



# final report

Project Code: M.465  
Prepared by: MLA  
Date published: October 1995  
ISBN: 1 74036 128 8

PUBLISHED BY  
Meat and Livestock Australia Limited  
Locked Bag 991  
NORTH SYDNEY NSW 2059

## Strategic Research into Smart Packaging

Meat & Livestock Australia acknowledges the matching funds provided by the Australian Government and contributions from the Australian Meat Processor Corporation to support the research and development detailed in this publication.

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### SUMMARY.

Many improvements have been made to the sachet formulations, and after many problems sachets have now been commercially manufactured.

The equipment for vacuum skin packaging and gas flush lidding is now set up at Melrina premises in Sydney and initial trials have begun.

Many problems were experienced with the equipment and with the films but these are now largely resolved. A new easier to use tray has been ordered.

The patent which covers the retail ready version of this technology and its use in masterpacks and vacuum packs has again been modified, and a PCT application which will allow world wide coverage has been lodged.

A promotional brochure illustrating the concept has been put together.

Bernard Bourke and myself aim to visit the MRC in the near future to discuss how we further develop this jointly owned technology, which we feel has immense scope.

## SACHET FORMULATIONS/ MANUFACTURE.

Much work has recently been carried out on optimal formulations for the sachets with good results.

The main aim has been to increase the rate of oxygen scavenging and its extent (target is less than 10ppm). A further aim was to reduce the cost of the formulations. Clearly the amount and rate of CO<sub>2</sub> production needs to be maintained.

The attached report from Warren Tully describes some of the formulation changes which we have made. In summary these are:

For a standard formulation in which the ultimate pH is alkaline:

1. The rate of oxygen uptake is greatly enhanced by changing from citric to fumaric acid. The downside is that fumaric acid is more expensive than citric (\$7 per kg versus \$4 per kg for citric acid) and is also less hydrophilic. If fumaric acid is used the rate of water uptake by the sachet is reduced. We compensate for this by using sodium ascorbate rather than ascorbic acid. Sodium ascorbate is more expensive than ascorbic acid (\$28.50 versus approximately \$34.50 per kg).
2. Increasing the proportion of ferrous sulphate increases the rate of reaction.
3. The addition of EDTA to formulations based on sodium bicarbonate and citric acid dramatically increases the rate of reaction - so much so that they are close to the speed of the fumaric acid formulations.
4. When EDTA is used the amount of ferrous chloride required becomes minimal.
5. Fumaric acid containing systems are less stable than citric acid formulations.
6. Carbon black and silica slow down these formulations.

Note from the above discussion that the oxygen absorbing component is the most expensive component (sodium bicarbonate costs \$1.50 per kg) and this explains why we are so interested in using iron in these formulations. Finely divided iron powder can be bought from laboratory chemical suppliers (traditionally the most expensive) for as little as \$21 per kg. 0.3g of iron can absorb up to 100ml of oxygen whilst 0.3g of ascorbic acid will only absorb up to 38ml of oxygen.

It would be highly desirable to produce these sachets from iron powder but this has been prevented by an unpleasant odour.

It appears that adding powdered zinc to these formulations is the most efficient way of ensuring that no smell is produced. EDTA and carbon, alone but not in combination increase the rate of reaction .

Manufacturing these sachets has been much more difficult than expected, and this is purely because an outside contractor is making them, and we do not have direct control.

Traditionally sachet manufactures have had little need for temperature control on their sealing equipment and consequently very little control is available. The microporous film we use for making the sachets is constructed from polypropylene and calcium carbonate. It is then stretched to delaminate the polymer from the filler giving the permeability to gases but not to liquid water. The film will shrink slightly on heating and also has a relatively small sealing window, so this is why the manufacturer had so many problems. After trying a variety of different films as one side of the sachet the manufacturer agreed to invest in some new heat controls which eventually produced the desired result. The sachets we have at the moment are not of the best appearance but show that they can be made commercially. Melrina currently have around 1300 sachets. Some problems with the powder reacting prematurely have been noticed in shifting from the 200g to 15kg scale (sachets typically contain 3-5g of power) but we believe we know the reasons for this. One is that all instructions about resealing packages and placing desiccant sachets in the machine hopper were ignored.

We have also observed that formulations based on citric acid seem to be more stable than those based on fumaric acid. A desiccant must be stored with the sachets.

#### MELRINA TRIALS.

I have visited Melrina twice in recent weeks.

The first visit was plagued by equipment failure.

The Intact machine supplied by Trigon was fitted with an inferior 1st vent valve and this meant that creases were a big problem. The film we are currently using is more susceptible to creasing than commercial Intact films. On the second visit a new 1st vent valve was fitted which allowed the film to be used. We are currently looking at the effect of manufacturing variables on this film to remove the creasing problem.

The lidding film would not peel sufficiently easily from the Intact film, for reasons unknown. Rolls of film from the same production run seemed to work very well in the lab on my return. On the second visit one of the earlier lidding films was substituted and worked OK. Some greater tear resistance would be useful.

The temperature on the lidding machine was reduced in order to by pass problems with the lidding film, but at this reduced temperature there were problems sealing through some of the creases caused by the venting valve. This led to browning of some of the samples due to pack leakage.

The lidding machine also required some attention before it would reliably evacuate and seal trays.

There are some major limitations in the use of Intact as regards the contraction of the tray and the positioning of meat in it. Particularly difficult to pack are thick cuts of meat with deep hard fat edges. These are not deformed by the film and the film tends to break as it becomes overstretched. These problems are made much worse when the tray has non compressable 90° walls like our present tray. We have ordered samples of a new tray from Flight Plastics which has the same seal area but angled edges. The previous supplier Derron gave us nothing but problems with very late delivery, wrong sizes, excessive lead times etc.

The second visit to Melrina solved all the problems except for the tray, and things are working well enough for Melrina to commence their own trials

I spent a good few hours showing Melrinas NSW Manager Daryl Fogarty the machines and what were the expected problems etc. I will follow this up with a simple manual.

On the first visit to Melrina some samples had been made and stored in their chiller which runs at -2°C. Beef samples were removed from this chiller and then packaged in the cold store at 2°C. The samples were semi solid when I next inspected them. The sachets had not worked because the temperature was too cold. The water which activates the sachet had frozen solid. We would not expect this to happen under normal conditions where the meat would be at 3-5°C when placed in the chiller.

#### OXYGEN ABSORBING FILMS.

This part of the project continues to proceed well.

A large number of formulations have been evaluated on the bench top extruder. These are all multi layer structures which are sequentially coated by the extruder. A brief report by Warren Tully is attached.

The photo exposed oxygen absorbing film project is also producing good results. A suitable switching mechanism has been identified and the team are now deciding on which is the most appropriate oxidisable substrate. A report from the student Craig Depree is attached.



Andrew Matthews

### Research into further sachet formulations

Although the CO<sub>2</sub> emitting/O<sub>2</sub> absorbing system is currently on line to be marketed there is always a need to minimise costs, with this in mind further research has continued into alternative substituents in the packs. At present sodium bicarbonate, sodium ascorbate, fumaric acid and ferrous sulphate are used, of which sodium ascorbate is the major cost. The aim is therefore to find cheaper alternatives that reduce the overall cost of each sachet whilst maintaining an appropriate rate of O<sub>2</sub> absorption/CO<sub>2</sub> emission.

One such alternative would be the use of ascorbic acid in lieu of sodium ascorbate, this has the added bonus that citric acid can be used to replace fumaric acid. Unfortunately the rate of oxygen absorption is significantly slower than its predecessor but we have found that this rate can be further enhanced by the addition of ethylenediaminetetraacetic acid (EDTA) {Table 1}.

Table 1						
code no.	NaHCO <sub>3</sub>	Citric A.	EDTA	Ascorbic A.	FeSO <sub>4</sub>	[O <sub>2</sub> ]
1	5.46	3.77		0.73	0.04	0.2 %
3	5.40	3.73		0.72	0.14	0.4 %
4	5.33	3.68		0.72	0.28	0.4 %
5	5.42	3.43	0.36	0.71	0.07	29 ppm
6	5.40	3.26	0.54	0.72	0.07	27 ppm
7	5.40	3.10	0.72	0.72	0.07	14 ppm
8	5.36	3.25	0.54	0.72	0.15	16 ppm

As can be seen EDTA dramatically increases the rate of oxygen uptake, presumably by complexing to the Fe(II) ions, also of note is that varying the amount of ferrous sulphate seems to have little effect on the rate. Further investigations (Table 2) showed that increasing the amount of EDTA (with respect to total acid content) increases the rate and that ferrous sulphate does need to be present albeit it in minute quantities.

Table 2						
code no.	NaHCO <sub>3</sub>	Citric A.	EDTA	Ascorbic A.	FeSO <sub>4</sub>	[O <sub>2</sub> ]
1	5.4	3.8		0.73	0.036	2.8
3	5.4	3.7		0.72	0.14	2.5
7	5.4	3.1	0.72	0.72	0.072	60 ppm
12	5.4	1.8	2.16	0.72	0.072	50 ppm
13	5.4	3.1	0.72	0.72	0.036	400 ppm
14	5.4	3.1	0.72	0.72	0.15	0.16
15	5.4	3.1	0.72	0.72		2
16	5.4	3.1	0.72	0.72	0.3	0.17
17	5.4	3.4	0.36	0.72	0.15	0.23
18	5.4	1.8	2.16	0.72	0.15	60 ppm
19	5.4	3.6	0.18	0.72	0.15	0.14
20	5.4	3.6	0.18	0.72	0.036	240 ppm

Further attempts to increase the rates of both the EDTA and standard formulation by the addition of active carbon proved unsuccessful (Table 3) with if anything a reduction in rates observed.

**Table 3**

code no	NaHCO <sub>3</sub>	Fumaric A.	Na Ascorbate	FeSO <sub>4</sub>	Active C	Ascorbic A	[O <sub>2</sub> ]
29	5.2	3.3	1.3	0.23			<10 ppm
30	5.2	3.3	1.3	0.23	0.05		<10 ppm
31	5.2	3.3	1.3	0.23	0.2		100 ppm
32	5.2	3.3	1.3	0.23	1		200ppm
EDTA							
36	5.4	2.4	1.5	0.08		0.72	100 ppm
37	5.4	2.4	1.5	0.08	0.1	0.72	100 ppm
38	5.4	2.4	1.5	0.08	1	0.72	100 ppm

More quantitative tests on the EDTA based system were performed (Table 4) in which 250 ml of air was introduced into the sample. This showed that in 5 days oxygen levels fell below 10 ppm, when EDTA replaced citric acid (77), and was somewhat higher when a citric acid/EDTA mix was used (78). However the mix was deemed to proceed at an appropriate rate, as confirmed (78\*) when oxygen levels were undetectable after 4 days in 150 ml of air.

**Table 4**

code no.	NaHCO <sub>3</sub>	Citric A.	EDTA	Ascorbic A.	FeSO <sub>4</sub>	[O <sub>2</sub> ]
77	2.0		1.3	0.8	0.05	<10 ppm
78	2.0	0.96	0.2	0.8	0.05	0.18
78*	2.0	0.96	0.2	0.8	0.05	<10 ppm

All these results confirm the suitability of this system. When considering that much higher quantities of oxygen have been removed than will be necessary in reality, and that the overall cost of each sachet is vastly reduced, we consider this system a winner and confident it has an application in the field.

A second alternative to the standard mixture is also being investigated, this being an iron based system. Iron is used for oxygen removal in numerous patents, having the advantages of being cheap and proceeding at a rapid rate (dependant on powder size). This would therefore seem the logical alternative, but as with most things there is a drawback in that iron powder and acid produce a pungent odour (apparently H<sub>2</sub>S). Removal of this aroma is therefore essential before any application can be considered. A literature search showed some possible hydrogen sulphide scavengers and tests on the more promising ones were carried out.

Initially Fe(II) salts were considered (Tables 5 and 6) but these still harboured

**Table 5**

code no.	NaHCO <sub>3</sub>	Citric A.	Fe	FeSO <sub>4</sub>	[O <sub>2</sub> ]
9	1.58	1.2	0.14	0.1	1.1
10	2.5	2.1	0.25	0.15	<0.5 ppb
11	2.4	2.1	0.3	0.2	2.5

**Table 6**

code no.	NaHCO <sub>3</sub>	Citric A.	Fe	FeSO <sub>4</sub>	Active C	[O <sub>2</sub> ]
33	2.5	2.1	0.25	0.15		1.41
34	2.5	2.1	0.25	0.15	0.05	0.6
35	2.5	2.1	0.25	0.15	0.5	<0.5 ppb

the unpleasant odour, however these tests did indicate that active carbon increases the rate of oxygen uptake. Conversely tests on various other scavengers (Tables 7 and 8)

<b>Table 7</b>							
code no.	NaHCO <sub>3</sub>	Citric A.	Fe	active C	Cu(NO <sub>3</sub> ) <sub>2</sub>	[O <sub>2</sub> ]	smell
39	2.55	2.05	0.25	0.1	0.05	3.92	no
Zinc							
40	2.55	2.05	0.25	0.1	0.1	<100 ppb	no

<b>Table 8</b>								
code no.	NaHCO <sub>3</sub>	Citric A.	Fe	active C	Zinc	[O <sub>2</sub> ]	[O <sub>2</sub> ] 6d	smell
59	2.3	1.9	0.3	0.05	0.08	240 ppm		no
Aspartic A								
60	2.3	1.9	0.3	0.05	0.1	2	0.5	yes
Glycine								
61	2.3	1.9	0.3	0.05	0.1	2.7		no
Copper								
62	2.3	1.9	0.3	0.05	0.1	0.14	<0.5 ppb	no
Zinc Oxide								
63	2.3	1.9	0.3	0.05	0.1	1.5	1.4	yes
Silica								
64	2.3	1.9	0.3	0.05	0.1	6 ppm	0.2 ppm	no
65	2.3	1.9	0.3		0.1	12 ppb		no

were far more successful with no hydrogen sulphide smell identifiable, although in some cases other odours were present. Of these results zinc powder appears the most promising with copper similarly showing some hope. Further investigations showed:

- (i) Zinc also removes oxygen (Table 9), though at a reduced rate (c.f. iron).
- (ii) Active carbon does increase the rate of oxygen absorption, whereas silica and salt do not (Tables 9, 10 and 11).
- (iii) Confirmation that copper powder is another alternative, glycine is not (Table 11).
- (iv) The presence of EDTA further increases the rate, but if EDTA is used in lieu of citric acid the rate is reduced. (Tables 13 and 14).
- (v) The inclusion of zinc increases the rate of oxygen uptake (Table 14).

<b>Table 9</b>							
code no.	NaHCO <sub>3</sub>	Citric A.	Fe	active C	Zinc	[O <sub>2</sub> ]	[O <sub>2</sub> ] 7d
46	2.3	1.8			0.3	0.12	50 ppm
47	2.3	1.8		0.2	0.3	0.2	140 ppm
48	2.3	1.8	0.3	0.2	0.1	<0.5 ppb	
49	2.3	1.9	0.3	0.2	0.1	<0.5 ppb	
50	2.3	1.9	0.3		0.1	0.2	
52	2.3	1.9	0.3	0.1	0.05	<0.5 ppb	
Cu(NO <sub>3</sub> ) <sub>2</sub>							
51	2.3	1.9	0.3		0.02	1.8	



**Table 10**

code no.	NaHCO <sub>3</sub>	Citric A.	Fe	active C	Zinc	[O <sub>2</sub> ]	smell
66	2.3	1.9	0.3	0.1	0.1	0.1 ppm	no
				Silica			
68	2.3	1.9	0.3	0.1	0.1	0.5	no
				NaCl			
70	2.3	1.9	0.3	0.1	0.1	0.3 ppm	no

**Table 11 (250ml air)**

code no.	NaHCO <sub>3</sub>	Citric A.	Fe	active C	Zinc	[O <sub>2</sub> ]	[O <sub>2</sub> ] 8d
65	2.3	1.9	0.3		0.1	2.2	<10 ppm
66	2.3	1.9	0.3	0.1	0.1	2.9	<10 ppm
				NaCl			
72	2.3	1.9	0.3	0.2	0.1	2.5	0.17
				active C	Cu		
71	2.3	1.9	0.3	0.1	0.1	2.1	<10 ppm
					glycine		
73	2.3	1.9	0.3	0.1	0.1	2.6	0.25

**Table 12 (250ml air)**

code no.	NaHCO <sub>3</sub>	Citric A.	Fe	active C	Zinc	[O <sub>2</sub> ] 6d
65	2.3	1.9	0.3		0.1	0.98
76	2.3	1.9	0.3	0.1	0.1	<10 ppm

**Table 13 (250ml air)**

code no.	NaHCO <sub>3</sub>	Citric A.	Fe	EDTA	[O <sub>2</sub> ] 5d
79	1.88		0.34	1.75	5
80	2.3	1.53	0.34		3

**Table 14 (150ml air)**

code no.	NaHCO <sub>3</sub>	Citric A.	Fe	EDTA	Zinc	[O <sub>2</sub> ] 4d
81	1.88	1.53	0.3			3.5
82	1.88	1.53	0.3		0.1	60 ppm
83	1.88	1.0	0.3	0.6		<10 ppm

From the above results it is clear that zinc (and possibly copper) powder are promising as scavengers of not only the unpleasant odour but also oxygen. Envisaged recipes may also include active carbon and/or EDTA to increase rates of oxygen absorption. However further trials are warranted before iron's use can be recommended.

#### Experimental

Readings taken after 3 days unless indicated otherwise. Two oxygen meters were used, one reading to 0.5 ppb and the other to 10 ppm. A standard method of injecting a known quantity of air into samples was introduced during these tests allowing for higher accuracy and reproducibility of results.

Samples have approximately 2.5 ml of added water to allow activation of sachets

### Summary of Oxygen Absorbing Iron Films

The first aim of this work involved determining how best to disperse the iron powder in films. It was found that when ionomers were used the iron adhered to the pellets thus requiring no special treatment. In all other cases powdered polymers were required to give adequate dispersion (in large scale applications compounding would be used).

Iron removes oxygen by rusting. This cannot occur without the presence of water and an electrolyte. Thus when iron and PEO (water absorbent) are put into the film we see minimal oxygen uptake. However when salt was included we found rusting did occur (Table 1).

Table 1					
Sample No.	Fe (%)	NaCl (%)	PEO (%)	Polymer	[O <sub>2</sub> ] (%)
1	15	3	5	LDPE	17.0 (3d), 10.4 (5d)
2	15	3	5	EVA 18	19.1 (1d), 8.7 (5d)
3	15		5	EVA 18	20.5 (1d), 20.4 (4d)
4	15		15	IONOMER	20.6 (1d), 20.6 (4d)

Interest was now focused on which resin gave the best results. It was found that the favourable resin to use was EVA with the higher % vinyl acetate the better. This preference for EVA may in part be due to the high oxygen and water vapour transmission rates of the films and also that on extrusion some acetic acid can be produced.

The next step was trying to speed up the rate of oxygen absorption. This was achieved by the use of acid in the formulation (Table 2). From the results it can be

Table 2					
Sample No.	Fe (%)	NaCl (%)	PEO (%)	Acid (%)	[O <sub>2</sub> ] (%)
5	15	3	10		8.1 (3d), 0.8 (5d)
6	15			3, Citric	12.9 (2d), 11.5 (3d)
7	10			1, Citric	18.1 (3d)
8	10	3		3, Citric	14.8 (6h), 10 ppm (4d)
9	10 <sup>1</sup>	3		3, Citric	13.0 (3h), 10 ppm (3d)
10	10 <sup>1</sup>	3		3, Ascorbic	16.3 (1d), 10.0 (9d)
11	10	3 FeSO <sub>4</sub>	5	3, Ascorbic	6.6 (8d)
12	10 <sup>1</sup>	3		2, Polyacrylic	18.4 (1d), 17.2 (9d)
13	10	3	5	4, NaCit	6.6 (3d)
14	10	3	5	3, Tartaric	13.9 (2d), 7.0 (3d)
15	10	3	5	4, Na <sub>3</sub> Cit	19.2 (1d), 9.7 (6d)
16	10	3		4, Na <sub>3</sub> Cit	18.6 (1d), 8.6 (5d)
17	10	3	5	3, Pot. Bitart.	15.2 (2d)
18	5 <sup>1</sup>	3	5	3, Citric	15.4 (6d)
19	5 <sup>1</sup>	3		2.3, NaCitA	19.9 (8d)

1. fine iron powder.

seen that the inclusion of citric acid with NaCl increases the rate dramatically. Unfortunately when the iron rusts we do get some leaching of this rust into the water which would not be consumer friendly. The use of citric acid also results in a small amount of gas which effects the film quality and resulting thickness.

The leaching is overcome by coating a thin film on the inner layer. This does slow the oxygen absorption but this effect can be reduced by using a high  $O_2/H_2O$  permeable film (such as EVA or Ionomer). Results (Table 3) confirm that rates of

Table 3 <sup>1</sup>					
Sample No.	Film	Coating	PEO (%)	Acid (%)	[O <sub>2</sub> ] % (days)
20	EVA 28	EVA 28	5	4 NaCitric	17.2 (1), 8.7 (4)
21	EVA 28	EVA 28	5	2, Tartaric <sup>2</sup>	17.6 (3)
22	EVA 28	EVA 28	5	3, Citric	11.6 (3)
23	EVA 28	EVA 28		3, Citric	6.7 (3)
24	EVA 28	EVA 28		2, Citric <sup>2</sup>	8.9 (3)
25	EVA 18	EVA 28		3, Citric	14.8 (1), 8.2 (4)
26	EVA 18	EVA 18		2, Citric	13.5 (3)
27	EVA 18	1901		2, Citric	14.3 (1)
28	EVA 18	1410		2, Citric	16.5 (3)
29	EMA	EVA 18		2, Citric	11.9 (3), 2.2 (7)
30	EVA 18	EVA 18		1, Citric	17.9 (3)
31	EMA	EVA 18		1, Citric	18.8 (1), 2.2 (14)
32	EVA 18	PF1140		1, Citric	18.5 (1)
33	EVA 18	EVA 18		0.3, Citric	17.9 (3)
34	EVA 18	EVA 18			18.9 (5)

1. All contain 10% Fe and 3% NaCl

2. Acid melted with Iron then reground before extrusion

3. EVA refers to EVA 18.

oxygen uptake are improved with citric acid concentration and highly permeable coatings. Also of note is that the water attracting additive (PEO) does not improve the rate when used in conjunction with citric acid. Further tests using mixed polymer films and gas flushed trays (Table 4) show that rates of oxygen uptake are sufficient in

Table 4					
Sample No.	mixed polymer Film	Coating	Acid (%)	[O <sub>2</sub> ] % (days)	gas flushed tray (0°C)
34	EVA 18/EMA 1:1	1901	3, Citric	14.4 (1)	1.5 ppm (1)
35	EVA 18/EMA 1:1	1901	1, Citric	16.2 (2)	0.3 (2)
36	EVA 18/EMA 1:3	1901	1, Citric	17.6 (2)	0.2 (2)
37	EVA 18/EMA 3:1	1901	1, Citric	14.7 (2)	0.2 (2)
38	EVA 18/1410 1:1	PF1140/EVA 18 1:1	1, Citric	19.1 (1)	2.4 (1)
39	EVA 18	PF1140/EVA 18 1:1	1, Citric	2.9 (8)	11.2 ppm (2)
40	EVA 18	EVA 18	0.73, Citric		27 ppm (3)
34	EVA 18	EVA 18			No Change

EMA/EVA mixtures only when the citric acid concentration is raised. The use of the polyacrylic acid (1410) also reduces the rate of absorption. Removal of oxygen from gas flushed trays kept at 0°C proceeds sufficiently even when only 0.73% citric acid is used however when no citric acid is present the absorption is practically halted.

Overall these results show that adequate rates of oxygen removal are achieved with films containing 10% Fe, 3% NaCl and as little as 0.7% citric acid in an EVA based film. The uptake of oxygen being further increased with higher concentrations of citric acid. These results are encouraging but the quality of the resultant film is reduced with the use of citric acid.

A second simpler system is now being investigated in which no acid is used. The rate is thus further reduced but the film quality is much better. Initial results (Table 5) are positive with the use of PEO improving the speed of oxygen uptake. It is hoped that further tests will reveal that the rates are sufficient for gas flushed trays.

Table 5				
Sample No.	Film	Coating	PEO (%)	[O <sub>2</sub> ] % (days) <sup>1</sup>
41	EVA 18			18.4 (3)
42	EVA 18		10	1.2 (3)
37	EVA 18	PF1140/EVA 18 1:1	10	17.8 (4)
38	EVA 18	PF1140/EVA 18 1:1	15	15.9 (3)

1. 150 ml air.

# Report

Films prepared so far have been prepared by one of two methods,

- (A)  $\text{Co}(\text{acac})_3$  and  $\text{Ph}_2\text{CO}$  (~150 mg of each) were dissolved in  $\text{CH}_2\text{Cl}_2$  and added to 6-8 grams of sunflower oil/squalene. The mixture was adsorbed onto silica (~5 grams),  $\text{CH}_2\text{Cl}_2$  removed before mixing with 45 grams of polymer (R3170; EVA-18).
- (B)  $\text{Co}(\text{acac})_3$  and  $\text{Ph}_2\text{CO}$  (~150 mg of each) were dissolved in  $\text{CH}_2\text{Cl}_2$  and mixed with 45 grams of EVA-18. The excess  $\text{CH}_2\text{Cl}_2$  was removed at 40 °C and sufficient silica (~2.5 g) was added to make the mixture "extrudable".

Mixtures from either method were extruded at 150 °C and a screw speed of approximately 80-85 rpm. Extrusion of these films requires "starve fielding" the extruder (adding small quantities at a time) and mixtures prepared via method B are easier to handle (less silica dust) and extrude.

$\text{Co}(\text{acac})_3$ ,  $\text{Mn}(\text{acac})_3$  and  $\text{Fe}(\text{acac})_3$  have been incorporated into EVA films (via method A). Co was by far the most active, Fe worked but was much slower and Mn for some reason showed no activity.

Much faster oxygen uptake observed when exposed for 4 min (rather than 2 min).

Although initially showed very promising results, subsequent films extruded using squalene as the oxidisable material were surprisingly unreactive compared to their sunflower seed oil counter-parts.

Still awaiting results from long term control experiments (same as experiment samples except no exposure to UV light). Results to date for the controls are largely for films prepared via method A (see below).

Control E1B (method A)	12.4 % after 19 days
Control E1H (method A)	~20.4 % after 26 days
Control E1Fa (method A)	~20.6 % after 26 days
Control E1Fb (method A)	~20.5 % after 26 days
Control E1M (method B)	~20.2 % after 14 days

Obviously more time is required to see how stable these controls are as ideally they need to be stable for at least a few months. The controls to date have been left at room temperature, storing these at cooler temperatures should lead to a significant increase in stability, however this may not be a feasible concept in the "real" world.

Samples made via method B have been prepared with 5, 6, 7 and 8 grams of sunflower seed oil and all exhibited oxygen scavenging (head space of bag typically between 450 and 550 mls). As expected performance decreases as the quantity of oil in the film decreases.

### Examples of oxygen uptake by "films"

- |     |                             |                                   |
|-----|-----------------------------|-----------------------------------|
| (I) | 45 g of EVA-18              | 2.7 g of silica                   |
|     | 8.0 g of sunflower seed oil | 0.156 g of Co(acac) <sub>3</sub>  |
|     | 0.164 g of benzophenone     |                                   |
|     | amount of film used 7.20 g  | exposure: 2 min each side of film |

Headspace Oxygen: 15.8 % (16 h), 1.25 (39 h), 0.21 (48 h), < 10 ppm (68 h)

- (2) Essentially the same as the above example except 7.0 g of sunflower seed oil was used.
- amount of film used 6.97 g                      exposure: 2 min each side

Headspace Oxygen: 12.6 % (20 h), 2.0 % (~2 days), <10 ppm (~3 days)  
cf. to similar sample only exposed for 2 min.

Headspace Oxygen: 20.1 % (20 h), 14.6 % (~2 days), 8.7 % (~3 days), 2.73 % (5 day)

- (3) Same as above except 6 g of sunflower seed oil used  
amount of film used 6.99 g exposure: 2 min each side

Headspace Oxygen: 8.7 % (20 h), 2.5 % (~2 days), 0.81 % (~3 days), <10 ppm (5 day)  
*cf. to 2 min exposure sample*

Headspace Oxygen: 19.7 % (20 h), 8.6 % (~2 days), 3.1 % (~3 days), < 10ppm (5 day)

- (4) Same as above except only 5 g of sunflower seed oil used  
amount of film used 6.9 g exposure: 2 min each side

Headspace Oxygen: 10.8 % (20 h), 4.5 % (~2 days), 3.1 % (~3 days), 1.2 % (5 day)

MRC CLAIMS TO DATE

1	MARCH 94	17,933.73
2	JUNE94	16,952.90
3	SEP 94	17,114.29
4	DEC 94	14,679.90
5	MARCH 95	35,699.24
6	JUNE 95	31,192.25
7	SEP 95	59,511.03
		<u>193,083.34</u>

MRC PAYMENTS TO DATE

1	MARCH 94	-30,765.00
2	JUNE 94	-30,017.48
3	SEP 94	-30,390.00
4	DEC 94	-30,060.00
5	MARCH 95	-29,835.00
6	JUNE 95	-27,805.00
7	SEP 95	-27,487.50
		<u>-206,359.98</u>

BALANCE

-13,276.64



Summary of the MRC Project Costs for the period ended 30/9/95Claim Number 7Project Salaries

	12075.00
Andy Matthews	8250.00
Russell Cassey	3825.00

Project Contractors

	34801.69
Warren Tully ( feb to jun)	15262.35
Warren Tully - jul/aug/sept	10666.59
eng recharge labour	664.75
mirinz trials	8208.00

Project Database

	1676.83
literature searches	20.17
patent CO2 gas pack	1484.74
patent codimer/kays	171.92

Project Materials

	10957.51
overhaul vac pump	347.00
pump	752.00
acetal rod	45.27
glass stirrers	25.00
meat for trials	308.40
gas cylinder	13.94
labour - eng recharge	75
sodium ascorbate	705.00
sodium bicarbonate	81.83
fumaric acid	177.50
iron powder/butadien	535.03
NAHCO3	9.02
trial FT74308	2087.52
TPSA trials	3200.00
TPSA trials	1820.00
TPSA trials	455.00
TPSA trials	90.00
TPSA trials	230.00

Project Travel

0

TOTAL CLAIM NUMBER SEVEN

\$ 59511.03

## PROBLEM:

M.465 - Strategic Research into Smart Packaging

Meat will absorb large quantities of carbon dioxide. For example, beef will generally absorb 1 litre of carbon dioxide per kg, while lamb will absorb up to 1.5 litres per kg. This has meant that high carbon dioxide packaging has not been used for tray based systems due to pack distortion.

## TRIGON'S SOLUTION

We have overcome this problem by developing a patented CO<sub>2</sub> generator / oxygen absorber sachet.

This produces CO<sub>2</sub> at a rate similar to the rate of absorption, and in an amount sufficient to saturate the meat. This allows minimal pack volume (ie very low headspace) and avoids pack distortion. CO<sub>2</sub> packaged red meat is very sensitive to oxygen, thus the use of an oxygen absorber as one component of the sachet.

Oxygen absorbers have been available for many years but many of these absorbers do not function effectively in high CO<sub>2</sub> atmospheres. Oxygen absorbers which release carbon dioxide to compensate for oxygen removed are also available. However, this is the first time a system has become available whereby the amount of CO<sub>2</sub> generated is independent of the amount of oxygen absorbed.



*Sachet added at the time of packaging*

These sachets may be used with a variety of package styles such as within vacuum and gas flushed pouches, (eg Masterpack) but for retail presentation the following package style has proved excellent.

The meat is vacuum skin packed onto a PET or PVC tray. This holds the meat in place on the tray and also retains the drip.

A sachet and a few mls of

water are placed on top of the skin film, or attached to the lid. Then the package is re-evacuated, gas flushed with CO<sub>2</sub> and sealed under the peelable barrier lid.

In this deoxygenated state the steaks may be stored for up to 12 weeks at -1°C yet still exhibit a full display life.

At the point of sale, the barrier lid is peeled back and the meat blooms to a bright red colour again.

This technology was developed by Trigon Packaging Systems under contract from the Meat Research Corporation of Australia.



*Lid and sachet removed at point of sale*



*Retail presentation*

**Further information and samples may be obtained from:**

**(Trigon Packaging Systems (NZ) Ltd. Fax Int 64-7-849 2230)**



**Sealed Air Corporation**

**TRIGON**

The information contained represents our best judgment based on work done to date, but the Company assumes no liability whatsoever in connection with the use of this information.

# RETAIL READY MEAT PACKAGES WITH THE FRESH RED MEAT COLOUR



## RETAIL READY FOR EXPORT PACKAGING

A tray based system allowing meat to be stored for extended periods under carbon dioxide. The trays are sealed with a removable barrier lid which allows the meat to rebloom to the bright red colour that consumers expect and trust.

## WHY CO<sub>2</sub> PACKAGING ?

It is generally accepted that use of high carbon dioxide packaging for red meat is superior to that of vacuum packaging.

**The benefits are :**

1. Reduced bacteria counts.
2. Longer storage life (up to twice that of vacuum packing).
3. Better colour and colour retention on retail display.

In order to fully exploit these advantages the meat must be saturated with CO<sub>2</sub> and the oxygen concentration should be less than 500ppm throughout the lifetime of the package.



Sealed Air Corporation

**TRIGON**