennema, O. R., 1986. Edible films and coatings: a review. *Food Technology*, 40: 47-59.
- Kester, J. J. and Fennema, O. R., 1989. Resistance of lipid films to water vapor transmission. *Journal of the American Oil Chemists' Society*, 66: 1139-1146.
- Lakshminarayana, S., Sarmiento, L., Ortiz, J. I. and Siade, G., 1974. Extension of storage life of citrus fruit by application of candelilla wax emulsion and comparison of its efficiency with Tag and Flavorseal. *Proceedings of the Florida State Horticultural Society*, 87: 325-330.
- Lau, O. L. and Yastremski, R., 1991. Retention of quality of 'Golden Delicious' apples by controlled- and modified-atmosphere storage. *HortScience*, 26: 564-566.
- Lau, O. L. and Meheriuk, M., 1994. The effect of edible coatings on storage quality of McIntosh, Delicious and Spartan apples. *Canadian Journal of Plant Science*, 74: 847-852.
- Magness, J. R. and Diehl, H. C., 1924. Physiological studies on apples in storage. *Journal of Agricultural Research*, 27: 1-38.

- Mellenthin, W.M. and Wang, C.Y., 1974. Friction discoloration of 'd'Anjou' pears in relation to fruit size, maturity, storage and polyphenoloxidase activities. *HortScience*, 9: 592-593.
- Mellenthin, W.M., Chen, P.M. and Borgic, D.M., 1982. In-line application of porous wax coating materials to reduce friction discoloration of 'Bartlett' and 'd'Anjou' pears. *HortScience*, 17: 215-217.
- Mannering, R., 1996. Pears pick up after determined effort. *The Orchardist*, 69: 18-19.
- Mannheim, C. H. and Soffer, T., 1996. Permeability of different wax coatings and their effect on citrus fruit quality. *Journal of Agricultural and Food Chemistry*, 44: 919-923.
- Martin-Polo, M., Voilley, A., Blond, G., Colas, B., Mesnier, M. and Floquet, N., 1992. Hydrophobic films and their efficiency against moisture transfer. 2. Influence of the physical state. *Journal of Agricultural and Food Chemistry*, 40: 413-418.
- Meheriuk, M., Prange, R.K., Lidster, P.D. and Porritt, S.W., 1994. Postharvest disorders of apples and pears. Agriculture Canada Publication 1737/E. 67pp.
- McHugh, T. H. and Krochta, J. M., 1994. Permeability properties of edible films. In: J.M. Krochta, E.A. Baldwin and M.O. Nisperos-Carriedo (Editors), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Company, Inc., Lancaster, pp. 139-187.
- Nanos, G. D., Romani, R. J. and Kader, A. A., 1992. Metabolic and other responses of 'Bartlett' pear fruit and suspension-cultured 'Passa Crassane' pear fruit cells held in 0.25% O₂. *Journal of the American Society for Horticultural Science*, 117: 934-940.
- Nisperos-Carriedo, M. O., Shaw, P. E. and Baldwin, E. A., 1990. Changes in volatile flavor components of pineapple orange juice as influenced by the application of lipid and composite films. *Journal of Agricultural and Food Chemistry*, 38: 1382-1387.
- Peppelenbos, H. W., Tijssens, L. M. M., van't Leven, J. and Wilkinson, E. C., 1996. Modelling oxidative and fermentative carbon dioxide production of fruits and vegetables. *Postharvest Biology and Technology*, 9: 283-295.
- Salisbury, F.B. and Ross, C.W., 1992. *Plant Physiology*. Wadsworth Publishing Co., California. 682 pp.
- SAS, 1990. SAS Institute INC. Cary, NC.
- Smith, S. M. and Stow, J. R., 1984. The potential of a sucrose ester coating material for improving the storage and shelf-life qualities of Cox's Orange Pippin apples. *Annals of Applied Biology*, 104: 383-391.
- Smith, S., Geeson, J. and Stow, J., 1987. Production of modified atmospheres in deciduous fruits by the use of films and coatings. *HortScience*, 22: 772-776.
- Toivonen, P.M.A., 1997. Non-ethylene, non-respiratory volatiles in harvested fruits and vegetables: their occurrence, biological activity and control. *Postharvest Biology and Technology*, 12: 109-125.

- Thomas, D.R., 1992. Interpreting discriminant functions: A data analytic approach. *Multivariate Behavioral Research*, 27: 335-362.
- Trout, S. A., Hall, E. G. and Sykes, S. M., 1953. Effects of skin coatings on the behaviour of apples in storage: I. Physiological and general investigations. *Australian Journal of Agricultural Research* 4: 57-81.
- Wang, C.Y. and Mellenthin, W.M., 1973. Relationship of friction discoloration to phenolic compounds in 'd'Anjou' pears. *HortScience*, 8: 321-323.
- Wang, C.Y. 1990. *Chilling Injury of Horticultural Crops*. CRC Press, Boca Raton, Florida. 313 pp.
- Watkins, C.B., Bramlage, W.J. and Cregoe, B.A., 1995. Superficial scald of 'Granny Smith' apples is expressed as a typical chilling injury. *Journal of the American Society for Horticultural Science*, 120: 88-94.
- Yearsley, C.W., 1996. Internal lower oxygen limits of apple fruit. PhD Dissertation, Massey University, Palmerston North, New Zealand, 366 pp.
- Yearsley, C.W., Banks, N.H., Ganesh, S. and Cleland, D.J., 1996. Determination of lower oxygen limits for apple fruit. *Postharvest Biology and Technology*, 8: 95-109.
- Yearsley, C. W., Banks, N. H. and Ganesh, S., 1997a. Temperature effects on the internal lower oxygen limits of apple fruit. *Postharvest Biology and Technology*, 11: 73-83.
- Yearsley, C. W., Banks, N. H. and Ganesh, S., 1997b. Effect of carbon dioxide on the internal lower oxygen limits of apple fruit. *Postharvest Biology and Technology*, 12: 1-13.

Appendix 1

Equilibration of surface chambers to the internal atmosphere of 'Doyenne du Comice' pear

The equilibration of surface chambers was characterized for fruit left at 20°C for 48 h, after one month cold storage. Two surface chambers (Fig. 5.1A) were adhered to each side (blushed and green sides) at the equator of 15 fruit and left to dry for 24 h. The surface chambers were flushed with O₂-free nitrogen and sealed with a septum and water seal. Samples of surface chamber atmosphere were taken 0, 1, 2, 4, 8, 16, 32, and 100 h after sealing the chamber. Gas samples were removed from surface chambers by gas tight syringe (Hamilton 100 mm³) and the values of $p_{O_2}^i$ and $p_{CO_2}^i$ were determined using an O₂ electrode (Citicell C/S type, City Technology Ltd., London, UK) in series with a miniature infra-red transducer (Analytical Development Company, Hoddesdon, UK), with O₂-free N₂ as a carrier gas (flow rate 580 mm³·s⁻¹).

The internal partial pressure of O₂ ($p_{O_2}^i$) and CO₂ ($p_{CO_2}^i$) with time at 20°C followed a Michaelis-Menten model (Fig. A1.1). The fitted models for $p_{O_2}^i$ {on the blushed side: $y = [16.74 (\pm 0.56) x] / [1.36 (\pm 0.23) + x]$ and $R^2 = 97.69\%$; on the green side: $y = [16.52 (\pm 0.57) x] / [1.41 (\pm 0.24) + x]$ and $R^2 = 97.66\%$ } and $p_{CO_2}^i$ {on the blushed side: $y = [3.52 (\pm 0.06) x] / [1.45 (\pm 0.12) + x]$ and $R^2 = 99.51\%$; on the green side: $y = [3.74 (\pm 0.06) x] / [1.45 (\pm 0.12) + x]$ and $R^2 = 97.51\%$ } indicated that equilibration between the fruit and the chamber internal atmosphere was achieved ~ 16 h after sealing the chamber.

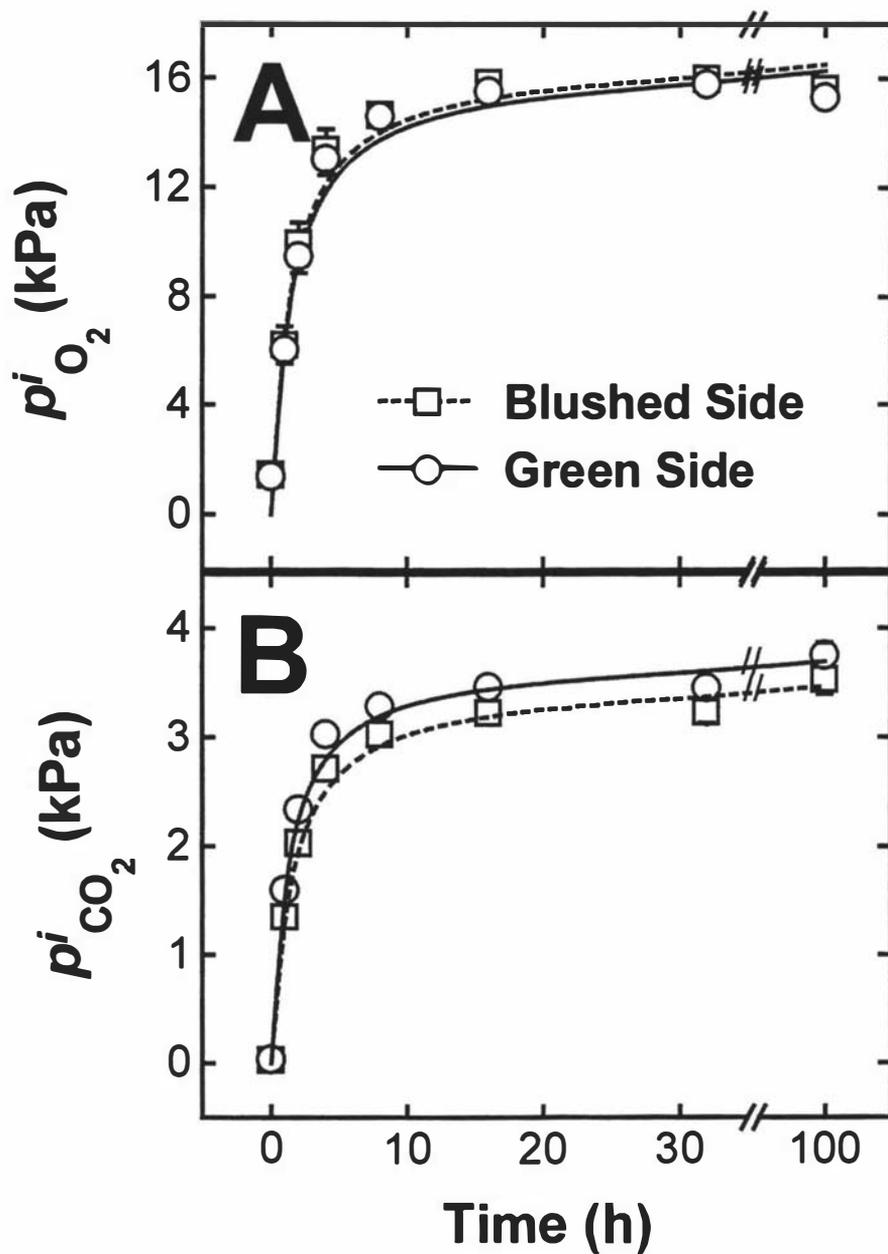


Figure A1.1 Equilibration of $p^i_{O_2}$ (A) and $p^i_{CO_2}$ (B) in surface chambers adhered to blushed and green sides of 'Doyenne du Comice' pears left at 20°C. Values are average of 15 fruit. Bars represent standard error of the means. Lines represent the best fit.