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THE DESIGN AND EVALUATION OF A QUASI-ISOSTATIC TEST SYSTEM FOR DETERMINING THE OXYGEN BARRIER PROPERTIES OF INTACT PACKAGES

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Robert Paul Adams

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Major professor

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THE DESIGN AND EVALUATION OF A QUASI-ISOSTATIC TEST SYSTEM FOR DETERMINING THE OXYGEN BARRIER PROPERTIES OF INTACT PACKAGES

By

Robert Paul Adams

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ABSTRACT

THE DESIGN AND DEVELOPMENT OF A QUASI-ISOSTATIC TEST SYSTEM FOR DETERMINING THE OXYGEN BARRIER PROPERTIES OF INTACT PACKAGES

By

Robert Paul Adams

A test cell was developed to determine the oxygen permeability of intact packages using a quasi-isostatic test technique. Oxygen permeability rates of selected composite cans were obtained and compared with data using an isostatic test method. The closure systems of these composite cans were then isolated to ascertain the seal integrity of the composite can container systems.

Good agreement was obtained between the quasi-isostatic test technique developed in this study and a commercially available isostatic test method. This study established the validity of the quasi-isostatic test system and supports its general applicability for determining the diffusion of gases and vapors through intact composite package systems.

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INTRODUCTION

Determination of the permeability of packaging materials in unfabricated forms is well documented (Karel et al., 1963; Talwar, 1974; Davis and Huntington, 1978; Linowitzki, 1978; ASTM D-1434, 1981; ASTM D-3985, 1981). However, there has been only limited published information concerning the permeability of the fabricated package. Concern is often voiced that discrepancies arise when permeability data for materials are used to estimate the permeability of an intact, finished package. The effects of fabrication of the package, distribution, storage and handling of the package can alter the permeability rate of a material to such a degree that it may be difficult to accurately utilize the permeability data for packaging material or materials for estimating the permeability of the fabricated package.

There is, therefore, a real need to compile and present information concerning the permeability of an entire package. This study examined the gas transmission rates of a selected number of composite can systems using a quasi-isostatic technique. Additionally, a method was used to isolate the closure systems of the various composite containers in order to examine the effectiveness of a variety of closure methods used in their manufacture.

Finally, this quasi-isostatic test procedure was compared with a commercially available isostatic test method, employing the Ox-Tran 100 (Modern Controls, Inc., Elk River, Minnesota). Good agreement between these two methods would seem to validate the quasi-isostatic test system as a viable method in determining the gas diffusion rates of intact packages.

LITERATURE REVIEW

Early work in determining the permeability of a fabricated package involved experimentation with a variety of methods. Smith and Kleiber (1944) designed an apparatus for use in measuring the rate of gas penetration through flexible materials. The permeability data for oxygen (O_2) diffusing through the packaging material were then used to give a measurement of O_2 permeating into a pouch fabricated from the same material.

Cartwright (1946, 1947) described an apparatus and method for determining the quantity and composition of gases in vacuum-packed and gas-packed food containers. Test packages were filled with Ottawa sand and stored at ambient (75^{o}F, 50% RH) conditions. The O_2 transmission rate of the package was then determined by measuring the change of the internal pressure of the package. O_2 transmission is the result of the difference between the external and internal pressure that acts as the driving force.

Ellickson, Hasenzahl and Hussong (1954) developed a method for determining the gas permeability of test films formed into packages. The effects of creasing, folding and sealing were included in this method of determining gas permeability. Brinkman (1957) reported a test method for determining the measurement of gas permeation into machine-made pouches. This method suggests testing can be adapted to a wet or dry atmosphere and to various relative humidities.

Lelie (1964) described a test procedure which examined the gas permeability of fabricated packages which had undergone stressing caused by fabrication, filling, sealing, distribution and final display. Leonard (1964) described an accelerated test for measuring the gas transmission of completed packages. The packages were exposed to higher concentrations of oxygen than normal atmospheric conditions, after which the change in the level of oxygen inside the package was measured over time.

Potter (1967) described the testing of frozen juice fiber composite cans. A standard gas transmission cell, using a manometric procedure, was modified to measure the passage of air through the can wall. Moeller and Lockhart (1967) described an accelerated isostatic permeability test method that was developed as a tool for predicting package shelf life. The effects of heat seals and other closure types on the permeability of pouches and low density polyethylene bottles were detailed by these authors.

Weinke and DeLong (1968) reported a test procedure for measuring the oxygen permeation of pouches and semi-rigid containers. This test method could be adapted for a wide range of temperatures and relative humidities. Calvano, Baummer and Speas (1968) offered an interesting test technique that consisted of filling plastic containers with strong ammonia solutions and metallic copper turnings. As O_2 permeated the test container, the solution turned blue as oxidation of the copper occurred. The color density of the solution was measured by colorimetry and compared with standard solutions to determine the amount of O_2 that had permeated the package.

Mack (1971) and Speas (1972) both described applications of this test method. Mack examined the oxygen barrier characteristics of thermoformed plastic food packages and their closures. Speas examined various packages to determine both their oxygen permeation rates and their effectiveness in preventing outward loss of volatile aromas.

Robertson and Scott (1969) outlined a method that was concerned with measuring the propellant loss of aerosol packages. A gas chromatograph was used to distinguish between leakage of the components of the propellant system and the volatile components of the pack. Loudenslagel and Floate

(1970) reported an isostatic test method that evaluated the permeability of an intact package. A test gas was passed over the outside of the whole package and a known quantity of isolated sweep gas was repeatedly circulated through the inside of the package. A gas chromatograph was used to determine the rate of concentration increase of the test gas over time.

Morrow and Gilbert (1971) described test procedures for the separate determination of gas phase permeation and gas leakage of plastic containers. This test technique used a specially designed "bottle cell" to examine bottles filled with product and closed with caps or crowns. Spiehler (1971) described a commercial instrument that measured the changing oxygen concentration in the headspace of gas-flushed flexible packages.

Amini and Morrow (1974) described a test method which evaluated a closure separately from its container. Applications included monitoring the loss of carbon dioxide from a carbonated beverage container, the entrance of O_2 into a package, and the loss of organic solvents from a product. In all cases, loss or gain of compounds was measured only through the closure. Demorest (1978) reported on commercial equipment that measured the O_2 and CO_2 permeability of intact packages. This test apparatus employed an isostatic test method.

The Composite Can and Tube Institute's listing of recommended Industry Standards considers testing procedures for:

1. The water vapor permeability of composite cans,
2. A method to determine the gas content of the headspace of composite cans,

3. An air pressure method to determine the leakage of composite cans, and

4. A test for measuring the gas tightness of composite cans with one end on.

As illustrated by the above listed standard methods of test, there is no industry approved method for determining the permeability of an intact composite can container system, or for evaluating the closure systems for a composite container. The test procedure that follows may be considered as one alternate test method in determining package permeability values. The quasi-isostatic test procedure described is based upon the assumption that once an equilibrium state of permeation is reached, the rate of permeation is equivalent in both directions.

MATERIALS AND METHODS

Composite Container Systems Examined

Three composite container systems were investigated. These were comprised of:

1. A 12 ounce paperboard 401 x 408 composite can with a liner of 12 pound Surlyn/0.00035 inch aluminum foil/7 pound low density polyethylene/25 pound kraft paper. The top closure was a flexible membrane constructed of 48 gram Mylar/1.5 pound adhesive/0.0025 inch aluminum foil/15 pound Surlyn. The bottom of the composite can was a 401 metal end, used with and without a compounding agent.

2. A one quart paperboard 401 x 509 composite can with a liner of 15 pound low density polyethylene/25 pound kraft paper. The top and bottom closures were 401 metal ends, used with and without a compounding agent.

3. A one quart paperboard 401 x 509 composite can with a liner of 0.00028 inch aluminum foil/25 pound kraft paper. The top and bottom closures were 401 metal ends, used with and without a compounding agent.

Analytical Methods

Both a quasi-isostatic test method and an isostatic test method were used to examine the permeability of the composite container systems. The respective test methods are described in detail below.

I. The Quasi-Isostatic Test Procedure

The quasi-isostatic test apparatus consists of a permeability cell constructed at the Michigan State University machine shop. The permeability cell is equipped with both inlet and outlet gas flush valves and a gas sampling port. The body of the test cell is manufactured from stainless steel, with an interior void volume of 2275 ml (Figure 1).

The composite container system to be tested is mounted in the permeability cell and the cell assembled. The cell is then purged with an inert gas (in this study, nitrogen) until a 100 percent oxygen-free environment, determined by gas chromatography, within the cell is obtained. The gas inlet and outlet valves are then closed. Oxygen permeating through the composite container into the cell chamber is monitored as a function of time until the permeation rate attains steady state.

Permeation Test Conditions. Permeation measurements were carried out at $23^{\circ}C$ and 50 percent $\pm$ 5% relative humidity (RH). For all studies where the oxygen permeation rates were determined by the quasi-isostatic test method, a gas chromatographic procedure was used to determine the oxygen concentration in the cell headspace. For analysis, a 500 μl gas sample was removed from the cell headspace by a gas-tight 500 μl syringe (Model 1750 RN, Hamilton Company, Reno, Nevada) and injected directly into the gas chromatograph.

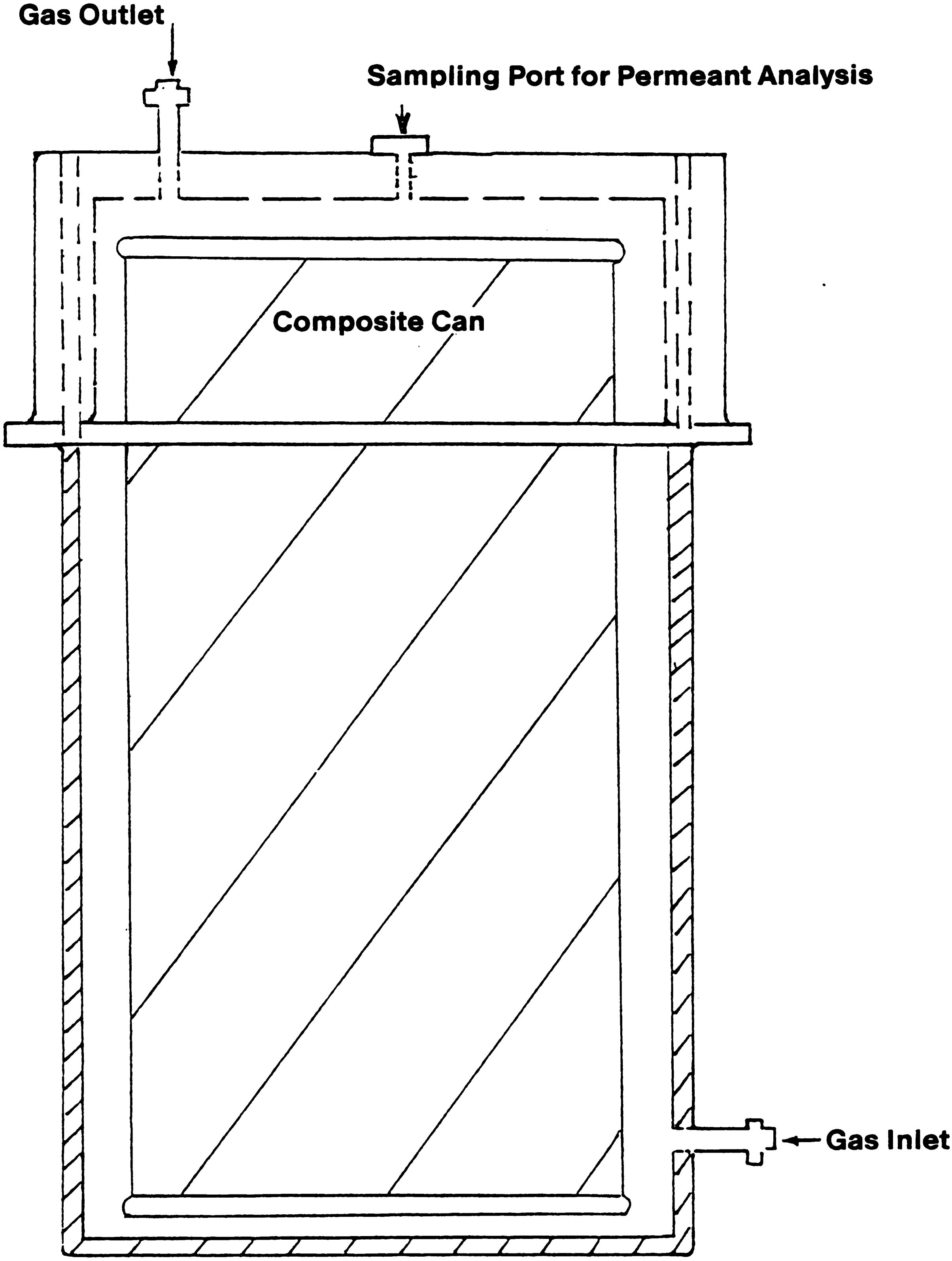

Figure 1. **SCHEMATIC REPRESENTATION OF PERMEATION CELL.**

For oxygen analysis, a Hewlett Packard Gas Chromatograph Model 5830A, equipped with dual thermal conductivity detection was used. Gas chromatographic conditions were: a 3 ft by 1/2 in (1.27 cm by 91.44 cm) stainless steel column, packed with Molecular Sieve 5A (Supelco, Inc., Bellefonte, Pennsylvania); Carrier gas, helium at 30 ml/minute; Injection port temperature of 150^{o}C; Detector temperature of 350^{o}C; Column temperature of 70^{o}C; Oxygen retention time of 1.86 minutes. The percent of oxygen was computed from the oxygen peak area and used directly as the concentration of oxygen present. The experiment was terminated when a steady state permeation rate was obtained.

Based on the quasi-isostatic test procedures described, the oxygen transmission rates were determined for the intact composite container systems. The respective composite container systems were evaluated for their oxygen barrier properties with and without a compounding agent.

<u>Determination of Closure Effectiveness</u>. The extent of oxygen permeation through the closure end unit of the respective composite container systems was determined by systematically isolating the membrane closure and/or the metal ends by application of a silicone rubber bead (Dow Corning Corporation, Midland, Michigan) to the body/closure seal area. Following an appropriate cure time, the oxygen transmission rates of the modified composite can systems were determined by the quasi-isostatic test method described.

<u>Cell Headspace Volume Determination</u>. Following termination of the permeability studies, the test cell was flushed with nitrogen and the headspace of each permeability cell was determined by a modification of

the procedure of Davis and Huntington (1978). The initial carbon dioxide concentration within the permeability cell was determined by gas chromatography using a 500 μl headspace gas sample. A known volume (5 ml) of pure carbon dioxide was then introduced into the headspace of the permeability cell, and after an appropriate equilibration period, the carbon dioxide concentration was determined again by gas chromatography. Gas chromatographic conditions were: a 6 ft by 1/8 in (0.32 cm by 182.88 cm) O.D. stainless steel column, packed with Chromosorb 102, 80-100 mesh (Johns-Manville, Celite Division, Denver, Colorado); Carrier gas, helium at 10 ml/minute; Injection port temperature of 150°C; Column temperature of 70°C; Carbon dioxide retention time of 0.97 minutes. The concentration was based on an external standard of 100 percent carbon dioxide.

The void volume (i.e. headspace of the permeability cells) was calculated from the relationship:

$$V = \frac{V_a \times 100}{C_1 - C_o} \tag{1}$$

where: V = headspace volume (ml)

V_a = volume of carbon dioxide added (ml)

C_1 = final carbon dioxide concentration (volume/volume %)

C_o = initial carbon dioxide concentration (volume/volume %)

The cell headspace or void volume determined by this method was 1400 ml for the 401 x 408 composite can system and 1265 ml for the 401 x 509 composite can system.

II. The Isostatic Test Procedure

The oxygen permeability for both the intact and modified composite container systems was also determined by a commercially available test instrument. The OX-Tran 100 (Modern Controls, Inc., Elk River, Minnesota) employs an isostatic technique and was used to determine the oxygen transmission rate of the intact composite container system. Testing was based on the instrument manufacturer's general test procedure for packages.

RESULTS

Experiments were carried out according to the previously described procedure. Results are shown as follows.

401 x 408 Composite Container Systems

I. The Quasi-Isostatic Test Procedure

The results of the studies for oxygen permeability through the flexible membrane end-noncompounded end composite container system, as determined by the quasi-isostatic test method, are tabulated in Tables 1 - 3.

For better illustration, representative samples are presented graphically in Figure 2. Here, the total quantity of oxygen which had permeated through the several composite container systems is plotted as a function of time. The total quantity of oxygen which had permeated was obtained from the relationship:

$$Q_t = \frac{C_t \times V}{100} \tag{2}$$

where: Q_t = quantity of oxygen which had permeated at time = t (ml)

C_t = oxygen concentration within the cell headspace at time = t (volume/volume %)

V = headspace volume of cell (ml)

Table 1. Data of Oxygen Permeability of the Entire 401 x 408 Composite Can System - Noncompounded Ends Obtained by Quasi-Isostatic Method.

Run No.	Time (Hours)	Total Quantity Oxygen Permeated (ml)
1	5	1.7
	17	5.8
	29	9.7
	43	14.1
	49	15.6
	54	17.3
	68	21.4
2	5	3.3
	12	4.4
	21	8.8
	46	18.0
	53	19.4

Table 2. Data of Oxygen Permeability of the 401 x 408 Composite Can System - Can Body and Flexible Membrane Only Obtained by Quasi-Isostatic Method.

Run No.	Time (Hours)	Total Quantity Oxygen Permeated (ml)
1	5	1.8
	11	3.7
	24	6.5
	55	15.0
	72	19.1
	78	20.3
2	5	2.0
	11	3.5
	24	7.3
	55	16.5
	72	20.7
	78	22.3

Table 3. Data of Oxygen Permeability of the 401 x 408 Composite Can System - Can Body Only Obtained by Quasi-Isostatic Method.

Run No.	Time (Hours)	Total Quantity Oxygen Permeated (ml)
1	10	3.1
	16	4.3
	24	6.3
	34	9.8
	40	10.2
	47	11.8
	67	16.2
2	17	5.5
	25	7.4
	35	10.2
	41	11.0
	48	12.7
	68	16.8

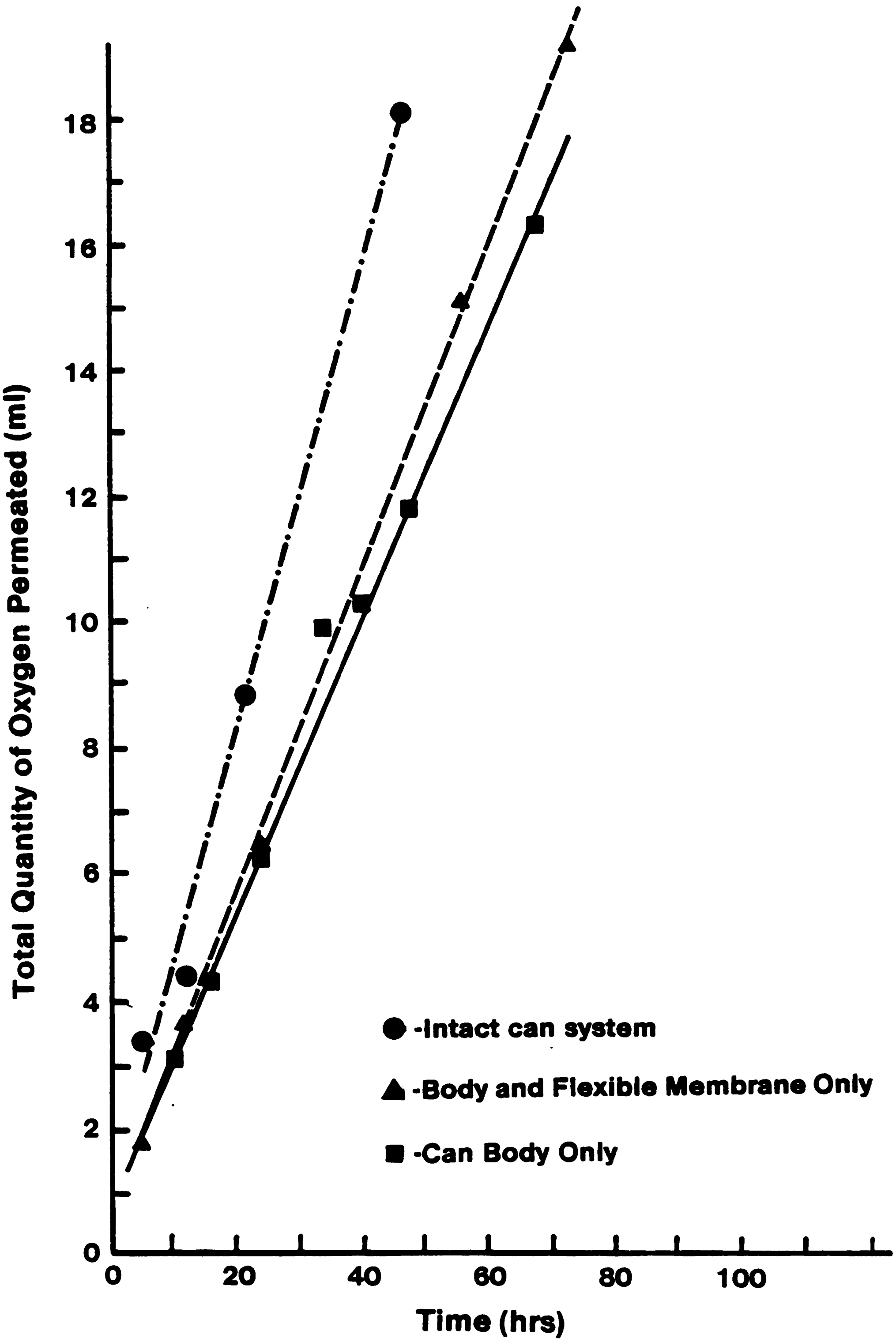

Figure 2. **Oxygen Permeation rates for the flexible membrane end-noncompounded end unit, 401 x 408 composite container system.**

The results of the studies for oxygen permeability through the flexible membrane end-compounded end composite container system, as determined by the quasi-isostatic test method, are summarized in Table 4.

For better illustration, a representative sample is presented graphically in Figure 3. For comparison, the oxygen permeation rate of a representative sample for the flexible membrane end-noncompounded end composite container system is also shown in Figure 3.

Table 4. Data of Oxygen Permeability of the Entire 401 x 408 Composite Can System - Compounded Ends Obtained By Quasi-Isostatic Method.

Run No.	Time (Hours)	Total Quantity Oxygen Permeated (ml)
1	358	2.6
	425	3.3
	531	4.1
	570	5.2
	738	6.3
	903	6.4
2	425	1.4
	531	1.8
	570	1.8
	738	2.3
	903	2.8

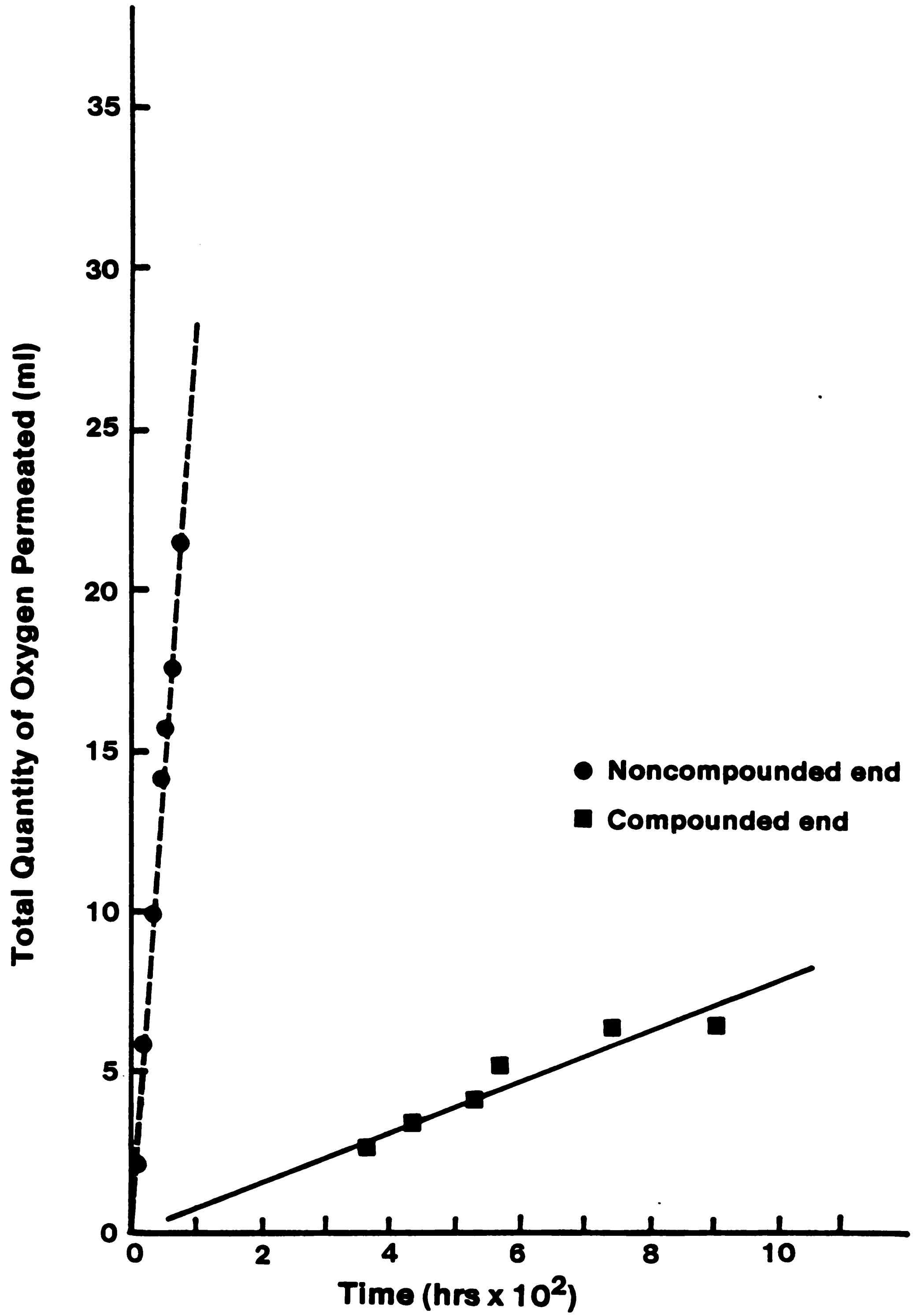

Figure 3. **Oxygen Permeation Rates of 401 x 408 Composite Container System.**

In analyzing the permeability data, the oxygen permeability rates were determined from the slope of the steady state or linear portion of the transmission rate profile curves. Linear regression analysis was then carried out on the data presented in Tables 1 - 4. The oxygen permeability rate and permeability constants for the respective 401 x 408 composite container systems, determined under the test conditions discussed, are summarized in Table 5.

Table 5. Summary of Permeability of the 401 x 408 Container/Closure Systems by the Quasi-Isostatic Method.

Container System	End Type	Permeability[a] $\left(\frac{ml\ O_2}{container \cdot 24\ hours}\right)$	Permeability Constant $\left(\frac{ml\ O_2}{container \cdot 24\ hours \cdot atm}\right)$
Entire Can	Noncompounded	7.9 ± 0.7	37.7 ± 3.2
Body and Flexible Membrane Only	Noncompounded	6.4 ± 0.5	30.3 ± 2.4
Can Body Only	Noncompounded	5.4 ± 0.2	25.7 ± 0.8
Entire Can	Compounded	0.12 ± 0.07	0.57 ± 0.35

[a] Values are the average of duplicate runs.

II. The Isostatic Test Procedure

The results of the isostatic studies for oxygen permeability through both the intact and modified composite container systems are tabulated in Table 6.

For comparison, the permeability values determined by the quasi-isostatic test method and the isostatic test method are shown in Table 7.

Table 6. Summary of Permeability of the 401 x 408 Container/Closure Systems by the Isostatic (Ox-Tran 100) Test Method.

Container System	End Type	Permeability [a] $\left(\frac{\text{ml } O_2}{\text{container} \cdot 24 \text{ hours}}\right)$	Permeability Constant $\left(\frac{\text{ml } O_2}{\text{container} \cdot 24 \text{ hours} \cdot \text{atm}}\right)$
Entire Can	Noncompounded	6.5 ± 0.4	31.0 ± 2.0
Body and Flexible Membrane Only	Noncompounded	4.6 ± 0.1	21.9 ± 0.7
Can Body Only	Noncompounded	4.0 ± 0.1	19.0 ± 0.7
Entire Can	Compounded	0.12 ± 0.07	0.57 ± 0.35

[a] Values are the average of duplicate runs.

Table 7. Comparison of the Oxygen Permeability of the 401 x 408 Composite Can System Using the Quasi-Isostatic and Isostatic (Ox-Tran 100) Test Methods.

Test Method	Container System	End Type	Permeability (a) $\left(\frac{\text{ml } O_2}{\text{container} \cdot 24 \text{ hours}}\right)$	Permeability Constant $\left(\frac{\text{ml } O_2}{\text{container} \cdot 24 \text{ hours} \cdot \text{atm}}\right)$
Quasi-Isostatic Isostatic	Entire Can	Noncompounded	7.9 ± 0.7 6.5 ± 0.4	37.7 ± 3.2 31.0 ± 2.0
Quasi-Isostatic Isostatic	Body and Flexible Membrane Only	Noncompounded	6.4 ± 0.5 4.6 ± 0.1	30.3 ± 2.4 21.9 ± 0.7
Quasi-Isostatic Isostatic	Can Body Only	Noncompounded	5.4 ± 0.2 4.0 ± 0.1	25.7 ± 0.8 19.0 ± 0.7
Quasi-Isostatic Isostatic	Entire Can	Compounded	0.12 ± 0.07 0.53 ± 0.01	0.57 ± 0.35 2.52 ± 0.07
Quasi-Isostatic Isostatic	Body and Flexible Membrane Only	Compounded	- 0.41 ± 0.01	- 1.93 ± 0.03
Quasi-Isostatic Isostatic	Can Body Only	Compounded	- 0.20 ± 0.01	- 0.94 ± 0.05

(a) Values are the average of duplicate runs.

401 x 509 Composite Container Systems

I. The Quasi-Isostatic Test Procedure

The results of the studies for oxygen permeability through Low Density Polyethylene (LDPE)/Paper composite container systems, as determined by the quasi-isostatic test method, are tabulated in Tables 8 and 9.

For comparison, the oxygen permeation rates of representative samples of noncompounded and compounded container systems are presented graphically in Figure 4.

Table 8. Data of Oxygen Permeability of the Entire LDPE/Paper 401 x 509 Composite Can System - Noncompounded Ends Obtained by Quasi-Isostatic Test Method.

Run No.	Time (Hours)	Total Quantity Oxygen Permeated (ml)
1	12	32.4
	17	42.2
	20	47.8
	23	52.9
	26	57.4
	37	72.4
2	12	32.6
	17	42.6
	20	48.3
	23	53.2
	26	58.2
	37	73.1

Table 9. Data of Oxygen Permeability of the Entire LDPE/Paper 401 x 509 Composite Can System - Compounded Ends Obtained by Quasi-Isostatic Test Method.

Run No.	Time (Hours)	Total Quantity Oxygen Permeated (ml)
1	12	16.4
	17	22.1
	22	27.8
	26	32.0
	36	41.6
2	12	17.2
	17	20.3
	22	25.2
	26	29.4
	36	38.0
3	3	6.4
	9	13.7
	12	17.5
	16	22.3
	24	31.2

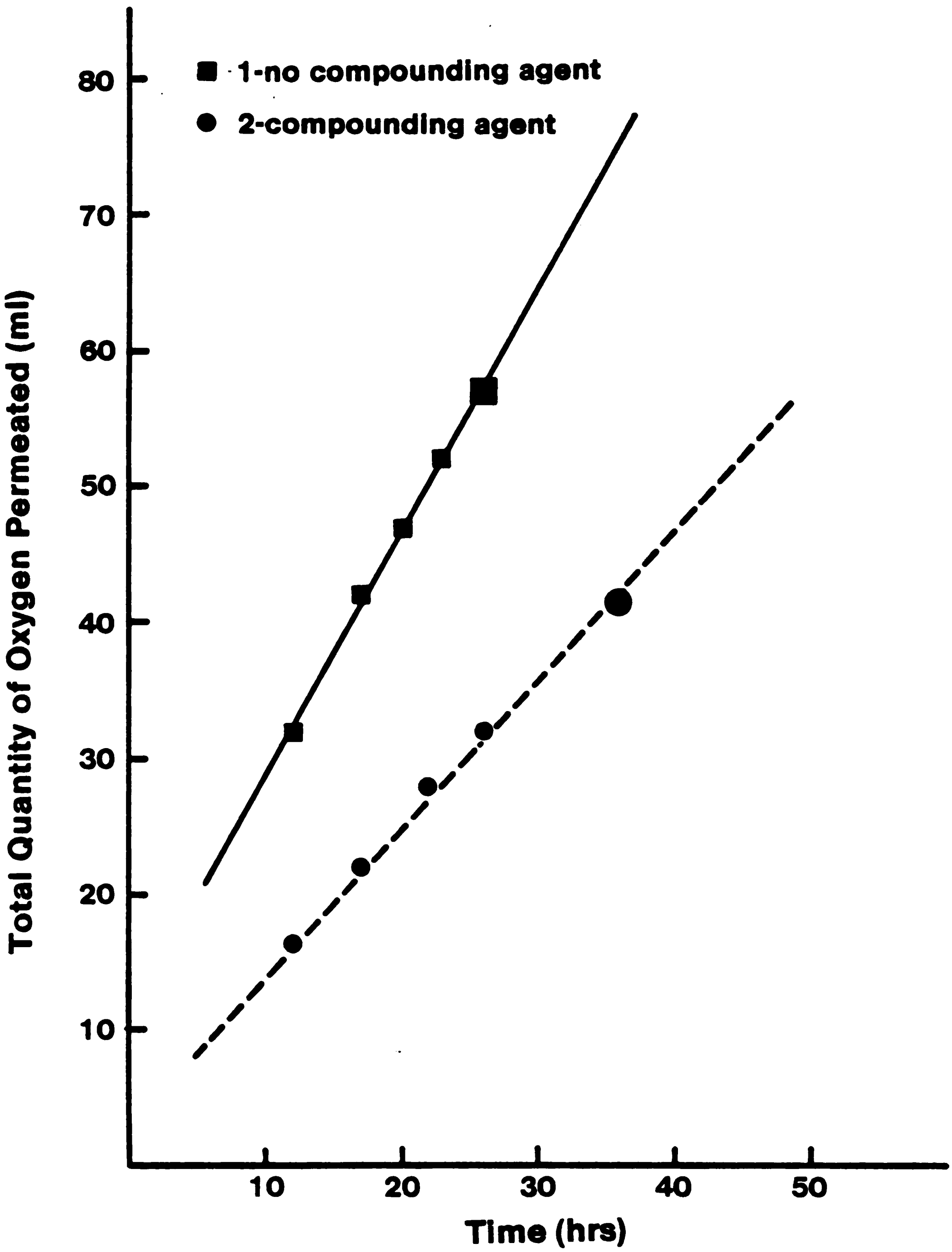

Figure 4. **OXYGEN PERMEATION RATES FOR THE 401 x 509 COMPOSITE CONTAINER SYSTEM (15# polyethylene/25# paper)**

The results of the studies for oxygen permeability through Aluminum Foil/Paper composite container systems, as determined by the quasi-isostatic test method, are tabulated in Tables 10 and 11.

For comparison, the oxygen permeation rates of representative samples of noncompounded and compounded container systems are presented graphically in Figure 5.

Table 10. Data for Oxygen Permeability of the Entire Foil/Paper 401 x 509 Composite Can System - Noncompounded Ends Obtained by Quasi-Isostatic Test Method.

Run No.	Time (Hours)	Total Quantity Oxygen Permeated (ml)
1	6	5.9
	22	11.3
	29	13.9
	49	21.8
	72	29.7
	97	37.9
	121	44.9
2	6	4.8
	22	9.6
	29	11.8
	49	18.7
	72	25.7
	97	33.0
	121	39.9
3	3	3.5
	10	6.1
	19	10.0
	27	12.8
	33	15.3
	43	18.7
	50	23.4
	56	24.8

Table 11. Data of Oxygen Permeability of the Entire Foil/Paper 401 x 509 Composite Can System - Compounded Ends Obtained by Quasi-Isostatic Test Method.

Run No.	Time (Hours)	Total Quantity Oxygen Permeated (ml)
1	5	1.5
	21	5.1
	27	6.1
	48	11.0
	70	16.4
	96	22.3
	120	27.6
2	6	2.1
	22	5.8
	28	6.9
	49	12.4
	71	18.4
	97	24.7
	121	30.3

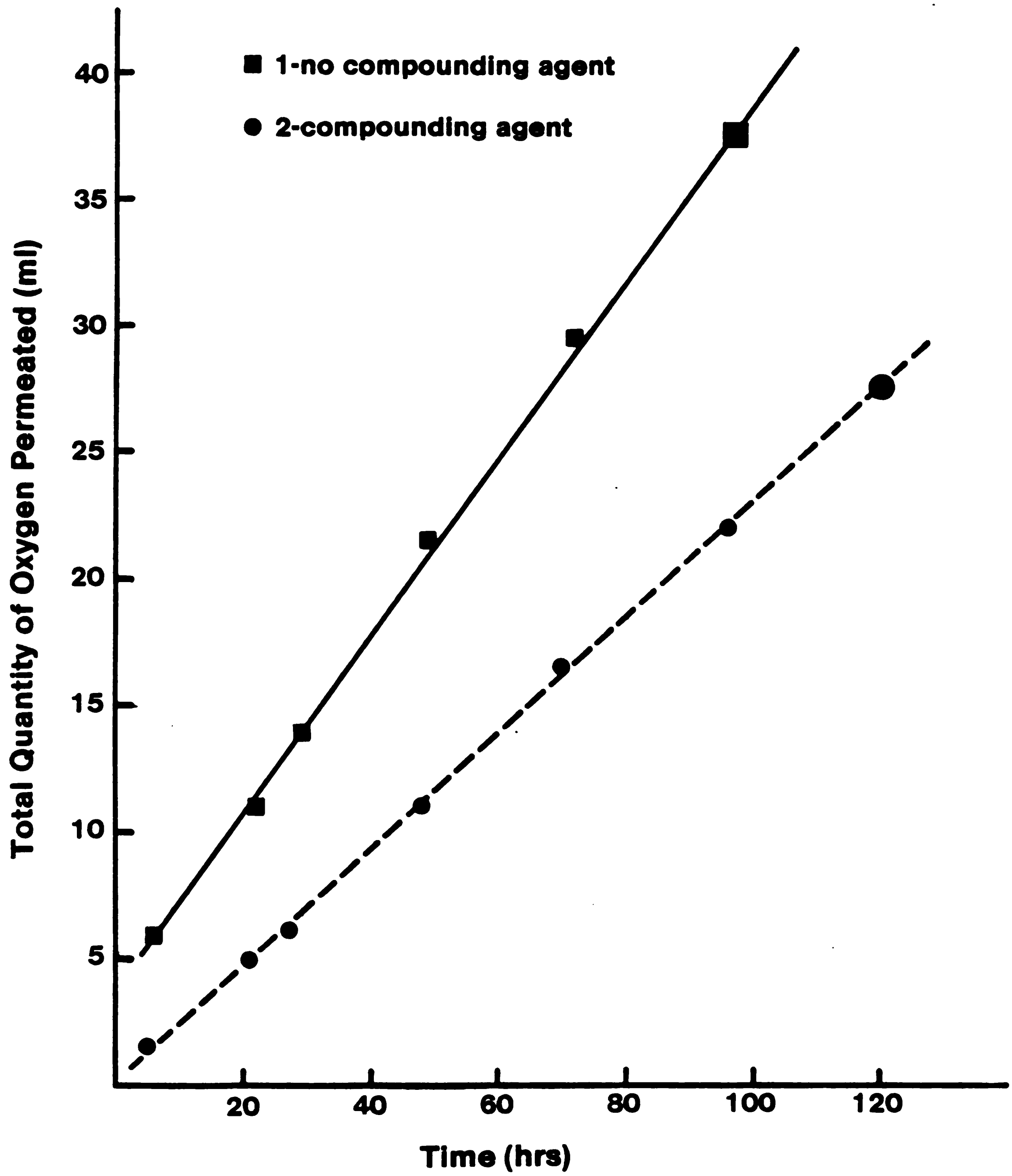

Figure 5. **OXYGEN PERMEATION RATES FOR THE 401 x 509 COMPOSITE CAN (.00028 foil/25# paper)**

As discussed previously, the oxygen permeability rates were determined for the slope of the linear portion of the transmission rate profile curves. The oxygen permeability rate and permeability constants for the respective 401 x 509 composite container systems, determined under the test conditions discussed, are summarized in Table 12.

Table 12. Summary of Permeability of 401 x 509 Composite Container Systems Obtained by the Quasi-Isostatic Test Method.

Container System	End Type	Permeability $\left(\frac{ml\ O_2}{container \cdot 24\ hours}\right)$	Permeability Constant $\left(\frac{ml\ O_2}{container \cdot 24\ hours \cdot atm}\right)$
LDPE/Paper	Noncompounded	38.2 ± 0.3[a]	181.7 ± 1.6
LDPE/Paper	Compounded	25.0 ± 3.5[b]	118.9 ± 16.6
Foil/Paper	Noncompounded	8.5 ± 1.2[b]	40.4 ± 5.9
Foil/Paper	Compounded	5.8 ± 0.3[a]	27.4 ± 1.6

[a] Values are the average of duplicate runs.

[b] Values are the average of triplicate runs.

II. The Isostatic Test Procedure

The results of the isostatic studies for oxygen permeability through the LDPE and Foil composite container systems are tabulated in Tables 13 and 14.

For comparison, the permeability values determined by the quasi-isostatic test method are also shown in Tables 13 and 14.

Table 13. Comparison of the Oxygen Permeability of the 401 x 509 Composite Can System Using the Quasi-Isostatic and Isostatic (Ox-Tran 100) Test Methods.

Test Method	Container System	End Type	Permeability $\left(\frac{\text{ml } O_2}{\text{container} \cdot 24 \text{ hours}}\right)$	Permeability Constant $\left(\frac{\text{ml } O_2}{\text{container} \cdot 24 \text{ hours} \cdot \text{atm}}\right)$
Quasi-Isostatic Isostatic	LDPE/Paper	Noncompounded	38.2 ± 0.3[a] 34.5 ± 4.9[a]	181.7 ± 1.6 164.3 ± 23.6
Quasi-Isostatic Isostatic	LDPE/Paper	Compounded	25.0 ± 3.5[b] 32.5 ± 2.8[a]	118.9 ± 16.6 154.8 ± 13.5

[a] Values are the average of duplicate runs.

[b] Values are the average of triplicate runs.

Table 14. Comparison of the Oxygen Permeability of the 401 x 509 Composite Can System Using the Quasi-Isostatic and Isostatic (Ox-Tran 100) Test Methods.

Test Method	Container System	End Type	Permeability ($\frac{ml\ O_2}{container \cdot 24\ hours}$)	Permeability Constant ($\frac{ml\ O_2}{container \cdot 24\ hours \cdot atm}$)
Quasi-Isostatic Isostatic	Foil/Paper	Noncompounded	8.5 ± 1.2[b] 13.0 ± 0.1[a]	40.4 ± 5.9 61.7 ± 0.3
Quasi-Isostatic Isostatic	Foil/Paper	Compounded	5.8 ± 0.3[a] 8.5 ± 0.4[a]	27.4 ± 1.6 40.5 ± 2.0

[a] Values are the average of duplicate runs.

[b] Values are the average of triplicate runs.

DISCUSSION

401 x 408 Composite Container Systems

Assuming the application of the silicone rubber bead provided complete isolation of the can body/metal closure seal area, a comparison of the data presented in Tables 1 and 2 indicated that for the composite container fabricated with a noncompounded end unit, oxygen permeation (or leakage) through the can body/metal end seal area was significant. A one-way analysis of variance with an improved estimate of error showed a statistically significant difference in O_2 permeation between the intact 401 x 408 composite can system - can body/flexible membrane at a 95 percent confidence interval.

Table 3 summarizes the oxygen transmission rate data of the composite can system where the can body/metal closure seal area and the can body/membrane closed end were both isolated by application of a silicone rubber bead to the respective closure seal areas. Again, it was assumed that the can body/seal areas were effectively isolated and permeation occurred only through the composite can body. A comparison of the data presented in Tables 2 and 3 using a one-way analysis of variance at a 95 percent confidence interval showed no difference statistically between the respective systems evaluated. These findings indicated good seal integrity between the can body and the membrane closure. A graphic representation of these data can be seen in Figure 2.

The oxygen transmission rate data of the 401 x 408 compounded end composite can system are summarized in Table 4 and presented graphically in Figure 3. For comparison, the oxygen permeation data for the flexible membrane end-noncompounded end system is also presented in Figure 3. As shown, the compounding agent had a marked effect on the oxygen permeation through the composite container system. Over a sixty-fold decrease in the oxygen permeation rate was observed when a compounding agent was used in fabricating the can body/metal closure end seal.

A summary of the oxygen permeability rates and permeability constants determined from the linear portion of the transmission rate curves is given in Tables 5 and 6. As noted, there was a significant amount of permeation (or leakage) through the can body/metal end seal.

A comparison of the permeability studies of the intact and modified composite container systems using both the quasi-isostatic and isostatic test methods is given in Table 7.

The isostatic method using the Ox-Tran 100 was utilized to validate the quasi-isostatic test procedure. As shown, relatively good agreement was obtained between the flexible membrane-noncompounded end systems. This can provide validity for the quasi-isostatic test method developed and also validity to the assumption that the permeability of the container is equivalent in both directions.

There was a certain lack of agreement between the quasi-isostatic and isostatic test methods for the flexible membrane-compounded end systems. This observed lack of agreement will be expanded upon in the error analysis portion of this work.

401 x 509 Composite Container Systems

Low Density Polyethylene (LDPE)/Paper Composite Can Systems

A comparison of the oxygen transmission rate data given in Tables 8 and 9 for the respective noncompounded and compounded end systems indicates a 52 percent decrease in the oxygen permeability of the composite can systems using the compounding agent.

Figure 4 graphically presents the comparison of the noncompounded and compounded can systems.

Aluminum Foil/Paper Composite Can Systems

A comparison of the oxygen transmission rate data given in Tables 10 and 11 concerning the respective noncompounded and compounded end systems indicates a 46 percent decrease in the oxygen permeability rate of the composite can system fabricated with a compounding agent.

Figure 5 graphically presents a comparison of the oxygen transmission rate data for the noncompounded and compounded can systems.

As noted previously, the use of a compounding agent reduced the overall oxygen permeability rate of all samples tested.

The addition of a layer of aluminum foil to the liner of the composite can is also noted as significantly reducing the oxygen permeability of the composite container systems. A reduction in permeability rate of 77 percent was noted in comparing the foil/paper and LDPE/paper noncompounded end systems. A reduction in the oxygen permeability rate of 76 percent was noted in comparing the foil/paper and LDPE/paper compounded end systems.

Tables 13 and 14 provide a comparison of the quasi-isostatic and isostatic (Ox-Tran 100) test methods for the respective LDPE/paper and

foil/paper composite cans. Again, relatively good agreement was obtained between the quasi-isostatic and isostatic test methods. There appears consistent agreement between the quasi-isostatic and isostatic test procedures throughout the course of this experiment, giving validity to each procedure.

Error Analysis

Various sources of error may be introduced in the experimental methods used. They include:

Temperature is assumed constant throughout all testing. Fluctuations in room temperatures could have had considerable impact upon the oxygen permeation rates and permeability constants reported.

The partial pressure gradient was assumed constant throughout the course of analysis by the quasi-isostatic procedure. With the cell being a closed system, after the trial run was started, there would gradually be a change in the oxygen partial pressure across the package. The permeation data reported were within the initial portion of the transmission rate curve, where a change in the partial pressure gradient would be minimal.

With any experimental procedure, the effects of operator error should be minimized. Consideration must be given to various portions of the test procedure where possible error may have been introduced. The following are some considerations.

Precision in obtaining the gas samples at the proper time intervals was necessary to assure an accurate transmission rate curve.

The proper maintenance of the gas chromatograph and the permeability cells was necessary to assure puncture free septa. A similar concern was the overall integrity of the respective permeability cells. It was assumed that no oxygen could leak into the cell headspace after the cell was gas flushed and sealed. The integrity of the cells was established in preliminary runs using a pressure drop method, assuring cell integrity during the actual test studies.

Proper calibration of the permeability cell headspace was necessary to determine the total quantity of oxygen peresent in the cell.

Care must be taken in applying the silicone rubber bead to the various composite cans and their closure systems. Poor application of this silicone bead could inadvertently result in permeation or leakage in the closure area. It is assumed no oxygen permeates the silicone rubber bead.

The total number of samples examined was limited by the quantity of test containers available. A larger sample size would reduce possible errors from inadequate sampling.

With regard to the isostatic test procedure, in addition to the considerations cited above, extreme care must be taken in mounting the test package to the Ox-Tran 100 package test station. The test package must be punctured and gas inlet and outlet ports affixed to the package. In our use of the isostatic method, two small holes were drilled in the metal end of the composite can. The 1/8 inch (0.32 cm) O.D. copper tubing used as the gas inlet and outlet ports was inserted into the container through the holes and silicone rubber was then applied to the package/gas port areas to prevent any leakage from occurring. If extreme care is not taken, a minimal amount of oxygen leakage can dramatically alter the permeability readings obtained using the isostatic procedure.

The prevention of this oxygen leakage is critical when the permeability of the container is extremely low, as in the situation with the 401 x 408 flexible membrane-compounded end composite container system. This possibility of error may account for the lack of agreement between the quasi-isostatic and isostatic test procedures with the 401 x 408 flexible membrane-compounded end composite can. With the quasi-isostatic test method, package integrity can be maintained since it is not necessary to mount the package for testing.

This lack of agreement may not be totally unexpected. Roy (1981) conducted oxygen permeability studies of various plastic films using the Ox-Tran 100 and an Isostatic Test Cell. Different permeability rates were determined for the different methods employed, and numerical factors were determined which compensated for the difference between methods.

Further studies comparing the quasi-isostatic and isostatic test methods may be warranted to determine if additional numerical factors are necessary.

SUMMARY AND CONCLUSIONS

A simple test cell was developed for determining the oxygen permeation rates through composite can systems. The quasi-isostatic method described may be applied to a variety of intact packages, providing the proper size test cell is available.

With respect to the various composite container systems examined, the use of a compounding agent in construction of the composite can greatly enhanced the oxygen barrier properties of the container. With minor modifications, the effectiveness of various closure systems for composite cans were evaluated by the test method developed.

Comparison of the quasi-isostatic test method described with an isostatic test procedure indicated reasonable agreement between the two test procedures and established the validity of the proposed test method.

APPENDIX

APPENDIX

ONE WAY ANALYSIS OF VARIANCE: IMPROVED ESTIMATE OF ERROR

C_1: $u_1 = u_2$, If $|t| \leq t_{\alpha/2}$, accept C_1

C_2: $u_1 \neq u_2$, If $|t| > t_{\alpha/2}$, accept C_2

$$MS_E = \frac{\left[\sum_{i=1}^{4}\sum_{j=1}^{2} Y_{ij}^2 - \sum_{i=1}^{4}\left(\frac{Y_i^2}{2}\right)\right]}{n - 4}$$

where: $Y_i = \sum_{j=1}^{2} Y_{ij}$

Group	Results
1	.31 .35
2	.25 .28
3	.23 .22
4	.0072 .000286

C_1: Group 1 = Group 2

C_2: Group 1 $\neq$ Group 2

$$MS_E = \frac{.46086 - .45950}{4} = .00036$$

$$t = \frac{\bar{x}_1 - \bar{x}_2}{MS_E(\frac{1}{n_1} + \frac{1}{n_2})} = \frac{.330 - .265}{.00036(1/2 + 1/2)} = 3.426$$

at a 95% C.I. and 3 d.f., $t_{\alpha/2} = \underline{\underline{3.182}}$

since $|3.426| \geq 3.182$, we accept C_2 that Group 1 $\neq$ Group 2

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