AN INVESTIGATION OF AN OXYGEN SCAVENGER PACKAGING FILM AS AN INNER PACKAGE ANTIOXIDANT DEVICE

Thesis for the Degree of M.S. MICHIGAN STATE UNIVERSITY RICHARD SCOTT ERHSBERGER, JR. 1975





This is to certify that the

thesis entitled

AN INVESTIGATION OF AN OXYGEN SCAVENGER PACKAGING FILM AS AN INNER PACKAGE ANTI-OXIDANT DEVICE

presented by

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#### ABSTRACT

# AN INVESTIGATION OF AN OXYGEN SCAVENGER PACKAGING FILM AS AN INNER PACKAGE ANTIOXIDANT DEVICE

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Richard Scott Ernsberger, Jr.

This investigation was conducted to support the use of an oxygen scavenger film as an inner package antioxidant device rather than the complete primary package. Samples of American Can's Maraflex 7-F oxygen scavenger film with different ratios of headspace volume to film surface area were examined for their oxygen consumption activity. It was found that by increasing the surface area of the material while maintaining a constant headspace volume, the half-life period for oxygen consumption would decrease. Specifically, for the three primary runs with volume to surface area ratios of 18.6:1, 8.3:1, and 2:1, the average half-life periods were 342.27, 108.47, and 47.56 hours respectively. The average oxygen consumption rate or material specific activity was established at  $5.46 \times 10^{-3}$  grams of  $0_2/cm^2/atms/hr$ .

Additionally, it was found that some inhibition of material activity occurs through its use resulting in a regression of activity through reuse. The cause or causes producing this phenomenon were not determined.

# AN INVESTIGATION OF AN OXYGEN SCAVENGER

# PACKAGING FILM AS AN INNER PACKAGE

# ANTIOXIDANT DEVICE

Ъy

Richard Scott Ernsberger, Jr.

# A THESIS

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# INTRODUCTION

Packaging affects the storage quality of food products in various ways. Its primary function is to control and protect against environmental factors affecting the quality and integrity of the product. Shelf-life of a product is the predominate concern of the food packaging engineer. Once a product has completed final processing and packaging, assurance must be provided that the product will not deteriorate significantly before its intended consumption. The shelflife of a packaged product is an established period of time, under assumed conditions, after which deterioration may cause it to be substandard. Environmental factors affecting the deterioration mechanisms of these products include thermal stresses, wavelengths of light, concentration of water vapor, oxygen concentration, and biological organisms. Although most degradation mechanisms of food products are influenced by a combination of these environmental factors, the primary mechanism for deterioration in most foods may be significantly attributed to one of these factors. The factor of primary concern in this study associated with primary food packaging is that of oxygen concentration. The investigation will analytically examine the antioxidative influence of an impregnated oxygen scavenger packaging film incorporated as a contingent inner package oxygen consumption device.

# OBJECTIVES

The primary objectives of this project are to quantitatively determine the effectual relationship of the above mentioned oxygen scavenger film as an inner package antioxidant device; to hypothetically apply this relationship to a packaged food product; and to provide information relevant to this material in association with the current state-of-the-art food packaging technology.

#### BACKGROUND

#### Oxygen Rancidity

Oxygen rancidity is primarily associated with the deterioration of fats and oils. This rancidity results from a chemical reaction where long chained unsaturated fatty acids are broken into smaller chained fatty acids. The reaction is based on the intermediate formation of peroxides where unsaturated fatty acids are subjected to oxidation at their double bonds. The resultant smaller chained fatty acids produce the familiar objectionable odors and are primarily responsible for the rancid taste (Desrosier, 1970)

## Material Description and Concept

There currently exist many FDA approved food additives which serve as antioxidative devices, each having its' own advantages and disadvantages. Recent developments in the area of oxygen scavenger mechanisms incorporated in packaging materials has shown great potential as a successful and efficient antioxidative device (Kuh, 1970; Food Processing, 1973; Peters, 1974: Zimmerman, 1974). One such film has been developed and is currently manufactured by the American Can Company, Greenwich, Connecticut. The material consists of polyester/ adhesive/foil/Surlyn/palladium catalyst/Surlyn. It is commercially

identified as Maraflex 7-F. The principal mechanism of antioxidation is the formation of water vapor from headspace oxygen and hydrogen within a moisture vapor impermeable cell. The gas barrier properties of the Surlyn film are such that they allow permeation of both oxygen and hydrogen molecules through and into the palladium catalyst area. Within this area the water formation reaction occurs.

A highly critical prerequisite to the successful implementation of this material, of course, is the need for hydrogen and oxygen to be present in the headspace. This is accomplished by gas flushing, with a gas mixture of 8% hydrogen and 92% nitrogen, prior to final package sealing. Commercial automated food packaging systems for employing a nitrogen gas flush operation will exhaust approximately 98% to 99% of the headspace oxygen.

## LITERATURE REVIEW

Kuhn, et al (1970) reports that work done by Mucha, et al (1961) involving flavor stability of foam spray dried whole milk over extended storage periods require low oxygen concentration to prevent detrimental flavors. Significantly, samples stored at 0.1% oxygen atmosphere resulted in a better flavor than those stored at 1.0%. In conjunction with this aspect. Kuhn further reports that a study by Berlin, et al (1963) concludes that residual oxygen levels above those necessary to maintain dry milk flavor stability may be accounted for by entrapped oxygen gas with the product particles. At the time of Kuhn's report, there were three general methods available for removing residual oxygen from packaged products. One was the employment of a product exposed to vacuum for an extended duration of time. Although somewhat successful, it proved to be an expensive operation (Kurtz, et al 1967). Second was the incorporation of Glucose Oxidase as a deoxidative device in nitrogen flushed packages. For dry products the mechanism must be separately packaged and implemented as an insert. This mechanism requires the presence of glucose and water for reaction. Although this method has been proven effective (Kurtz et al, 1957), problems occur which are solely generic to the package insert and its integrity. The third and final method

reported by Kuhn is the use of palladium or platinum pellets for catalyzing the reaction 2H +0  $\rightarrow$  2H 0 as devised and proven by King (1955). 2 2 and Abbott et al. 1961. Initial tests conducted on a film constructed of paper/PE/foil/scavenger/PE proved successful. However, the effectiveness was short lived due to excessive pinholing in the foil. A second laminate construction consisted of polyester/Saran/polyvinyl alcohol/PE/ scavenger/PE resisted flex cracking and pinholing previously foil attributed. Furthermore, the residual oxygen levels of the packages were between 0.15% and 0.5%. A storage study conducted on 10 pouches held at 73 F and 50% R.H. over a 24 week period resulted in concentration levels between 0.00% and 0.38%. An article published in the 1973 September issue of Food Processing entitled "Oxygen Scavenger Package Stops Oxidation, Extends Shelf-Life" further illuminated the successful use of American Can's oxygen scavenger film. This current film represents a third laminate and is constructed of polyester/adhesive/ foil/Surlyn/catalyst/Surlyn. With efficient commercial packaging machines that exhaust about 98% of oxygen gas, approximately 2% residual oxygen remains in the package headspace. By applying the 8% hydrogen/92% nitrogen gas mixture flush, the inherent attributes of the scavenger mechanism have efficiently consumed most residual oxygen. In a six month study involving packaged spray dried whole milk, packages stored at extreme temperatures and relative humidity (100 F and 90% R.H.) were organoleptically rated the same as the control stored at 0 F. Furthermore, a storage test conducted on fresh meat employing the scavenger film stored at 32 F doubled the original shelf-life of four weeks to that of eight weeks.

Peters (1974) offers further evidence in support of the scavenger film's effectiveness for extending shelf-life of oxygen sensitive

packaged products. He reports that pouches containing from one to four ounces of powdered milk with initial oxygen levels between 0.5% and 2.5%, after 24 hours, had been reduced to between 0.1% and 0.2%. And, after an additional 24 hours levels were reduced to zero. Peters suggests that with this film such antioxidant ingredients as BHA and BHT may be removed from products to the advantage of marketing strategies. Additional reference is made to a study by Bishov et al (1971) on freeze-dried food items representing vegetables, fruits, meat, fish, and poultry. These items were separately containerized with an oxygen catalyst of palladium pellets and sealed after being flushed by a mixture of 5% hydrogen and 95% nitrogen, and stored for 6 months at 100 F. The results rated the experimental items comparable to the original products.

An article entitled "Scavenger Pouch Protects Oxygen-Sensitive Foods," by Zimmerman, et al (1974) explains American Can's development of the current scavenger films designated as Maraflex 7-F. Evolution of their previous laminate film (polyester/Saran/polyvinyl alcohol/ polyethylene/scavenger/polyethylene) to the present construction of polyester/foil/Surlyn/catalyst/Surlyn as primarily the result of improved laminating qualities and increased barrier properties. With the incorporation of Surlyn, seal area contamination and activity level problems were resolved. "Activity" as defined by the authors is derived from the amount of time consumed in obtaining one-half of the initial headspace oxygen concentration in a calibrated pouch. Twelve hours is generally accepted by the authors to be adequate for most food products. Furthermore, Surlyn provided greater gas permeation rates than did the polyethylene, thus allowing greater flow of both oxygen and hydrogen into the catalytic cell area. Additionally, the

water vapor transmission rate of the Surlyn provided a positive barrier against permeation of reaction produced moisture. Together with the Surlyn, the external layer of foil and polyester provided additional barrier and strength characteristics. Corresponding with previous shelf-life studies, it was further reported that American Can has recently concluded a 1 year storage study on 4-ounce, gas flushed, scavenger packages containing whole milk powder. Samples were stored at the following conditions: 45 F/90% R.H.; 73 F/50% R.H.; 100 F/20% R.H.; and 100 F/90% R.H. The control sample was stored at 0 F. The flavor taste panel evaluating the product recorded no flavor change during the 12 month period.

Marcus Karel (1974) in an excellent article entitled "Packaging Protection for Oxygen-Sensitive Products" presents and discusses the effects packaging has on the control of oxygen against oxygen sensitive food products. This includes information regarding oxidation as a function of oxygen pressure, the effect of diffusion on final oxidation, deterioration of organoleptic quality, and an explanation and mathematical derivation of activated diffusion as associated with a materials permeability coefficient. Additionally, Karel offers data generic to various material properties and their effect on permeability as well as determining optimal material combinations in achieving maximum use of steady state concentrations for respirating food products. In concluding his article, Karel refers to three antioxidation systems previously mentioned by Kuhn (197) available for food packaging: 1) The use of a separate container employed as an inner package oxygen scavenging device similar to a desiccant package;

2) the use of enzyme glycose oxidase; and 3) the incorporation of an oxygen scavenger impregnated film pouch as produced by the American Can Company to remove residual headspace oxygen concentration, the subject for which this thesis is directed.

#### MATERIALS AND METHODOLOGY

#### 3-Phase Design

The research design entailed a 3-phase integrated study. The first phase involved the preparation of oxygen scavenger film samples, equipment, and apparatus. The second phase measured oxygen uptake of the various sized samples of the scavenger film. The third and final phase of this study applied the derived data from phase two to a hypothetical packaged food product for design consideration.

#### Equipment

The study employed a Gilson model GR 20 differential respirometer as the primary apparatus for the second phase of this study. The respirometer was used to analytically measure oxygen uptake of the oxygen scavenger film. The respirometer is based on the principle that at constant temperature and constant gas volume any changes in the amount of gas can be measured by changes in its pressure (Umbreit, 1964). The primary component of the respirometer is the volumometer. The volumometer consists of a manometric tube with indicating fluid, sample flask, reference flask, micrometer, periscope, and inlet port valve. The volumometer measures gas changes effected by the sample. This is accomplished in a closed system whereby the volume of gas

absorbed is replaced by an equal volume of dyed indicating fluid. The fluid is in a manometer located upstream from the sample flask. The fluid level of the manometer is returned to its original position, as viewed through the periscope, by manually turning the micrometer shaft. The shaft is digitally indexed in microliters and upon final equilibration, total volume change may be directly read off the shaft. Figure I offers a representation of the initial gas flushing followed by equilibration, oxygen consumption, and reequilibration. Although the flasks are submerged in a constant temperature water bath, the reference flask is used to compensate for any extraneous temperature and pressure changes affecting manometer sensitivity.

#### Sample Preparation

Film samples were prepared from American Can Company's oxygen scavenger film laminate identified as "Maraflex 7-F." The scavenger web construction is 0.5 mil polyester/0.35 mil Al. foil/15 lb Surlyn/ 1 lb Palladium catalyst/12 lb Surlyn. Note that the basis area is 3000 ft<sup>2</sup>, so that 15 lb Surlyn represents approximately 1 mil thickness. The web material (2500" x 9 9/16) was received from American Can in September 1974.

Individual samples were measured with a standard rule and cut to size by an exacto knife. Approximately 3 feet of leader material was run off prior to sample preparation to reduce the probability of sample contaminations. Samples were prepared and handled as aseptically as possible using metal tongs, surgical gloves and a wiped down work area using a 70% solution of ethanol. After sample preparation, they were



Figure I - The four basic stages of manometer utilization

grouped by size and placed into a closed container awaiting experiment implementation. Sample dimensions for the 3 primary runs are given in Table I.

The ratios were established from the active surface area of the material samples and volumeter headspace volume. The headspace volume was determined to be 30 cc. Slight differences were noted in headspace volumes, and were attributed to variance in manometer indicating fluid and glassware dimensionable integrity. It was felt that these variances were not significant enough to critically effect the results of the study and, therefore, 30 cc of headspace volume was used in the calculations.

The ratio for Run 1 of 18.6:1 was derived at the convenience of the  $1/2" \ge 1/2"$  dimension. Run 2 however, at a ratio of 2:1 was obtained by predetermining the required surface area equivalent to that ratio and then physically providing this area. Due to the configuration of the sample flasks, the resulting scavenger material was of two pieces. One piece of rectangular dimensions, encircled the neck area while the second was of frustum construction adhering to the internal conical profile of the flask. Run 3 of ratio 8.3:1 was designed such that the combination of two Run 3 samples would produce a 4:1 ratio (i.e., 3.63 cm<sup>2</sup>x2 = 7.62 cm<sup>2</sup>; 30 cc/7.26 cm<sup>2</sup> = <u>4.1:1</u>). Therefore, it provided data of comparability with not only Run 3 at 8:1 but also Run 2 with a 2:1 relationship. Similarity of material samples were determined by correlating the computed specific activity coefficients.

Sample flasks were 17 ml of the Erlenmeyer configuration. All sample flasks were cleaned prior to the experiment using a dichromate

	Surface Area	2 2 0.25 in (1.613 cm )	2 2 0.625 in (4.032 cm)					$\begin{array}{ccccc} 2 & 2 \\ \underline{1.703 \ in \ (10.990 \ cm \ )} \\ 2 & 2 \\ 2.328 \ in \ (15.022 \ cm \ ) \end{array}$	2 2 0.563 in (3.63 cm )
								al Area	
SNOISN								) Tota	
RUN RATIOS AND SAMPLE DIME	Dimension	1/2" x 1/2"	a. 1" x 5/8"	b. frustum:	0 = 2.496 R	r = 1.719 in 1	r = 1.261 in 2	Area = $0/2 (r_1^2 - r_2^2)$	3/4" x 3/4"
		(ratio 18.6:1)	(ratio 2:1)	two pieces					(ratio 8.3:1)
		Run 1	Run 2						Run 3

TABLE I

method. Sample flasks were readied by placing a scavenger film sample of prescribed surface area into each of sixteen sample flasks using metal tongs. The flasks were then attached to the manometer and readied for the gas flushing and sealing phase. All glass joints and valves requiring lubrication were so checked and prepared. Manometer indicating fluid was checked for proper levels and purity. Application of lubricant to the interfacing surfaces securing the sample flask was accomplished after insertion of the sample material. This was to preclude possible contamination of sample material.

Gas flushing was accomplished using a certified gas mixture of 91.5% N<sub>2</sub> and 8.5% H<sub>2</sub>. To facilitate the flushing process, a 1/8" copper tube 6 inches in length was attached to a regulated gas source. With the inlet port valve removed, the 1/8" tube was inserted through the inlet port valve sleeve and into the sample flask. The sample flask was then flushed with the gas mixture for a period of 30 seconds at 3 psig. Immediately following flushing the inlet port valve was quickly replaced. The replacing of this valve requires a practiced technique which prohibits a blow back of indicating fluids if done too quickly or compromization of headspace gases if done too slowly.

Prestudy flushing practice, checked with a Varian 90-P gas chromatograph containing a 5A molecular 50/80 column for analysis, resulted in a consistent technique whereby the average gas flushing and sealing resulted in oxygen headspace content of 1-3%. The technique for determining headspace oxygen content is shown in Appendix A. Additionally, it was found that by presetting the manometer micrometer at 40 ul, an optimum starting registration, after gas flushing and instrument equilibration, could be achieved.

After flushing and micrometer readjusting, the manometer was attached to the respirometer and submerged in a water bath held at a constant temperature of  $22.5^{\circ}C \pm 0.5C$ . Micrometer readings and time were then recorded. A total of 20 manometers were used for Runs 1, 2, and 3, 16 of which contained sample material and were gas flushed. The remaining 4 manometers were used for reference, and contained no sample material. Of these four, two were gas flushed and two were not, yet all four were submerged with the others.

#### General Comments

Data obtained from the experimental runs was submitted to statistical evaluation employing a computer program developed by Dr. Wayne Clifford of the School of Packaging, Michigan State University. This program is offered at Appendix B. Much of the oxygen uptake exceeded the measuring capacity of the manometers. Hence, total volume uptake could not be directly determined. The computer program utilized mathematical and statistical techniques to arrive at an estimation of final volume uptake. The program entails 3 parameter functions of which 2 parameters utilize the least squares method, and the third uses a 1 dimensional search technique. This search technique is described by Wilde (1964) as the golden section search. Essentially, this 3 parameter functional program combines both mathematical and statistical models, and estimates total oxygen uptake. In a bracketing procedure, the estimates applied to linear regression analysis were correlated in arriving at the final estimate of total volume uptake. Data produced by the program for each sample included values for total

initial oxygen, A and B parameters for the linear equation, correlation coefficient for the regression model, and the error for the sum of squares of the deviation for the time satisfying the data.

#### RESULTS AND DISCUSSION

A total of 5 runs were conducted for this study. Fifty samples were initially started out of which 40 survived their periods of investigation, and were used in the compilation and analysis of this study. A breakdown by run is offered in Table II.

Ratios were based upon headspace volume versus the surface area of sample material. Headspace volume of the sample cells was established as 30 cc and was assumed to be final and, therefore, held constant throughout the study. Surface area of the samples was varied, hence, the variability of ratios for Runs 1, 2, 3, and 4.

Raw data recorded for each run by sample is available in Table III through Table VII. These values represent actual readings taken during the extent of the experiment. Tables VIII through Table XII offer the computerized interpretation of the raw data. Included with these generated data are calculated values establishing the estimated half-life and specific activities for the samples studied.

Specific activity is defined as the amount of oxygen consumed in grams-per surface area of material-per hour-at one atmosphere of oxygen pressure. This is mathematically defined by the following:

$$\begin{bmatrix} \text{Rate of } 0_2 \\ \text{Consumption} \end{bmatrix} = -\begin{bmatrix} \text{Film Specific} \\ \text{Activity} \end{bmatrix} \begin{bmatrix} \text{Area of} \\ \text{Material} \end{bmatrix} \begin{bmatrix} \text{Concentration} \\ \text{of } 0_2 \end{bmatrix}$$
to find the rate of  $0_2$  consumption, an expression for the mass of  $0_2$ 
inside the container is needed. This will come from the ideal gas
law:
$$P_{0_2} \quad V = \frac{m}{M} \text{ RT} \tag{1}$$
where:

P<sub>02</sub> = Partial pressure of 0<sub>2</sub> V = Volume (cc) m = Mass (grams) M = Molecular wt (32g/mole) R = Gas constant (82.06 cc-atm/<sup>o</sup>K-mole) T = Temperature <sup>o</sup>K Solving Equation 1 for m;

$$m = \frac{VM}{RT} P_{0}$$
(2)

the mass of oxygen in the container may be determined.

The time rate of change of m is simply the first time derivative of Equation 2:

$$\frac{dm}{dt} = \frac{VM}{RT} \frac{\frac{dP_0}{2}}{dt}$$
(3)

So the equation governing this situation is:

$$\frac{VM}{RT} \frac{\frac{dP_0}{2}}{dt} = -Sa \cdot A_f \cdot P_0$$
(4)

This equation may be simplified to:

$$\frac{dP_0}{dt} = -BP_0 \tag{5}$$

where:

$$B = Sa \cdot A_{f} \cdot \frac{RT}{MV}$$
(6)

where:

Sa = Specific Activity 
$$(g/cm^2/atm/hr)$$
  
 $A_f$  = Area  $(cm^2)$   
B = Straight line parameter (slope)  
When Equation 5 is solved, it yields:

$$P_{0_2} = P_{0_2} e^{-Bt}$$
 (7)

An alternative expression is:

$$\ln P_{0} = \ln P_{0} - Bt$$
 (8)

Half-life is defined as that period of time expended during the consumption of one-half the volume of headspace oxygen. It is mathematically defined as:

$$t_{1/2} = \ln 2/B$$
  
or  
 $t_{1/2} = .693/B$ 

It was anticipated that by increasing the surface area of the oxygen scavenger material while maintaining a constant headspace volume the half-life expectancy of oxygen uptake would decrease. This was evidenced in Runs 1, 2, and 3. Mean results may be seen in Table II. Run 1 with a volume to surface area ratio of 18.6:1 TABLE II

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GENERAL DATA FOR ALL RUNS

+3		2	T		-	
Avg. Sa x 10	4.33	4.80	7.24	1.364	0.14*	
Avg. t 1/2	342.27	47.56	108.47	243.34*	2,134.26*	
Avg. V 0	782.57	2,461.27	736.95	787.49*	4,433.03*	
Avg. Duration of Run (hrs.)	336.0	21.9	123.05	147.93	239.09	
Avg. No. Read/Run	18.0	10.9	11.4	11.8	12.0	
No. End Samples	6	7	14	S	ŝ	
No. Begin Samples	16	8	14	5	'n	
Ratio	18.6:1	2:1	8.3:1	4:1	4:1	
Run	н	2	ε	4A	4B	

\*These values do not include Sample 4 of this Run.

	I					L	I	22	2														
						hrs	52.0	74.0	96.0	100.0	120.0	126.5	144.0	151.0	175 D	192.0	199.0	240.0	249.5	264.0	488.0	312.0	336.0
					10	uls	199.0	216.0	239.0	243.0	263.0	271.0	288.0	295.0	309.0	332.0	338.0	381.0	390.0	404.0	424.0	440.0	453.0
						hrs	52.0	74.0	96.0	100.0	120.0	126.5	144.0	151.0	175 0	192.0	199.0	240.0	249.5	264.0	288.0	312.0	336.0
		KUN 1	(1		7	uls	137.0	151.0	165.0	169.0	174.0	184.0	195.0	199.0	200.0 211 0	218.0	222.0	248.0	252.0	263.0	273.0	281.0	292.0
-	III E	DATA FOR F	5:1 (cc/cm <sup>2</sup>	les		hrs	52.0	74.0	96.0	100.0	120.0	126.5	144.0	151.0	175 0	192.0	199.0	240.0	149.5	264.0	288.0	312.0	336.0
	TABLE	VS. TIME	RATIO 18.6	Samp	9	uls	155.0	202.0	245.0	254.0	283.0	294.0	314.0	325.0	342.U 348 D	363.0	368.0	408.0	416.0	430.0	447.0	461.0	473.0
		NOLUME	OF			hrs	52.0	74.0	96.0	100.0	120.0	126.5	144.0	151.0	175 D	192.0	199.0	240.0	249.5	264.0	288.0	312.0	336.0
					Ŷ	uls	149.0	182.0	219.0	225.0	256.0	268.0	295.0	306.0	0.100 337 0	361.0	370.0	423.0	436.0	450.0	474.0	492.0	509.0
						hrs	52.0	74.0	96.0	100.0	120.0	126.0	144.0	151.0	175 0	192.0	199.0	240.0	249.0	264.0	288.0	312.0	336.0
					4	uls	137.0	173.0	211.0	215.0	248.0	257.0	285.0	296.0	325 0	246.0	254.0	399.0	407.0	423.0	443.0	460.0	473.0
							-	7	ო	4	ഹ	9	~ 0	ωc	10 م	11	12	13	14	15	16	17	18

TABLE III (Cont'd)	VOLUME VS. TIME DATA FOR RUN 1	OF RATIO 18.6:1 (cc/cm <sup>2</sup> )	Samples	12 15 16	s uls hrs uls hrs uls hrs		0 168.0 52.0 1/1.0 52.0 185.0 52.0 0 201 0 74 0 201 0 74 0 205 0 74 0	0 237.0 96.0 231.0 96.0 226.0 96.0	0 242.0 100.0 238.0 100.0 230.0 100.0	.0 275.0 120.0 262.0 120.0 247.0 120.0	.5 288.0 126.5 272.0 126.5 254.0 126.5	0 316.0 144.0 295.0 144.0 268.0 144.0	0 329.0 151.0 304.0 151.0 277.0 151.0	0 353.0 168.0 322.0 168.0 288.0 168.0	0 361.0 175.0 327.0 175.0 293.0 175.0	0 381.0 192.0 345.0 192.0 306.0 192.0	0 389.0 199.0 349.0 199.0 311.0 199.0	.0 437.0 240.0 388.0 240.0 347.0 240.0	.5 446.0 249.5 398.0 249.5 359.0 249.5	.0 462.0 264.0 407.0 264.0 370.0 264.0	0 485.0 288.0 425.0 288.0 385.0 288.0	0 499.0 312.0 436.0 312.0 397.0 312.0	0 511.0 336.0 449.0 336.0 408.0 336.0
				12	uls		168.0 201 0	237.0	242.0 1(	275.0 12	288.0 13	316.0 1/	329.0 15	353.0 16	361.0 17	381.0 19	389.0 19	437.0 24	446.0 2/	462.0 26	485.0 28	499.0 31	511.0 33
				11	hrs	( ( )	52.0 74.0	96.0	100.0	120.0	126.5	144.0	151.0	168.0	175.0	192.0	199.0	240.0	249.5	264.0	288.0	312.0	336.0
					uls		89.0 110.0	137.0	143.0	165.0	173.0	193.0	201.0	221.0	227.0	245.0	251.0	301.0	310.0	326.0	247.0	365.0	380.0
						•	<b>ч</b> с	n 4	4	Ŝ	9	2	œ	б <u>і</u>	10	11	12	13	14	15	16	17	18

				16	hrs	.50	1.02	2.02	4.76	5.56	6.01	7.50	9.25	12.54	15.79	23.82	27.00
					uls	107.0	133.0	162.0	189.0	200.0	203.0	221.0	238.0	263.0	286.0	328.0	339.0
				5	hrs	.52	1.04	2.03	4.79	5.58	6.04	7.51	9.26	12.57			
	UN 2			1	uls	117.0	139.0	190.0	276.0	317.0	338.0	413.0	489.0	625.0			
E IV	DATA FOR R	1 (cc/cm <sup>2</sup> )	ples	13	hrs	.52	1.04	2.03	4.76	5.58	6.04	7.54	9.30	12.63	15.86	23.89	
TABL	VS. TIME	F RATIO 2:	Sam		uls	80.0	89.0	117.0	167.0	190.0	202.0	243.0	289.0	366.0	428.0	539.0	
	VOLUME	Ö		12	hrs	.53	1.05	2.05	4.77	5.57	6.05	7.52	9.27	12.58			
					uls	136.0	164.0	221.0	301.0	334.0	356.0	423.0	493.0	640.0			
				11	hrs	.55	1.05	2.05	4.80	5.60	6.05	7.55	9.29	12.60	15.85	23.88	27.04
					uls	4.0	13.0	38.0	87.0	111.0	124.0	166.0	218.0	308.0	383.0	510.0	542.0
						Ч	7	ო	4	ŝ	9	2	∞	6	10	11	12

TABLE IV (Cont'd)	UME VS. TIME DATA FOR RUN 2	OF RATIO 2:1 (cc/cm <sup>2</sup> )	Samples		10	50	02	02	76	56	01	50	25	54	62	32	38
	VOL			18	hrs	·.	1.0	2.0	4.7	5.5	6.0	7.5	9.2	12.5	15.7	23.8	26.9
					uls	32.0	45.0	74.0	117.0	139.0	143.0	177.0	213.0	263.0	306.0	390.0	416.0
				7	hrs	.52	1.02	2.02	4.75	5.52	5.98	7.48	9.25	12.57	15.79	23.82	
				1	uls	59.0	71.0	106.0	148.0	164.0	172.0	212.0	251.0	326.0	398.0	557.0	
						Ч	7	ო	4	ъ	9	7	∞	6	10	11	12

						hrs	3, 30	7.73	18.26	23.82	29.71	42.98	48.96	66.64	72.11	79.27	91.27	151.14
					8	uls	0, 00	112.0	141.0	157.0	174.0	202.0	216.0	256.0	268.0	283.0	304.0	398.0
						hrs	UE E	7.75	18.27	23.84	29.73	43.00	49.00	66.64	72.14	79.30	91.30	151,18
		£			7	uls	127 0	147.0	195.0	217.0	242.0	286.0	305.0	362.0	376.0	395.0	423.0	531 0
	٨	A FOR RUN	(cc/cm <sup>2</sup> )			hrs	7 83	7.27	17.81	23.38	29.25	42.53	48.51	66.18	71.68			
	TABLE	. TIME DAT	TIO 8.3:1	Samp1e	9	uls	0 88	150.0	258.0	308.0	352.0	422.0	447.0	517.0	536.0			
		VOLUME VS	OF RA			hrs	77	7,17	17.68	23.25	29.13	42.40	48.38	66.06	71.56	78.71	90.71	150 59
					4	uls	0 09	85.0	126.0	143.0	165.0	205.0	226.0	283.0	301.0	321.0	351.0	473 D
						hrs	7 V V	7,88	18.42	24.00	29.88	43.15	49.13	66.81	72.31	79.46	91.46	151 34
					3	uls	0 811	135.0	176.0	195.0	212.0	243.0	257.0	270.0	289.0	309.0	413.0	
							-	10	ا n	4	Ś	9	7	œ	6	10	11	12
(p,																		
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(Cont																		
۵																		
TABLE																		

VOLUME VS. TIME DATA FOR RUN 3 OF RATIO 8.3:1 (cc/cm<sup>2</sup>)

		hrs	3.22	/.68 18.20	23.76	29.65	42.92	48.90	66.56	72.06	49.21	91.21		
	14	u1s	83.0	124.0 199.0	234.0	269.0	326.0	351.0	421.0	443.0	473.0	507.0		
		hrs	3.25	7.68 18.22	23.77	29.66	42.94	42.94	48.92	66.56	72.06	49.22	91.22	151.10
	13	uls	146.0	171.0	186.0	193.0	219.0	230.0	265.0	276.0	290.0	310.0	406.0	
Samples		hrs	3.25	/.69 18.23	23.79	29.68	42.94	48.94	66.60	72.10	49.25	91.25		
	12	uls	92.0	133.0 212.0	253.0	286.0	341.0	363.0	420.0	438.0	458.0	483.0		
	10	hrs	2.72	7.17 17.70	23.25	29.13	42.40	48.38	66.06	71.56	78.71	90.68	150.59	
		uls	141.0	162.0 218.0	244.0	272.0	327.0	349.0	406.0	423.0	443.0	466.0	557.0	
		hrs	3.30	د/./ 18.26	23.82	29.71	42.98	40.96	66.64	72.14	79.27	91.27		
	5	uls	133.0	1/9.0 263.0	296.0	328.0	384.0	406.0	465.0	480.0	502.0	527.0		
			<del>г</del> і (	n n	4	2	9	7	∞	6	10	11	12	

					hrs		3.16	7.62	18.13	23.70	29.57	42.86	48.84	66.48	71.98	79.11		
	3			18	uls		143.0	196.0	282.0	320.0	352.0	405.0	427.0	485.0	506.0	529.0		
t'd)	A FOR RUN	(cc/cm <sup>2</sup> )			hrs		3.18	7.62	18.15	23.72	29.59	42.86	48.84	66.52	72.02	79.14	91.14	
BLE V (Con	. TIME DAT	TIO 8.3:1	Samples	17	uls		121.0	158.0	215.0	239.0	265.0	313.0	328.0	381.0	398.0	420.0	441.0	
TA	VOLUME VS	OF RA			hrs		2.18	6.63	17.17	22.73	28.59	41.88	47.86	65.52	71.02	78.15	90.15	150.05
				16	uls		207.0	174.0	174.0	194.0	215.0	244.0	263.0	313.0	330.0	355.0	374.0	470.0
					hrs		3.22	7.67	18.20	23.75	29.63	42.90	48.88	66.56	72.03	79.18	91.18	151.09
				15	uls		110.0	131.0	170.0	192.0	212.0	254.0	271.0	322.0	340.0	360.0	386.0	499.0
						2	1	2	m	4	Ś	9	7	œ	6	10	11	12

						ų	0	õ	0	0	0	0	0	6	و	6	6
					hrs	12.1	21.9	23.9	26.9	29.9	44.9	49.9	52.9	70.8	128.4	140.8	147.8
				10	uls	48.0	80.0	84.0	94.0	104.0	154.0	164.0	171.0	220.0	343.0	365.0	374.0
					hrs	12.14	21.92	23.92	26.92	29.92	44.92	49.92	52.92	70.92	128.48	140.92	147.92
	4A			6	uls	23.0	43.0	46.0	53.0	60.0	95.0	102.0	107.0	143.0	243.0	262.0	269.0
Ц	TA FOR RUN	(cc/cm <sup>2</sup> )	ß		hrs	21.94	23.94	26.94	29.94	44.94	49.94	52.94	70.93	128.51	240.94	147.94	
TABLE V	VS. TIME DA	RATIO 4.1:1	Sample	7	uls	20.0	20.0	26.0	31.0	61.0	69.0	73.0	103.0	196.0	217.0	228.0	
	VOLUME V	OF I			hrs	12.17	21.95	23.95	26.95	29.95	44.94	49.94	52.94	70.94	128.52	140.95	147.95
				4	uls	16.0	35.0	40.0	46.0	51.0	87.0	95.0	98.0	131.0	226.0	247.0	252.0
					hrs	12.20	21.97	23.97	26.97	29.97	44.96	49.96	52.96	70.97	128.54	140.96	147.96
				e	uls	53.0	70.0	47.0	49.0	83.0	114.0	120.0	124.0	152.0	231.0	242.0	246.0
						Ч	7	ო	4	S	9	7	∞	6	10	11	12

1					1			50									
				0	hrs	5.06	11.07	23.06	28.06	47.07	52.07	72.56	97.06	143.06	191.06	223.06	239.06
					uls	36.0	43.0	63.0	69.0	104.0	110.0	146.0	200.0	298.0	409.0	464.0	505.0
				6	hrs	5.07	11.08	23.07	28.07	47.07	52.07	72.57	97.07	143.07	191.07	223.07	239.07
	g				uls	111.0	111.0	117.0	122.0	236.0	138.0	154.0	174.0	211.0	256.0	283.0	303.0
	A FOR RUN 4	(cc/cm <sup>2</sup> )	w	7	hrs	5.10	11.10	23.09	28.09	47.09	52.09	72.60	97.10	143.10	191.10	223.10	239.10
TABLE VI	. TIME DAT	NTIO 4.1:1	Sample		uls	87.0	0.06	105.0	109.0	133.0	137.0	161.0	196.0	260.0	336.0	383.0	414.0
	VOLUME VS	OF RI		4	hrs	5.12	11.12	23.11	28.11	47.11	52.11	72.61	97.11	143.12	191.12	223.12	239.12
					uls	39.0	49.0	72.0	80.0	119.0	123.0	165.0	219.0	325.0	443.0	503.0	548.0
				3	hrs	5.13	11.13	23.13	28.13	47.13	52.13	72.63	97.13	143.12	191.12	223.12	239.12
					uls	60.0	67.0	89.0	95.0	122.0	133.0	168.0	214.0	305.0	397.0	441.0	474.0
						ы	7	ო	4	ŝ	9	7	8	6	10	11	12

VIII	
TABLE V	

TABLE VIII COMPUTED RESULTS FOR RUN 1

			(RATIO 18.6:1)			
Sample No.	v 0 (cc)	t 1/2 (hrs)	+3 Sa x 10 (gm/cm <sup>2</sup> /atm/hr)	Correlation Coefficient	Erroț <sub>2</sub> x 10	Parameter B x 10 <sup>+2</sup>
4	649.78	179.82	6.07	19997-	0.09176	-0.3854
Ŋ	791.89	231.25	4.72	-0.9995	0.1165	-0.2997
Q	582.59	146.83	7.43	-00.9994	0.3367	-0.4720
7	667.78	560.27	1.95	-0.9989	0.04191	-0.1237
10	1,298.75	715.39	1.52	-0.9991	0.01979	-0.09687
11	960.62	463.95	2.35	-0.9992	0.04288	-0.7494
12	690.58	175.59	6.21	-0.9992	0.2955	-0.3947
15	590.91	177.09	6.16	-0.9996	0.1443	-0.3913
16	810.19	430.25	2.54	-0.9988	0.07263	-0.1611

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COMPUTED RESULTS FOR RUN 2

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5,878.45 93.74 951.71 21.01 5,490.91 84.53 385.54 10.70 2,987.62 86.59	5.69 1.25 5.57 1.39 10.94 1.35	Coefficient -0.9975 -0.9982 -0.9980 -0.9987 -0.9991	x 10 x 10 0.4674 0.0036 0.1997 0.0037 0.9065 0.0057	<pre>Parameter B x 10 -0.3364 -0.0739 -0.3299 -0.0819 -0.6474 -0.0800</pre>
591.24 15.74	7.44	-0.9996	0.1161	-0.4403

TABLE X

COMPUTED RESULTS FOR RUN 3 (RATIO 8.3:1)

Sample No.	v 0 (cc)	t 1/2 (hrs)	+3 Sa x 10 (gm/cm <sup>2</sup> /atm/hr)	<b>Correlation</b> <b>Coefficient</b>	Error x 10 <sup>+2</sup>	Parameter B x 10 <sup>+2</sup>
۳ ۳	707.93	159.56	3.04	-0.9880	9.015	-0.4343
4	777.93	120.33	4.03	-0.9998	0.3251	-0.5759
Q	655,80	31.35	15.46	-0.9995	2.389	-2.211
7	699.91	83.89	5.78	-0.9999	0.1059	-0.8261
ø	642.80	128.19	3.78	-0,9999	0.1145	-0.5406
6	641.47	41.92	11.56	-0.9994	2.941	-1.653
10	641.67	57.24	8.47	-0,9999	0.5870	-1.211
12	594.48	41.25	11.75	-0.9995	2.534	-1.680
13	1,470.17	461.11	1.05	-0.9996	0.03187	-0.1503
14	770.70	65.03	7.45	-0.9993	1.360	-1.066
15	724.59	102.43	4.73	-0,9999	0.1726	-0.6766
16	728.68	129.44	3.74	-0.9848	17.46	-0.5354
17	600.26	56.30	8.61	-0.9993	2.009	-1.231
18	660.92	40.50	11.97	-0.9982	6.776	-1.711

		ameter x 10 <sup>+2</sup>	.4863	.3994	.1335	.3684	.5607
		Par		0	0	0	0 I
		Erroț <sub>3</sub> x 10	0.4815	0.2153	1.085	0.1017	
KUN 4A	[sture]	Correlation Coefficient	-0.9996	-0.9997	-0,9999	-0,9999	-00.9999
COMPUTED RESULTS FOR R	(RATIO 4:1 - before moi	+3 Sa x 10 (gm/cm <sup>2</sup> /atm/hr)	1.70	0.93	0.47	1.29	1.96
		t 1/2 (hrs)	142.50	173.51	519.14	188.10	123.60
		v 0 (cc)	459.69	586.74	1,370.10	656.28	663.87
		Sample No.	e.	44	7	6	10

TABLE XI

\*Sample No. 4 ratio = 2.75:1

TABLE XII COMPUTED RESULTS FOR RUN 4B	(RATIO 4:1 - before moisture)	7 t $-1/2$ $-1/$	<b>32.99 1,089.28 0.22 -0.9990 0.6016 -0.6362</b>	<b>36.</b> 44 1,142.99 0.14 -0.9987 0.8769 -0.6063	<b>35.51 3,051.52 0.08 -0.99</b> 87 0.1773 -0.2271	14.62 2,946.43 0.08 -0.9976 0.2108 -0.2352	L9.00 1,449.79 0.17 –0.9985 0.6175 –0.4778
		v 0 (cc)	3,092.99	3,896.44	6,405.51	3,714.62	4,519.00
		Sample No.	£	*7	7	6	10

\*Sample No. 4 ratio = 2.75:1

has a mean half-life of 342.27 hours while Run 3 with a ratio of 8.3:1 has a computed mean of 108.47 hours and the 2:1 ratio of Run 2 produces an average half-life of 47.56 hours. Specific activity on the other hand was assumed to remain fairly constant with differences attributable to minor variations associated with catalytic application during material fabrication. This was substantiated by similar mean values for specific activity of  $4.33 \times 10^{-3}$ ,  $4.80 \times 10^{-3}$ , and  $7.24 \times 10^{-3}$ for Runs 1, 2, and 3 respectively.

In an effort to validate the profile of results established by these 3 runs, a 4th run was conducted. Run 4A was a modification of Run 3. A comparison of specific activity values derived from this third run was conducted. The pairing combinations of samples for Run 4A is seen in Table XIII. With the exception of sample number 4 of Run 4A, samples 3, 7, 9, and 10, each contained 2 pieces of similar sample material as established by specific activity. Sample 4, in this case, contained 3 pieces of sample material and was to be used as a further validation of this experiment.

Essentially, it was assumed that by doubling the surface area, as was accomplished in samples 3, 7, 9, and 10, the resultant data would show a correlating reduction in half-life as earlier displayed by the previous 3 runs. As may be noted by the results of Run 4A, this was hardly the case. In fact, the mean half-life for these 4 samples (3, 7, 9, and 10) was 243.34 hours. The ratio here was 4.1:1. This is one-half the ratio of Run 3 at 8.3:1. Yet, Run 3 had a mean value of 108.47 hours. An investigation of 2 references on catalytic behavior and processes indicated that the entrapment of the converted water vapor on and around the catalyst sites may produce an

	PAII	RING COMBINATION FROM RUI	К З		
		FOR RUNS 4A AND 4B			
Sample No. for 4A & 4B	Sample No. from Run 3	0 0	t 1/2	+3 Sa x 10	
£	en .	707.93	159.56	3.04	
	14	770.70	65.03	7.45	
4	4	777.93	120.33	4.03	1
	Ø	642.80	128.19	3.78	
	16	728.68	129.44	3.74	
7	7	699.91	83.89	5.78	1
	15	724.59	102.43	4.73	
6	6	641.47	41.92	11.56	1
	12	594.48	41.25	11.75	
10	10	641.67	57.24	8.47	
	17	600.26	56.30	8.61	

TABLE XIII

inhibiting effect on the activity of the material (Augustine 1965, Rylander 1967). With this assumption, moisture content analysis was performed using a vacuum oven method, described in Appendix C, for a period of 16 hours.

The results of this analysis produced loses between 0.03% and 1.9%. This data is available in Table XIV. Following this analysis, Run 4B was conducted to see whether this moisture loss may have had a significant effect on the specific activity of the samples. As may be noted by Table XV, it did not. Degradation of the specific activity is obvious by the further reduction in the computed values. Additional evidence is seen by sample number 4 where the ratio was 2.75:1. Both half-life and specific activity values closely parallel those of the other 4 samples in both Runs 4A and 4B.

It was felt that at this point further investigation of catalytic phenomena to determine a probable cause for explaining loss of activity was beyond the scope of this project and therefore, unwarranted.

For a better understanding of the reaction profiles of these varied relationships, a graphical description of each run is offered in Figures II through III. Figure II provides a composite description of an average sample for each of the 5 runs. Figures III through VII each describe a run by presenting linear plots of those samples representing the high, low, and average half-lives. The vertical axis represents recorded volumes in ul with the horizontal axis representing time values in hours. As may be seen in Figure II, the composite representation, the steeper the linear slope the lower the

			% Moisture Loss	0.032%	0.457%	1.833%	1.665%	1.931%	
	DATA		W2	12.13610	12.26550	12.56004	11.22910	12.37500	
TABLE XIV	MOSITURE ANALYSIS	FROM RUN 4A	M1	12.13612	12.26597	12.56131	11.23025	12.37632	
			W (TARE)	12.07190	12.16307	12.49200	11.16114	12.30795	
			Sample	3	4	7	6	10	

% moisture loss =  $100 - \frac{(w_2 - w)}{(w_1 - w)}$ 

TABLE XV DATA COMPARISON BETWEEN RUN 4A AND 4B		Sa x 10 <sup>+3</sup>	1.70	0.22	0.93	0.14	0.47	0.08	1.29	0.08	1.96	0.17	
	0 4B	t1/2	142.50	1,089.28	173.51	1,142.99	519.14	3,051.52	188.10	2,946.43	123.60	1,449.79	
	RUN 4A ANI	٥	459.69	3,092.99	586.74	3,896.44	1,370.10	6,405.51	656.28	3,714.62	663.87	4,519.00	
			Run	4A	4B	4A	4B	4A	4B	44	4B	4A	4B
			Sample	£		4		7		6		10	







Figure III - High, low, and average half-life of Run 1

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Figure VII - High, low, and average half-life of Run 4B

associated ratio. These graphical descriptions are offered as further support of the previously discussed results.

As has been implied throughout this section, data representing half-life and specific activity values were of primary importance for interpretation of this study's results. This is not to say that the accompanying data lacks significance. Quite the contrary. The values for estimated maximum volume were required to effectively describe the linear plots and, in conjunction with the computed B parameter, produce the resultant values for half-life and specific activity. Values derived for the correlation coefficients and errors have provided a means for evaluating the accuracy of the statistical computations. However, it is felt that further explanation and development within these areas lies beyond the scope of this report. These peripherary data are provided as supportive information accenting the results of the primary data.

The results of this study render strong indications that secondary or reusage of the scavenger film would be unproductive. The specific mechanisms at work which have impaired the activity of the material are not known. It is assumed that contamination in one form or the other during the initial use of this material is the cause for deterioration of its specific activity. However, as previously mentioned, the additional investigation involving Runs 4A and 4B were designed to be supportive in nature and not of primary concern to this project. The primary objective was to evaluate this material as an inner package antioxidation device in support of the protective attributes of a food package. This in itself implies a

one-time use as with most hermetically sealed food containers. Furthermore, application of such was not assumed to be by one means alone. An inner package application may be considered to take the form of any one design. This may include its incorporation as a lidding closure of which various styles are available, ranging from beverage container cap inner seals, through formed semirigid and rigid package closures. An additional application would be that of a package insert. The applications are limited primarily by the package designer's imagination and the constraints of the product. As an example of inner package application, the following illustration of design approach is offered.

Assume a typical flexible pouch fabricated of an impermeable laminate such as Surlyn/foil/Surlyn. Total package volume is 89.43 cc. It is estimated that 10% of the volume remains as headspace after product fill. Within this pouch, freeze dried beef hash, an oxygen sensitive product, will be packaged. This food product is packaged during a conventional form-fill-sealing process. Incorporated in the filling and sealing operation is the gas flushing phase which introduces in a flushing manner, the prescribed mixture of 8% H<sub>2</sub> and 92% N<sub>2</sub> gas. Residual oxygen in the headspace is estimated to be 2%. The 0<sub>2</sub> scavenger material previously attached inside or inserted into the pouch is of 20 cm<sup>2</sup> surface area. The derived oxygen uptake rate found for the specific activity was 5.46 x  $10^{-3}$  grams of  $0_2/cm^2/atms/hr$ . Applying the above values in Equation 7 or more specifically:

$$P_{0_2} = P_{0_2}' e^{-Sa(RT/MV)(A_f)(t)}$$

where:

Sa = 
$$5.46 \times 10^{-3}$$
  
R =  $82.06 (cc-atm/^{0}K-mole)$   
T =  $298^{0}K$   
M =  $32g/mole$   
V =  $8.943 cc$  (headspace vol)  
A<sub>f</sub> =  $20 cm^{2}$  (film surface area)  
P'\_{0\_{2}} =  $2.344 \times 10^{-4} grams 0_{2}$ 

From Equation 6, B = 9.33 and from Equation 7:

$$P_0 = 2.344 \times 10^{-4} e^{-9.33t}$$

Applying Equation 9,  $t_{1/2} = 0.074$  hours. Therefore, at  $t_{1/2}$ ,  $P_{0_2} = 1.172 \times 10^{-4}$ . This is verified alternately by  $P'_{0_2}/2$  which defines  $t_{1/2}$ .

Table XVI offers a range of data of which the reduction of headspace oxygen over time is represented graphically in Figure VIII. Permeability is a function of many variables as may be seen in the above example. The imbalance of internal and external partial gas pressures will seek equalibrium. The time involved is primarily associated with the generic properties of the film such as the rate at which the gas will dissolve into the surface of the material, diffuse through, and evolve into the reduced atmosphere. The determined rate for catalytic activity is based upon this phenomenon of gas diffusion with the rate of diffusion being somewhat proportional to the partial pressure of the gas.

	%	0.10	0.20	0.25	0.50	0.67	1.00	1.50	1.75	1.90
HEADSPACE OXYGEN REDUCTION OVER TIME	cc	8.956x10 <sup>-3</sup>	1.791x10 <sup>-2</sup>	2.239x10 <sup>-2</sup>	4.478x10 <sup>-2</sup>	5.971×10 <sup>-2</sup>	8.956x10 <sup>-2</sup>	1.343x10 <sup>-1</sup>	1.567x10 <sup>-1</sup>	1.702x10 <sup>-1</sup>
	Po2	0.1172x10 <sup>-4</sup>	0.234x10 <sup>-4</sup>	0.293x10 <sup>-4</sup>	0.586x10 <sup>-4</sup>	0.781x10 <sup>-4</sup>	0.1172x10 <sup>-3</sup>	0.175x10 <sup>-3</sup>	0.2051x10 <sup>-3</sup>	0.223x10 <sup>-3</sup>
	Min.	19.26	14.82	13.38	8.94	7.08	4.44	1.85	0.84	0.33
	Hrs.	0.321	0.247	0.223	0.149	0.118	0.074	0.0308	0.0143	0.0055
	TX	5/100	1/10	1/8	1/4	1/3	1/2	3/4	7/8	95/100

TABLE XVI

COMPUTED DATA FOR





Sa	Specific Activity (g/cm <sup>2</sup> /atm/hr)
<sup>A</sup> f	Area (cm <sup>2</sup> )
A	Straight line parameter (y intercept)
В	Straight line parameter (slope)
v	Volume (cc)
Р	Pressure (1 atm)
P0,	Partial pressure of 0 <sub>2</sub>
T	Temperature (K <sup>O</sup> )
t	Time (hrs)
М	Molecular wt (32g)
R	Gas constant (82.06 ml-atm/ <sup>0</sup> K-mole)
m	Mass of gas

### SUMMARY

The objectives of this investigation were to examine American Can's oxygen scavenger laminate film as an inner package antioxidant device rather than its employment as the complete primary package. This laminate material provides a means by which residual headspace oxygen can be consumed through a catalytic hydrogenation within the film structure.

The literature survey revealed investigations which were conducted on oxygen scavenger films, concluding that their conceptual implementation as the primary package was quite significant in extending the shelf-life periods of oxygen sensitive food products.

The methodology for this investigation was of a three phase design requiring: 1) Initial preparation of samples, equipment, and apparatus; 2) Submitting samples to the system measuring this oxygen uptake; and, 3) Applying the derived data to a hypothetical package design. The primary instrument for data gathering was a gas differential respirometer designed to measure changes in volume through changes in pressure. Samples were submitted to a closed system whereby their activity of headspace oxygen consumption was readily measured. Due to the limited measuring capacity of the

instrument, a computer program was incorporated to estimate total volume uptake from which the specific activity of the sample material was calculated.

Five different experiments were run, three of which involved different ratios of headspace volume (30 cc) to film surface area, with the remaining two of the same ratios and material yet under different conditions.

The first three runs of ratios 2:1, 8.3:1, and 18.6:1 showed a progressive increase in half-life period or that period required to consume one-half the original volume of headspace oxygen.

The remaining two runs, 4A and 4B, were designed to support the results of the previous findings. Run 4A incorporated a selective doubling of samples of similar specific activity used and found in Run 3. Presumably by doubling the sample material (surface area) a one-half reduction in half-life periods should be produced. Such was not the case. The evidence indicates that some inhibition of film specific activity had occurred. Run 4B was conducted under the assumption that the converted water vapor might be causing a blockage of the supported catalyst sites and thus, inhibiting the material's specific activity. Prior to Run 4B, moisture content analysis was performed as a design to establish the amount of moisture formed and held by the material and, secondly, provide a dehydrating effect and thereby reactivating the activity of the film. The results of Run 4B showed a further regression of specific activity.

# CONCLUSIONS

From this investigation it is concluded that:

- 1. Maraflex 7-F Oxygen Scavenger film may be effectively used as an antioxidative inner package device.
- 2. Increasing the ratio of headspace volume to film surface area increases the half-life period of oxygen consumption.
- 3. Inhibition of film specific activity develops through its use.
- 4. Reuse of this material (everything held constant) will produce less effect on oxygen consumption than its previous effect.
- 5. The linear logarithmic relationship of oxygen uptake data is supported by the mathematical model.

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### PRESENTATION

Kuhn, P. E., K. F. Weinke, and P. L. Zimmerman, "Oxygen Scavenging System for Flexible Packaging of Whole Dry Milk," Ninth Milk Concentrates Conference, Sept. 15, 1970. APPENDICES

APPENDIX A

Appendix A

Headspace Oxygen Analysis Procedure

The following procedure describes the methodology, apparatus, and technique used in the quantitative determination of residual headspace oxygen of a package.
### APPENDIX A

### Headspace Oxygen

### I. GENERAL

The amount of oxygen remaining in the headspace of packages containing food products is very critical. The amount of oxygen present has a definite influence on shelf-life and product quality. The amount of oxygen in the headspace can be quantitated by gas chromatographic techniques. The percentage of oxygen is quantitated by ascertaining the peak areas of the different gases present in the headspace.

II. APPARATUS

- 1. Gas chromatograph (5A molecular sieve column)
- 2. Gas chromatograph recorder
- 3. Integrator
- 4. Helium carrier gas and regulator
- 5. Standard gas
- 6. Gas-tight sampling syringe
- 7. Headspace plunger
- 8. Vacuum gauge
- 9. Vacuum source
- 10. Headspace gas sample extracting apparatus
- III. PROCEDURE
- A. Analysis of Standard Gas
  - Standard gas is analyzed at the beginning and the end of a series of analyses which indicate analytical and

APPENDIX A (Cont'd) -

III.

- A. (Cont'd)
  - 1. (cont'd)

instrumentation performance. This is accomplished simply by injecting a standard of air into the chromatograph and thereby verifying the satisfactual operation of the chromatograph, integrator, and recorder.

- 2. Operating condition of gas chromatograph and recorder.
  - i. Column temperature 150°C (302°F).
  - ii. Helium carrier gas flow rate approximately 30 cc/min.
- B. Analysis of Headspace Gas
  - Place food can under the headspace plunger (5) (see Figure 1) and secure with wing nut level bar to seal plunger rubber septum to the can. Make sure needle is in the retracted position.
  - 2. Insure that all valves are in the closed position.
  - 3. Turn on vacuum source.
  - Insert needle through rubber septum until contact with metal lid is made.
  - 5. Open valves (1) and (2), and evacuate the whole system to maximum allowable limits available.
  - Close valve (1) for 15 seconds and check for leaks. (Drop in vacuum gauge reading is an indication of a leak).
  - 7. Open valve (3) until vacuum is lost, then close valve (3).

APPENDIX A (Cont'd) -

III.

- B. (Cont'd) -
  - 8. Open valve (1) and restore vacuum.
  - 9. Repeat steps 9 and 10 once.
  - 10. Close valve (1).
  - 11. Open valve (3) and closely monitor the loss of vacuum until it reaches "0" then close valve (3). Because the flushing gas is under positive pressure, one should minimize an overload of positive pressure upon reaching equilibrium.
  - 12. Inject the needle through the lid surface until a vacuum is noted on the gauge. Do not inject excessively for fear of incorporating product material in the needle orifice.
  - Equalize pressure by opening valve (3) until "o" vacuum is noted. (Allow same positive pressure to exist).
  - 14. Close valve (2).
  - 15. Open valve (1) until full vacuum is registered.
  - 16. Close valve (1).
  - 17. Allow 1 to 2 minutes for the stabilization of partial pressures.
  - 18. Open valve (2). The capacity of the system will allow headspace gas to be drawn into the sample removal area.
  - 19. Close valve (2).
  - 20. Allow 1 to 2 minutes for gas stabilization.

APPENDIX A (Cont'd) -

- B. (Cont'd) -
  - 21. With a gas tight syringe, remove gas sample from septum
    - (4) and inject into chromatograph.
  - 22. Results are recorded on a strip chart recorder.
- C. Calculation

Computation for  $0_2$  concentration derived from integrated data

will be the following:

$$N_2 + 0_2 = X$$
  
 $0_2/X = Y$ 

- **IV.** REFERENCES
  - 1. Whirlpool Corporation Document No. 24-00333, "Food

Can Headspace Oxygen Analysis Procedure."

## FIGURE 1

Diagrammatic Sketch of Sampling Device

and Gas Chromatograph



- 1. Vacuum on-off valve (Hoke-Tomco Solenoid)
- 2. System on-off valve (Hoke-Homco Solenoid)
- 3. H gas flushing on-off valve (Whitney)  $e^{-2\pi i \theta}$
- 4. Sample gas removal septum port
- 5. Headspace gas sampling device (Hamilton)
- 6. G. C. sample injection septum port

APPENDIX B

# FIGURE 2

Headspace Gas Sample Flow

and Reporting



## Appendix B

Computer Program

This program was generated by Dr. Wayne Clifford of the School of Packaging, Michigan State University. The program utilizes mathematical and statistical models for the conversion of raw data into applicable information. Critical values establishing the initial volume of headspace oxygen, A and B Parameters of the linear models, and correlation coefficients along with the error for variance, were computed from raw data of incremental time (hrs) and volume of headspace oxygen consumed (ul).

## APPENDIX B

# COMPUTER PROGRAM

	COMMON T(50), X(50), Y(50), QTT, ST, SGN, N
90	READ(5,200) N, ERROR
	IF (N.LE.O) CALL EXIT
	WRITE(6,205) N, ERROR
	READ(5,210) $(X(I), T(I), I=1,N)$
	IF(N.LT.O.O) GO TO 1000
	WRITE(6,215) (x(I), T(I), I=1,N)
	SGN=FSN(X(N) - X(1))
	DEL=5.0*(X(N-1) - X(N))
	ST=0.0
	STT=0.0
	DO 100 I=1,N
	ST=ST + T(I)
	STT=STT + T(I) * T(I)
100	
	QTT=N*STT - ST*ST
	CALL LLSQ(DEL,NCHG,SS,))
	DELX=0.0^DELX NOUC CCX b)
	(ALL LLSQ (DELA, NORG, SSA, 9)
100	17(55x - 55) = 120, 120, 140
120	
125	
	CALL LISZ(DELX NCHC SSX 0)
	IF(SSX - SSM) = 125, 125 = 130
130	DMIN=DFLX
100	GO TO 160
140	DMIN=DELX
145	SSM=SS
	DEL=3.0*DEL
	CALL LLSZ (DEL, NCHG, SS, O)
	IF(SS - SSM) 145, 145, 150
150	DMAX=DEL
160	DELL=DMIN + 0.618*(DMAX - DMIN)
	CALL LLSQ (DELL, NCHG, SSL, 0)
170	IF(ABS(DMAX - DMIN).LT.ERROR) GO TO 190
	WRITE (6,330) DMIN, DMAX
	IF(ABS(DMIN-DELL).GT.ABS(DMAX-DELL)) GO TO 180
	DEL=DMIN + 0.618*(DMAX - DMIN)
	CALL LLSZ (DEL, NCHG, SS, 0)
	IF(SS.GT.SSL) GO TO 1/5
	DMIN=DELL
	DELL≃DEL 081-88
	55L=55 CO TO 170
175	
1/2	ина-иев Со то 170
	GO TO T/O

APPENDIX B (Cont'd)

180	DEL=DMIN + 0.382*(DMAX - DMIN)
	CALL LLSQ(DEL,NCHG,SS,0)
	IF(SS.GT.SSL) GO TO 185
	DMAX=DELL
	DELL=DEL
	SSL=SS
	GO TO 170
195	DMTN=DFL
10)	CO = TO = 170
100	CALL LISO (DELL NCHC SS 10)
190	CO = TO = OO
000	GO = 10, 70 EODMAT(12, E10, 5)
200	FORMAT(111) = 121 = 11 = 1200 = 115 = 5
205	FORMAI(1H1, 5X, 18, 13H = N, ERROR = , E15.5)
210	FORMAT(2F10.5)
215	FORMAT (20X, 2F15.8)
330	FORMAT (38X, 2HGS, 2F14.7)
1000	STOP
	END
	SUBROUTINE LLSQ (DEL, NCHG, HQQ, KPRT)
	COMMON T(50), X(50), Y(50), QTT, ST, SGN, N
	DIMENSION E (50)
	DATA KQQ / 0 /
	XZ=X(N) - DEL
	KQQ=KQQ + 1
	IF(KQQ,LE.50) GO TO 90
	WRITE(6,220)
	KPRT=5
220	FORMAT(10X,30HABORT, TOO MANY CALLS TO LLSQ )
90	SY=0.0
	SYY=0.0
	SYT=0.0
	DO 100 I=1,N
	Y(I)=ALPG((XZ - X(I))*SGN)
	SY=SY + Y(I)
	SYY=SYY + Y(I)*Y(I)
	SYT=SYT + Y(I)*T(I)
100	CONTINUE
	B=(N*SYT - SY*ST)/QTT
	A=(SY - B*ST)/N
	R=B*SQRT(QTT/(N*SYY - SY*SY))
	NCHG=0
	XQ=A + B*T(1)
	E(L)=Y(L) - XO
	SS=E(1) * E(1)
	I=1
	<b>IF(KPRT.GT.O)</b> WRITE(6.210) $T(T)$ X(T) Y(T) XO F(T)
	SL = FSN(E(1))

```
APPENDIX B (Cont'd)
210
      FORMAT(1X, 5E14.6)
      DO 130 I=2,N
      XQ=A + B*T(I)
      E(I)=Y(I) - XQ
      IF(KPRT.GT.0) WRITE(6,210)T(I),X(I),Y(I),XQ,E(I)
      SS=SS + E(I) * E(I)
      SN=FSN(E(I))
      IF(SN.EQ.SL) GO TO 130
      NCHG=NCHG + 1
      IF(NCHG, EQ.1) K1=I
      K2=I
      SL=SN
130
      CONTINUE
      K=0.5*(K1+k2)
      NCHG=NCHG*FSN(E(K))
      NCHG=NCHG*FSN(E(K))
      WRITE(6,200) XZ, DEL, A, B, R, NCHG, SS
200
      FORMAT(5X,4E16.9,/,E16.9,15,E16.9)
      IF(KPRT.EQ.10) KQQ=0
      IF(KQQ.GT.60) CALL EXIT
      RQQ=L.) - ABS(R)
      RETURN
      END
      FUNCTION FSN(X)
      IF(X) 100, 120, 120
100
      FSN=-1.0
      RETURN
120
      FSN=1.0
      RETURN
      END
```

APPENDIX C

## Appendix C

Moisture Content Analysis Procedure

The following procedure is an excert from <u>Methods of Analysis</u>, 11th ed. (1970), AOAC. This procedure was employed as a guide for moisture content determination applied here. Essentially, under controlled conditions, the conditioned sample dish is weighed, followed by sample introduction. The dish with sample is weighed after which it is subjected to a controlled vacuum-oven drying period, succeeded by reweighing and moisture loss computation.

### APPENDIX C

## 3.0 ANALYTICAL PROCEDURES

3.1 MOISTURE - A Vacuum Oven Method

### I. GENERAL

The determination of the moisture content of a food is not only an important proximate analysis, but also provides a means for converting all other nutrient composition on an absolute dry weight basis. This method is based on the removal of water from the food solids by drying in a vacuum oven heated at 70  $\pm$  2°C to a constant weight. The resulting loss of weight of the sample is a measure of the amount of water in the sample.

Although the moisture determination is the most simple of analytical operations, it is not free from problems when an accurate analysis is desired. To completely separate all the water from the product without simultaneously causing decomposition of the product is difficult. Errors may be introduced by loss of some volatile components and during weighing a low moisture-content food such as dried and freeze-dried foods through a small weight change and water resorption from the atmosphere. In fruits, vegetables and similar products, and in products containing syrup, difficulties in expelling water arise from hardening of the surface causing occlusion of water. A thin layer of the product evenly spread in the evaporating dish facilitates the release of water from the product.

APPENDIX C (Cont'd)

**II.** APPARATUS

- 1. Balance, analytical
- Metal dish, flat bottom, with tight fitting slip in cover,
   5 cm to 8 cm in diameter
- 3. Oven, vacuum
- 4. Dessicator
- 5. Tong

#### III. PROCEDURE

A. Sample Preparation

All dehydrated and freeze-dried products should be comminuted finely enough to pass a 20 mesh sieve as the coarser particles do not release water readily. All liquid and semi-liquid samples should be well blended before proceeding for moisture analysis.

B. Sample Size

Sample size depends on the solid content of the food. In general, weigh an amount of sample that would give approximately 2 g of the dry residue.

C. Oven Drying of Samples

- Weigh the moisture dish along with its cover, which has been previously dried at 100+ 5°C and kept in a dessicator. Do not handle the dish with fingers.
- Transfer the sample to the dish and spread it evenly at the bottom of the dish. In general, take about 2 g for dried and freeze-dried sample, 5-10 g for semidry and wet products, 10 g for fresh or canned fruits and vegetables. For liquids containing low amounts of solids, use 25-50 g sample.

### APPENDIX C (Cont'd)

III. (Cont'd)

- 3. Partially uncover the dish and dry the sample at  $70\pm 2^{\circ}$ C under pressure not to exceed 100 Torr for a period of 5 hours. For meats and meat products, use a drying temperature of  $95^{\circ}$  to  $100^{\circ}$  for 5 hours.
- 4. During drying admit a slow current of air into the oven (about 2 bubbles per second) which has been dried by passing through concentrated sulfuric acid.
- 5. After a 5 hour druing period is over, cover the dish tightly and transfer it to a dessicator to cool to room temperature.
- 6. Weigh the dish to determine the loss in moisture in the food sample.
- Repeat Steps 3 6 for a 30 minute period of drying. Compare results to the weight previously obtained.
- D. Calculation

Water content, g/100 g =  $(W_2 - W)$  100  $(W_1 - W)$ 

Where

W = weight of dish with cover, g

 $W_1$  = weight of dish with cover + sample

- $W_2$  = weight of dish with cover + residue
- **IV. REFERENCES**

AOAC. Methods of Analysis, 11th Edition (1970) p. 211

