DEVELOPMENT OF THE DIFFERENTIALLY PERMEABLE FRUIT COATING "NUTRI-SAVE[R]" FOR THE MODIFIED ATMOSPHERE STORAGE OF FRUIT

Clive M. Elson, Ernie R. Hayes
Nova Chem Limited, P. O. Box 1030, Armdale,
Nova Scotia, Canada, B3L 4K9

Perry D. Lidster
Agriculture Canada, Kentville, Nova Scotia, Canada, B4N 1J5

The development of a preservative coating that simulates controlled atmosphere storage should offer several advantages to the apple industry. Potential advantages of using a differentially permeable fruit coating to create a modified atmosphere in apples and pears are: 1) improved retention of texture and titratable acids in cold storage; 2) maintenance of post-storage fruit quality during shipping; and 3) reduction of storage disorders. To achieve these benefits, the film coating must reduce the rates of respiration and desiccation. Nova Chem Limited has developed a coating, carrying the trademark "Nutri-Save[R]", that meets these requirements.

Description of "Nutri-Save" Coating

The "Nutri-Save" compound is a water soluble polysaccharide derived from a naturally-occurring biopolymer. Apples which are either dipped, drenched or sprayed with a 1-2% solution of "Nutri-Save" containing a surfactant take on a slight sheen but otherwise their appearance is unchanged. The coating process leaves approximately 3-5 mg of "Nutri-Save" polymer on the apple surface corresponding to a film of 1-3 microns in thickness (Fig. 1). Solutions of "Nutri-Save" have a pH of about 7.5 and a viscosity of 100-300 centipoise (1% solution). The material is biodegradable but won't support either fungal or bacterial growth. The "Nutri-Save" solutions are not compatible with all additives but they are compatible with benomyl fungicide. Tests have been performed on several different crops, e.g. apples, pears, tomatoes, peppers, pears, squash, cauliflower, strawberries, Brussel sprouts and broccoli, with encouraging results. Full scale toxicological studies at Hazleton Laboratories America will start in mid-June; however, a range finding study in which 2 rats of each sex were fed "Nutri-Save" polymer at dose levels up to 5% of diet has been completed. The rats' growth was normal and no effects were observed in either the gross necropsy procedures or in the histopathology examinations confirming our belief that the material is non-toxic.

Gas Permeability Studies

"Nutri-Save" films were prepared by pouring a solution onto a glass plate and allowing the water to evaporate. The films were transparent, firm, flexible and approximately 10-12 microns in thickness. When samples of the film were transferred from an environment of low relative humidity to one of high relative humidity, they absorbed water, increased in weight by up to 40% and became rubber-like, in fact when air was blown into a piece of film it stretched and expanded like a rubber balloon. To measure the permeability of the "Nutri-Save" films, pieces were mounted between the 2 halves of a glass O-ring joint which were attached by ground glass joints to 2 round bottom flasks. Sidearms on the flasks allowed gases to be introduced into one or other of the flasks and also to be withdrawn for gas chromatographic analysis. The variation of O_2 and CO_2 permeability with relative humidity at 20°C are shown in Figures 2 and 3, respectively. Below 70% relative humidity, the "Nutri-Save" films are impermeable to both gases; at 100% relative humidity 44 µl O_2 or 31 µl CO_2 will penetrate the film per square centimeter per hour. Hence, the permeability of "Nutri-Save" films can be governed by the water content of the air as well as the thickness of the film. From the above studies, it is inferred that the absorption of water by the films not only opens the structure of the film but also facilitates the transport of the gases through the film since these gases have a finite solubility in water. The rate of migration of water through the films was also measured at 20°C and was 0.8 mg $H_2O/cm^2/hr$. A comparison of the relative permeabilities to CO_2 of a series of polymeric films is presented in Table 1. A dry "Nutri-Save" film was comparable to Saran wrap and even when moistened a "Nutri-Save" film was superior to an inexpensive sandwich bag. The film designated "Nutri-Save-methylated" is interesting since it was twice as permeable to CO_2 and five times less permeable to H_2O than the standard "Nutri-Save" film. Such films, once improved, may have potential as coatings for citrus crops.

Respiration Studies

To demonstrate that the "Nutri-Save" coating did have an effect on the rate of respiration of apples, McIntosh apples were treated and placed in a respiration chamber at 20°C. Ambient air headspace gas which was free of CO_2 and ethylene was passed over the fruit at 1 liter/h and analyzed over a 7 day period (Table 2). A reduction in the rate of evolution of CO_2 and C_2H_4 (>50% reduction) was observed and the extent of the reduction was proportional to the concentration of "Nutri-Save" polymer in the coating mixture. Professor E. C. Lougheed (University of Guelph, Guelph, Ontario) in tests done on McIntosh apples that had been stored for 6 months at 1°C, warmed to 20°C and 70% RH, then treated with "Nutri-Save" coating and CO_2 and C_2H_4 monitored for 6 days (Table 3), found that the coating significantly reduced the respiration rate of post-storage apples. Professor Lougheed also studied Spartans, Idareds and Red and Golden Delicious cultivars. For Spartans, the ratio of CO_2 to O_2 was considerably greater than 1.0 indicating to him that fermentation may have occurred. Since Professor Lougheed's experiments were performed at a relative humidity where the film had been rendered relatively impermeable to O_2 penetration, the Spartan cultivar may be susceptible to low oxygen injury. For McIntosh apples, the "Nutri-Save" coating may have been moistened by water lost from the fruit as McIntosh are more susceptible to desiccation than Spartan. Furthermore, it is expected that different varieties will require different coating formulations to create identical MA conditions.

Storage Trials

Application of "Nutri-Save" solutions to McIntosh apples at concentrations of 1.5 percent (wt/v) or less showed no significant retention of fruit firmness or titratable acids in storage at 3°C (Table 4). However a 2 percent coating did indicate retention of firmness and titratable acids in the 1984 study but was less than the quality retention found in conventional CA (5% CO_2 plus 3% O_2) or low oxygen (0.7% CO_2 plus 1.0% O_2) storage regimens. In a separate commercial study, preclimacteric McIntosh apples were coated with 0.5% "Nutri-Save" and held for 161 days at 1° in air (Table 5). Treated fruit showed no incidence of scald or core flush compared to 9.6 and 8.3% respectively for the untreated fruit. A slight reduction in the incidence of decay was also found. Applications of 0.75 or 1.5% (wt/v) "Nutri-Save" to Spartan or 0.75% "Nutri-Save" to Golden Delicious apples did not suppress fruit firmness or titratable acids loss in air storage at 0°C (Tables 6, 7). However application of 2% "Nutri-Save" to Golden Delicious retained fruit firmness and titratable acids over a 9 month storage duration and were comparable to fruit held in conventional CA (3% CO_2 + 2.5% O_2, 0°C). Similar retention of fruit firmness have been observed on Idared apples (1) and by Dr. Sam Lau (personal communication) on Golden Delicious and Red Delicious treated with a 2% "Nutri-Save" solution without a surfactant added. Dr. Lau also determined that a 2% "Nutri-Save" application (without a surfactant) did not suppress fruit softening in McIntosh or Spartan apples stored for 5 months in air at 0°C. McIntosh, Golden Delicious and Red Delicious apples treated with "Nutri-Save" lost firmness at one-half the rate as compared to untreated CA-stored fruit during a simulated shelf life test of 7 days at 20° and 90% RH.

Application of 1 or 2% "Nutri-Save" to either Clapps Favorite or Bartlett pears stored for 90 days at 0°C significantly retarded the rate of fruit softening and titratable acids loss (Table 8). In 1 year of testing a 1% "Nutri-Save" coating resulted in firmness and titratable acids retention comparable to that in pears stored in conventional CA (3% CO_2 + 2.0% O_2) while a 2% "Nutri-Save" gave results similar to that found in pears stored in 0.3% CO_2 plus 1.0% oxygen. All storage treatments resulted in significant chlorophyll retention as compared to pears held in air storage and ripened to commercially acceptable standards at 20°C and 95% RH. However pears stored in either 1.0% oxygen or 2% "Nutri-Save" failed to ripen after 120 days of storage.

Conclusions

The permeability of the water soluble coating, "Nutri-Save", to oxygen and carbon dioxide was found to be dependent upon relative humidity, solution viscosity and molecular structure. The coating when applied to apples was able to suppress CO_2 and ethylene evolution from the fruit and oxygen penetration into the fruit at 20°C. Golden Delicious apples stored at 0°C appear to be the most responsive to coating application but quality retention response to coating application was also observed on McIntosh, Red Delicious, and Idared apple cultivars. Significant quality retention in Clapps Favorite and Bartlett pears in response to the coating application was observed in intermediate term (90 day) air storage.

The present evidence indicates commercial potential for the modified atmosphere storage of specific cultivars of apples and pears. Greatest potential for fruit quality retention using "Nutri-Save" appears to be for short to intermediate cold storage durations (60-180 days) in air. There does not appear to be a single universal coating recommendation for apples but rather each cultivar-coating combination must be formulated for optimum quality retention. Lot-to-lot and crop year-to-year response variations must also be considered prior to commercial implementation. However, with the appropriate testing and fruit selection, some of the quality benefits achieved through the use of CA storage may be realized by modified atmospheres created by fruit coatings in air storage.

Acknowledgements

The authors wish to acknowledge partial funding of this project provided by the Canada/Nova Scotia Food Development Programme. The authors are grateful to Dr. E. C. Lougheed and Dr. Sam Lau for sharing their results.

Literature Cited

1. Lidster, P. D. 1984. Modified atmosphere systems for individual fruits. Proc. Nova Scotia Fruit Growers Assn. Annu. Rpt. 121: (In press).

Table 1. Relative rates of migration of CO_2 through a series of polymeric films at 21°C and 100% R.H.

Film	Thickness (microns)	CO_2 Penetration (relative scale)
Nutri-Save	12	47
Nutri-Save - low R.H.	12	0
Nutri-Save - low viscosity	12	118
Nutri-Save - methylated	12	97
Nutri-Save +0.02 M NaCl	12	22
+0.02 M NaBr	12	42
+0.02 M LiF	12	30
Polyethylene	41	4
Saran Wrap	8	0
Quikki Sandwich Bag	21	128
"Zip-loc" Freezer Bag	44	6

Table 2. Carbon dioxide and ethylene evolution from McIntosh apples held at 20°C.

Treatment	Days	$ml\ CO_2\ kg^{-1}hr^{-1}$					$\mu l\ C_2H_4\ kg^{-1}hr^{-1}$				
		1	4	5	6	7	1	4	5	6	7
None		11.48[z]	12.68	11.93	11.50	11.86	75.09	90.16	103.60	65.93	80.94
Water Dip		11.21	12.51	11.57	11.72	11.94	62.86	93.03	93.76	93.09	76.18
0.65% Nutri-Save		8.79	6.03	5.77	5.97	6.20	20.31	27.11	34.39	42.01	39.74
1.0% Nutri-Save		8.20	5.74	5.33	5.24	5.35	21.66	21.33	23.90	30.93	28.73

[z] n=4

Table 3. Carbon dioxide (ml $kg^{-1}hr^{-1}$) and ethylene evolution and oxygen consumption (ml $kg^{-1}hr^{-1}$) in McIntosh apples held at 20°C.

Days at 20°C	Treatment*[z]	O_2 (ml $kg^{-1}hr^{-1}$)	CO_2 (ml $kg^{-1}hr^{-1}$)	CO_2/O_2	C_2H_4 (μl $kg^{-1}hr^{-1}$)
1	Nutri-Save[y]	6.7	6.2	0.9	42
	Untreated	13.3	11.9	0.9	119
2	Nutri-Save	6.5	6.9	1.0	38
	Untreated	12.4	12.4	1.0	146
3	Nutri-Save	5.7	6.4	1.1	38
	Untreated	11.4	11.4	1.0	156
6	Nutri-Save	6.0	6.2	1.0	46
	Untreated	11.6	11.2	1.0	144

[z]Apples stored for 6 months in air at 1°C prior to coating application.

[y]Nutri-Save coating applied at 1% with 0.1% Agral 90.

Table 4. Effects of controlled and modified atmosphere storage on firmness and titratable acids loss in McIntosh apples

Storage treatment (3°C)	Storage duration (months)	Fruit firmness (N)		Titratable acids (mg malic/100 mls juice)	
		1983	1984	1983	1984
Harvest	0	71	69	905	929
Air	3	48	50	827	542
	6	45	41	436	466
	9	41	36	365	306
Nutri-Save	3	45	45	730	584
A[z]	6	44	42	415	375
	9	41	37	308	301
Nutri-Save	3	50	53	643	680
B[y]	6	47	45	469	532
	9	42	41	312	365
0.7% CO_2 +	3	70	68	941	696
1.0% O_2	6	68	65	603	580
	9	67	59	606	573
3% CO_2 +	3	59	59	854	755
+ 2.5% O_2	6	56	50	512	529
	9	53	44	409	486

[z]Nutri-Save concentrations were 0.75% (wt/v) and 1.0% (wt/v) in 1983 and 1984 respectively.
[y]Nutri-Save concentrations were 1.0% wt/v and 2.0% (wt/v) in 1983 and 1984 respectively.
All solution contained a 0.1% (v/v) Tween-20 surfactant.

Table 5. Effects of 0.5% Nutri-Save coating on quality loss of McIntosh apples.

Treatment	Disorder Incidence[z]		
	Scald (%)	Core Flush (%)	Decay (%)
Control	9.6	8.3	5.4
0.5% (wt/v) Nutri-Save	0	0	1.3

[z]Examined after 161 days of air storage at 1°C.

Table 6. Effects of controlled and modified atmosphere storage on CO_2 and C_2H_4 evolution and on firmness and titratable acids loss in Spartan apples, 1983 crop year.

Storage treatment (0°C)	Storage duration (months)	Fruit firmness (N)	Titratable acids (mg Malic/100 mls juice)	CO_2 evolution (ml CO_2/kg.hr)	C_2H_4[y] evolution (μl C_2H_4/kg.hr)
Harvest	0	72	665	12.4	11.40
Air	3	62	570	15.8	51.40
	6	49	469	19.0	11.81
0.75% (wt/v) Nutri-Save[z]	3	58	563	15.3	59.10
	6	48	455	15.7	106.60
1.5% (wt/v) Nutri-Save[z]	3	64	657	12.7	38.00
	6	49	479	14.3	94.80
0.7% CO_2 + 1.0% O_2	3	70	677	12.2	33.90
	6	63	603	10.7	38.50
3% CO_2 + 2.5% O_2	3	68	640	13.1	36.40
	6	65	519	10.4	34.30
SE (n=5)		0.7	12.4	0.46	0.76

[z]0.1% (%) Tween-20 surfactant included in Nutri-Save solution.

[y]Values are averages over 3 day examinations at 20°C.

Table 7. Effects of controlled and modified atmosphere storage on firmness and titratable acids loss in Golden Delicious apples.

Storage treatment (3°C)	Storage duration (months)	Fruit firmness (N)		Titratable acids (mg malic/100 mls juice)	
		1983	1984	1983	1984
Harvest	0	73	78	670	616
Air	3	50	61	439	429
	6	48	49	302	315
	9	48	48	157	147
Nutri-Save A[z]	3	49	73	442	556
	6	49	67	312	399
	9	46	64	164	332
Nutri-Save B[y]	3	58	77	503	556
	6	55	72	365	529
	9	55	68	211	338
0.7% CO_2 + 1.0% O_2	3	72	77	600	549
	6	70	75	496	482
	9	70	71	399	452
3% CO_2 + + 2.5% O_2	3	72	76	640	570
	6	64	70	513	479
	9	61	69	389	399

[z]Nutri-Save concentrations were 0.75% (wt/v) and 1.0% (wt/v) in 1983 and 1984 respectively.
[y]Nutri-Save concentrations were 1.0% wt/v and 2.0% (wt/v) in 1983 and 1984 respectively.
All solution contained a 0.1% (v/v) Tween-20 surfactant.

Table 8. Effects of controlled and modified atmosphere storage on firmness and titratable acids loss in Clapps Favorite and Bartlett pears, 1984

Storage treatment[z]	Clapps Favorite		Bartlett	
	Fruit firmness (N)	Titratable acids (mg Malic/100 mls juice)	Fruit firmness (N)	Titratable acids (mg Malic/100 mls juice)
Air	56	173	61	200
1% (wt/v) Nutri-Save[y]	59	222	68	308
2% (wt/v) Nutri-Save[y]	62	237	72	298
0.3% CO_2 + 1.0% O_2	63[x]	278	72	306
0.3% CO_2 + 2.0% O_2	60	259	66	258
SE (n=5)	0.8	15.2	0.7	14.1

[z]Stored for 90 days at 0°C and 90% RH
[y]0.1% (v/v) Tween-20 surfactant included in Nutri-Save solution
[x]Flesh cavitation present indicating low oxygen injury.

FIG. 1. SCANNING ELECTRON MICROGRAPH OF "NUTRI-SAVE" COATING ON AN APPLE.

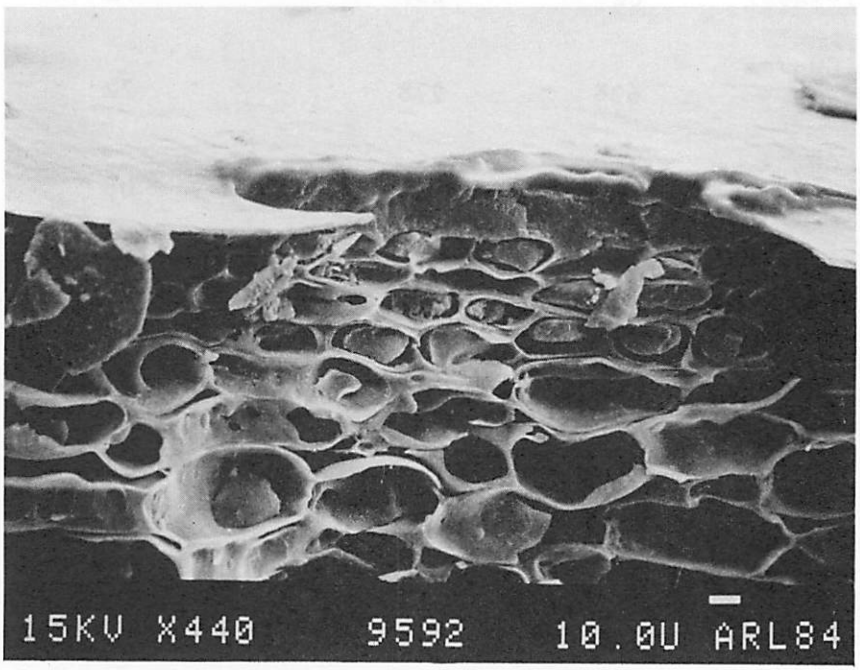

FIG. 2. PERMEABILITY OF "NUTRI-SAVE" FILM TO O_2 AS A FUNCTION OF RELATIVE HUMIDITY AT 20°C.

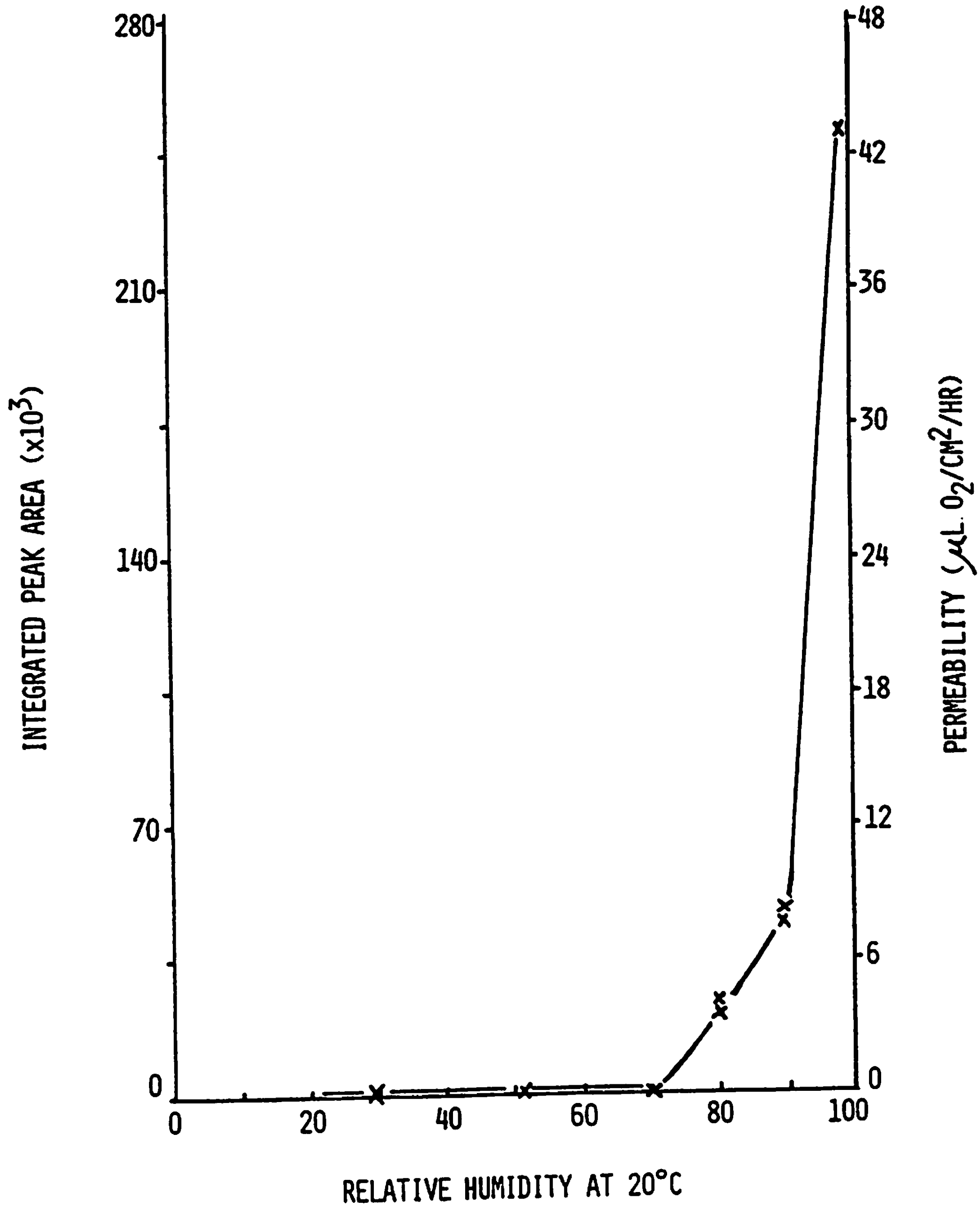

FIG. 3. PERMEABILITY OF "NUTRI-SAVE" FILM TO CO_2 AS A FUNCTION OF RELATIVE HUMIDITY AT 20°C.