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THE INFLUENCE OF SELECTED BARRIERS AND OXYGEN ABSORBERS ON PRODUCT QUALITY

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M.S. degree in PACKAGING

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THE INFLUENCE OF SELECTED BARRIERS AND OXYGEN ABSORBERS ON PRODUCT STABILITY

By

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ABSTRACT

THE INFLUENCE OF SELECTED BARRIERS AND OXYGEN ABSORBERS ON PRODUCT STABILITY

By

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Packages made from polyethylene (PE) and PVDC-coated polypropylene (PP)/polyethylene were filled with oat cereal and flushed with a known concentration of oxygen. Some were packed with an oxygen absorber. The oxygen absorber is packed in a small pouch made of low barrier material. Lipid oxidation was monitored monthly throughout the five month storage period using a modified TBA method. Head space oxygen was also determined. In general, the oxygen absorber retarded or delayed lipid oxidation in the oat product during storage. The effectiveness of the absorber was reduced over the length of the storage period when product was packed in the low barrier material (PE) and stored at high humidity and temperature ($65^{o}C$). There was a five-fold increase in the TBA index between product in the PE pouch without absorbers and product in the PVDC-coated PP/PE package with absorber at $41^{o}C$. Loss of product quality, as measured by sensory evaluation, was in general agreement with the TBA index and amount of O_2 consumed by the oat cereal.

ACKNOWLEDGMENTS

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INTRODUCTION

The use of preservatives in food products has allowed the development of many food items which can be stored for long times with lower risk of food poisoning. Recently, low salt, low sugar and use of less food preservatives have been demanded in processed foods, in view of the concern for human health. These treatments usually shorten the product's shelf life. Therefore in order to lengthen shelf life, manufacturing processes, packaging, and the distribution system are optimized. Many products now require inert gas atmosphere packaging to attain the desired shelf life when stored at ambient conditions. Sophisticated methods of obtaining inert gas atmospheres in packages, called a gas flush system, have been developed. The residual oxygen level of these processes is usually reduced to 1-2% with most commercial packaging systems. Still, some products such as whole dried milk become unacceptable from a flavor standpoint after 3-6 months storage in these levels of oxygen at ambient conditions.

Recently, pouched type oxygen absorbers (OA) have been developed and commercialized in Japan. OA are packed in small pouches made of low barrier materials. The agents

inside the pouch function by absorbing oxygen. The powdered oxygen absorber and food are packed together in a container of high barrier material. The objective of this study was to evaluate the storage stability of flaked, oat cereal product packed in different materials, with and without the oxygen absorber. The oat cereal is known to be very susceptible to lipid oxidation. The influence of initial oxygen concentration (1, 5, and 21%), storage temperature (21, 41, and 65^{o}C), relative humidity and light exposure on product quality was evaluated.

LITERATURE REVIEW

Oxygen Absorbers (OA)

Mucha et al. (1961) showed that extremely low oxygen concentrations are necessary to prevent oxidative flavors in reconstituted foam-spray-dried whole milk. Flavor evaluation confirmed differences in products stored in 0.1%, 1.0%, and 20% oxygen concentration. Berlin and Pallansch (1963) reported that to reduce the oxygen level trapped inside dry milk particles to less than 0.1%, it was necessary to use an efficient gas flush system with a scavenging system to absorb any oxygen entrapped in the product or permeating through the packaging material.

Maude et al. (1925) developed a free oxygen absorber which consisted or iron powder, ferrous sulfate and a hygroscopic substance in order to assure the safety of electric transformers against explosion in the United Kingdom (UK). The first application of OA for preserving the quality of a dry food was reported by Isherwood (1943) in the UK. Brinkmann and Schlebush (1953) introduced an OA in West Germany which consisted of active carbon and metal. In the United States (USA), Loo et al. (1958) developed an

oxygen absorber composed of sulfate and sulfite. A gas replacement system, where both a gas flush and a catalyst were employed, was developed by American Can Co. in the late 1960's, this was known as the Palladium Catalyzed Oxygen Scavenging System. With this method, the package head space was first flushed using a gas mixture (92% nitrogen, 8% hydrogen) and the package was sealed. The palladium catalyst was laminated between the film layers. Hydrogen in the head space reacted with residual oxygen to form water. Palladium catalyzed the oxygen scavenging reaction in the presence of hydrogen as follows:

$$H_2 + 1/2\ O_2 \xrightarrow{Pd} H_2O$$

Several studies using this catalyst impregnated film (PET/PVDC/Polyvinyl alcohol/PE/catalyst/PE or PET/foil/ionomer catalyst/ionomer) were conducted in the early 1970's. Kuhn et al. (1970) concluded that such a scavenger system containing polyvinyl alcohol as the principal gas barrier medium is very effective in achieving and maintaining very low residual oxygen concentrations in packages containing foam-spray-dried milk. Kuhn et al. (1970) also described three possible scavenging systems. The first one used a separate container employed as an oxygen scavenging device for head space oxygen, placed in the head space of a packaged product. The second one was achieved by using glucose

oxidase and glucose. Mixtures of glucose oxidase, glucose and water were packaged in low barrier materials and placed in the packaged food. The scavenging reaction could absorb 2% of the oxygen in the package. The scavenging reaction occurred only if ample water was present. The third one was the oxygen scavenger impregnated film system as mentioned before.

Zimmerman et al. (1974) changed the structure of the oxygen scavenger impregnated film, to PE/foil/ionomer/catalyst/ionomer in order to prevent seal failure and also improve the reliability of the scavenging activity. They performed a 1-year storage study on 4 ounce gas flushed scavenger packs containing whole milk powder, at four storage conditions (45^{o}F/90% RH, 73^{o}F/50% RH, 100^{o}F/20% RH and 100^{o}F/90% RH). There was no flavor change during storage for one year at any condition except 100^{o}F. In this study, Zimmerman et al. made observations for 6 months. They pointed out that cereal products and citrus crystals can be effectively packaged using the same technique. In spite of such results, these systems were not commercially successful. The most critical problem was the presence of hydrogen gas in the package and concern for product safety.

In Japan an inorganic oxygen absorber based on a dithionite (sodium hyposulphite and hydrosulphite) was developed by Fujishima (1977). It was claimed that sulfur

dioxide (SO_2) was formed and trapped in the food product during the reaction. Inorganic materials such as iron, and organic materials called reductons were chosen for the deoxidizer. Saito (1979) conducted storage studies with vegetable oil, dry instant noodles and fried beans packed with OA. He measured acid value (AV) and peroxide value (PV) as indexes of oxidation. He observed an increase of PV packed without an oxygen absorber, little change with the oxygen absorber (OA) and little change in AV for samples packed with and without an OA during 2 months of storage. Saito concluded that oxygen absorbers can effectively reduce the oxidative degradation of the processed food. Uematsu and Someya (1978) researched the effect of oxygen concentration and exposure to light on the lipid oxidation of fried rice cake and buttered peanuts. During 3 months storage at 30°C, they found that a nitrogen gas (N_2) flush of the fried rice cake (97% exchanging efficiency) did not prevent oxidation. The use of an ultraviolet absorbing film, a foil laminated film and a high barrier film with an OA did reduce oxidation of the fried rice cake. For the buttered peanuts in two conditions, a N_2 gas flush and use of an OA did effectively prevent oxidation. For the fried rice cake, preventing exposure to light was effective. Their results indicated that extent of lipid oxidation depends on each products' characteristics, however, eliminating oxygen is always effective. Oxidation

cannot occur in the absence of oxygen which is recognized as a physical requirement in the mathematical model for oxidation of potato chips by Quast et al. (1972).

Oat Lipids

Oat products are known to be very susceptible to lipid oxidation. In general, the lipid portion, extracted with nonpolar solvent, ranges from 2.0 to 11.0% (Hammond, 1983). Pokorny et al. (1961) first applied gas-liquid chromatography (GLC) to the analysis of oat lipids in order to classify the fatty acids. Lindberg et al. (1964) reported the first GLC results that gave resolution of all the major oat fatty acids. Since then GLC has been used in many studies relating to fatty acid composition of oat lipids. These results are summarized in Table 1 (Hammond, 1983). As shown 18:1 and 18:2 are the major fatty acids (FA) with a large contribution from 16:0, whereas 18:0 and 18:3 are minor components (0.5-4.0% and 0.5-5.0%) respectively. Price and Parsons (1975) showed that oat lipids contained from 70 to 76% nonpolar lipids (NL), from 3 to 10% phospholipids (PL) and from 7 to 17% glycolipids (GL). The major component of the NL is triglyceride (TG). Free fatty acids were reported to be between 2 to 12%, but this was strongly affected by lipase activity as well as variety and location where they were grown (Hammond, 1983).

Table 1. Fatty acid composition of oats (Hammond, 1983).

Reference	No. of varieties	Percentage composition						Location
		14:0	16:0	18:0	18:1	18:2	18:3	
Lindberg et al. (1964)	2	0.1-0.2	14.6-17.8	0.6-1.3	37.1-41.4	39.1-43.1	1.4-2.3	Sweden
Forsberg et al. (1974)	24	0.1-1.3	20.0-28.0	0.5-2.1	24.5-32.0	38.4-47.7	0.7-2.0	U.S.A.
Frey and Hammond (1975)	64	-	14.0-23.0	0.5-4.0	29.5-51.0	26.0-47.0	0.5-5.0	U.S.A.
Welch (1975)	6†	-	15.4-23.9	0.9-2.4	18.7-35.0	43.5-53.0	1.8-3.6	Britain
Youngs and Puskulcu (1976)	15	0.4-0.8	16.2-21.8	1.2-2.0	28.4-40.3	36.6-45.8	1.5-2.5	U.S.A.
de la Roche et al. (1977)	9	-	17.2-23.6	0.8-1.8	26.5-47.5	33.2-46.2	0.9-2.4	U.S.A.
Sahasrabudhe (1979)	12	0.5-4.9	14.9-25.8	1.6-3.9	25.8-41.3	31.3-41.0	1.7-3.6	Canada
Dehghan (1979)	6	0.2-1.2	17.5-21.6	1.0-1.9	30.4-35.8	40.0-46.3	0.7-1.0	U.S.A.
Pan (1981)	103§	-	13.0-21.0	1.0-4.0	33.0-48.0	28.0-44.0	1.2-4.0	U.S.A.

†12:0, 14:1, 16:1, 17:0, 17:1, 20:0, 20:1, and 22:0 reported trace amounts.

‡Includes both winter and spring sowings.

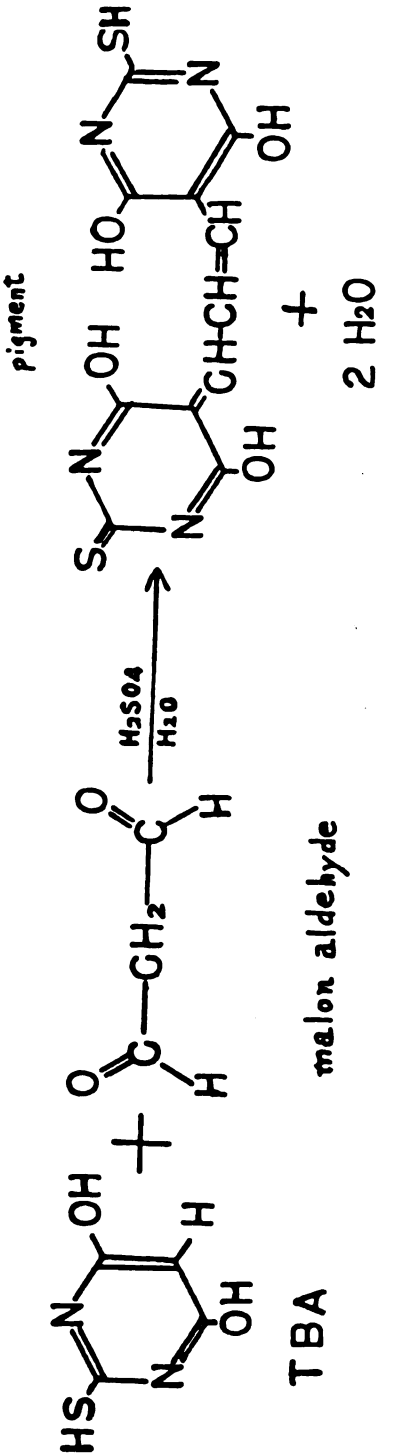
§Includes 43 A. sterilis strains.

TBA Test for Evaluating Lipid Oxidation

The thiobarbituric acid (TBA) test is one of the most widely used methods for the evaluation of lipid oxidation. Sinnhuber et al. (1958) attempted to clarify the nature of the colorimetric reaction which occurs during the TBA test. They proposed that the chromogen is formed through the condensation of two molecules of TBA with one molecule of malonaldehyde (Figure 1). Later they confirmed this chromogen formation by analyzing the chromogen crystal by mass spectrometry, nuclear magnetic resonance and infrared spectrometry.

Dahle et al. (1962) proposed a mechanism for the formation of malonaldehyde, a secondary product in the oxidation of polyunsaturated fatty acids, based upon the autoxidizing theory of Farmer and Sutton (1943). The investigators showed that linoleate developed no TBA color even at peroxide values of 2000 or greater, while fatty acids with three or more double bonds yielded the color. These results proved that only peroxide radicals which possessed β, γ unsaturation to the peroxide group were capable of undergoing cyclization with the final formation of malonaldehyde. Such peroxides could only be produced from fatty acids containing three or more double bonds. Since oat lipids contain few fatty acids containing three or more double bonds (Hammond, 1983), it would seem appropriate that lipid

Figure 1. Formation of TBA pigment.


TBA
malon aldehyde
H2SO4
H2O
pigment
+ 2 H2O

oxidation be measured by other evaluation methods. However, Caldwell and Grogg (1955) reported that the TBA test is well suited to oat cereal. They used TBA to evaluate the storage stability of two different oat cereals stored at 38°C and confirmed a five to ten fold increase in optical density at 532 nm until rancidity was apparent.

There are several variations in methodology for the TBA test. TBA can be directly reacted with a food product, or a portion of a steam distillate of the food, or a separatory acid portion of the extracted fat. Comparison between the direct TBA method and the distillation method for rancidity in fish (mackerel) was carried out by Vyncke (1975). Excellent correlation between the two methods was observed, although the TBA number, as determined by the distillation method, was twice as large as that by the direct extraction method.

Color development during the TBA test is usually assessed by measuring the absorbance of the red pigment at 532 nm. However, other pigments have been observed notably a yellow pigment with maximum absorbance at 450 nm. Marcuse and Johansson (1973) studied the reaction of TBA with various classes of aldehydes and found that alkanals, 2-alkenals, and 2-4-alkadienals produce a yellow (450 nm) pigment with TBA, while only 2-4 alkadienals and 2-alkenals produce the red pigment at 532 nm. They proposed that absorbance at 450 nm could be used as an index of rancidity as well as the

value at 532 nm. However, Patton (1974) has questioned the value of the absorbance at 450 nm, since these pigments can be produced by the reaction of TBA with aldehydes which are not oxidation products such as glyceraldehydes and aromatic aldehydes. Caldwell and Grogg (1955) removed the yellow pigment as an interfering color by selective absorption on a cellulose column.

There is some evidence that TBA can react with compounds other than those found in oxidizing systems to produce the red pigment. Dugan (1955) reported that sucrose and some compounds in wood smoke react with TBA to give a red color. Baumgartner et al. (1975) found that a mixture of acetaldehyde and sucrose produced a 532 nm absorbing pigment identical to that produced by malonaldehyde and TBA.

On the other hand, malonaldehyde can condense with some amino acids. The condensation product is not hydrolyzed under the conditions used in the TBA test (Buttkus and Rose, 1972). Lower color yields might occur in an oxidizing system in the presence of proteins.

METHODOLOGY

Sample Preparation

Fresh flaked oat cereal (without antioxidants) was obtained from a local producer for use in this study. The initial composition of the oat cereal was 64% carbohydrate, 14% protein, 7% fat and other materials (company's data). Fifty grams of oat cereal were deposited into a plastic pouch. An OA consisting of iron powder, water, and catalysts, and weighing 4.8 gm was placed into certain samples. Two different materials were used to make the sample pouches. One pouch material was composed of Polyvinylidene chloride (PVDC) coated Polypropylene (PP)/ polyethylene (PE). The total thickness of this film was 86 μm. The other pouch material was made from 84 μm polyethylene. The original pouch size was 20.5 cm x 18 cm (length x width). After filling, every sample pouch was vacuumed and heat sealed using the Super Vac^{R} Type GK 165R vacuum machine (Smith Equipment). After sealing, 150 ml of air was inserted using a 1000 ml volume airtight syringe. A square shaped gum sheet (2.5 cm x 2.5 cm x 0.1 cm; length x width x thickness), which had an adhesive surface on one wide, was attached to the top portion of the pouch by

using the adhesive side. This gum sheet was utilized to prevent gas leakage during sampling. The total inner volume of the package was determined by submerging the package into water in a 1000 ml graduate cylinder. Volume increase of the water indicated the total volume of the package. Internal volume was calculated by subtracting the volume of pouch material (corresponding to 10 ml) from the total volume. The internal volume was adjusted to 255 ml using a 5 ml airtight syringe. The top of the pouch was heat sealed, with a minimum amount of head space remaining in the discarded part of the pouch. The final pouch dimensions were 18 cm x 15 cm (length x width) and had been four side sealed. The surface area of the pouch was 540 cm^2. Head space volume of these samples was measured by an Oxygen Analyzer (Appendix 1 and 2) and found to be 185 ml.

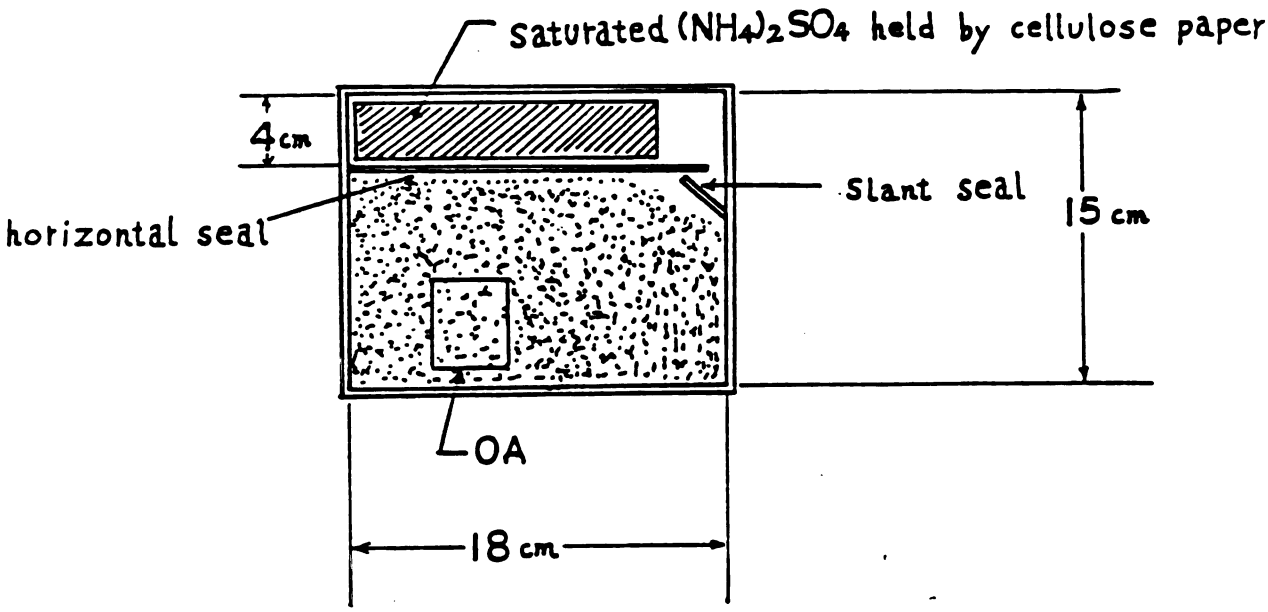
Initial head space oxygen concentrations (1.0% and 5.0%) were prepared by the same procedure with the exception of nitrogen gas flush. After the cereal was put into the pouch, nitrogen was introduced into the pouch by the Super Vac^R Type GK 165R. The desired oxygen concentration was obtained by injecting air or extracting the head space gas by the air tight syringe. The O_2 concentration was monitored using the O_2 analyzer. The internal volume was maintained at 255 ml. A sample package stored at high relative humidity (RH), was modified to hold the saturated salt solution (ammonium sulfate; $(NH_4)_2SO_4$) inside the

pouch. One horizontal and one slanted heat seal were added to the pouch in order to separate the saturated salt solution ($(NH_4)_2SO_4$). In Figure 2 is shown the modification. These samples could not be vacuumed, so the internal volume was regulated using the 50 ml airtight syringe. After the oat cereal (with or without OA) was deposited into the plastic pouches (20.5 cm x 18 cm), horizontal and slanted heat seals were added as mentioned previously. The top of the pouch was also heat sealed. The internal volume was regulated by the same manner except a 50 ml airtight syringe was used instead of a 5 ml airtight syringe. The final internal volume and dimensions were maintained at 255 ml and 18 cm x 15 cm respectively.

Sample Storage

Samples were placed into one of five storage conditions. The conditions were derived from combinations of three factors - temperature, humidity and exposure to light. Storage at 21°C and 45% RH was accomplished using a controlled temperature and humidity room. Storage at 41°C was accomplished using a temperature regulated chamber. Relative humidity inside the chamber was held at 40% RH by allowing water to evaporate from a bucket filled with water. Humidity was monitored using a psychrometer. A PE bucket (90 mil) containing a saturated salt solution ($(NH_4)SO_4$) was used to maintain high RH (80% RH) at this temperature. A

Figure 2. Package modification for high RH (41^{o}C, 80% RH).


Saturated $(NH_4)_2SO_4$ held by cellulose paper
4 cm
horizontal seal
Slant seal
15 cm
OA
18 cm

light exposure box made of corrugated board was maintained in this chamber to create another condition. A 15 W fluorescent light was installed underneath the top flap of the exposure box. The light intensity ranged from 40 to 90 foot candles (Appendix 3).

Another temperature regulated chamber was utilized for storage at 65^{o}C. In order to maintain a moderate RH (45% RH) packaged samples were stored in a PE bucket containing saturated salt solution (Chromium trioxide; CrO_3). Sample conditions are shown in Table 2. Samples were withdrawn periodically from each condition. Two pouched samples were used for the modified TBA test, head space oxygen concentration, and sensory evaluation. Temperature and RH tolerances were ±3^{o}C and ±5% RH respectively.

Index for Lipid Oxidation

Modified TBA Test

Caldwell and Grogg (1955) first applied the thiobarbituric acid test (TBA test) to cereal products including oat cereal. In this technique, extracted lipids were mixed with water, TBA reagent and trichloroacetic acid. After completion of the reaction, the aqueous layer was transferred to a cellulose adsorption column in order to remove the yellow pigments from the reacted solution. Optical density (O.D.) of the (red) solution was measured at 532 nm. Caldwell and Grogg (1955) reported that their method was

Table 2. Experimental conditions.

Temperature	RH	Material	Exposure to light	OA	Initial O_2 concentration
21°C	45%	PVDC coated PP/PE	No	No	21%
21°C	45%	PVDC coated PP/PE	No	Yes	21%
41°C	40%	PVDC coated PP/PE	No	No	21%
41°C	40%	PVDC coated PP/PE	No	No	5%
41°C	40%	PVDC coated PP/PE	No	No	1%
41°C	40%	PVDC coated PP/PE	No	Yes	21%
41°C	40%	PE	No	No	21%
41°C	40%	PE	No	Yes	21%
41°C	40%	PVDC coated PP/PE	Yes	No	21%
41°C	40%	PVDC coated PP/PE	Yes	Yes	21%
41°C	80%	PVDC coated PP/PE	No	No	21%
41°C	80%	PVDC coated PP/PE	No	Yes	21%
65°C	45%	PVDC coated PP/PE	No	No	21%
65°C	45%	PVDC coated PP/PE	No	Yes	21%

applicable to oat cereal.

The modified method used in this study is basically a combination of Caldwell's (1955) and Sidwell's (1954) techniques. In Sidwell's methodology sample lipids were melted with benzene. The reactive material in the benzene layer was extracted with an acid solution (glacial acetic acid) of TBA. The aqueous layer containing the reactive material and TBA was transferred to a test tube using a separatory funnel. The aqueous layer underwent reaction in a boiling water bath with development of the red color. Sidwell did not use an adsorption column. Separation between benzene layer and aqueous layer was very difficult when Sidwell's methodology was applied to the oat cereal used in this study. After vigorous mixing of the solution containing the two layers in the separatory funnel, the two layers formed an emulsion which caused an unproportional separation of reactive material into the aqueous TBA reagent layer. This separation ratio is critical for the TBA test and was improved by centrifugation.

Modified TBA Test (M-TBA Test)

Twenty grams of oat cereal were utilized for each measurement. Two M-TBA tests were executed for each pouched sample. Therefore, a total of four M-TBA tests were performed for a specific condition in each sampling time. Twenty grams of the cereal were placed into a 200 ml beaker

and extracted with 100 ml of hexane overnight at room temperature. The hexane layer was filtered using a glass suction funnel with an aspirator. Hexane (50 ml) was added to the sample to complete the filtration. The filtered hexane layer was transferred to a 250 ml flat bottom boiling flask and vacuum distilled using a rotary evaporator at 48^{o}C. Drying of the lipid sample was completed by gently nitrogen flushing the sample. The dried lipid extract was weighed and then added to 10 ml of benzene. After 10 ml of TBA reagent (0.67 gm of thiobarbituric acid diluted to 100 ml with distilled water, plus glacial acetic acid 100 ml) had been added to the flask, it was swirled and shaken vigorously for four minutes. The samples were then centrifuged in a 50 ml centrifuge tube for 15 minutes at maximum speed (Model CL of International Chemical Centrifuge manufactured by International Equipment Co.) to separate the benzene and aqueous layers. After the top layer (benzene) had been removed by a disposable pipette, the aqueous layer containing TBA and reactive material was transferred to a screw capped glass test tube. The test tube was placed in boiling water for exactly 30 minutes. After reacting, the aqueous layer became orange colored. A seven milliliter aliquot of the orange colored liquid was transferred to the cellulose adsorption column (6 mm inside diameter x 430 mm height) containing cellulose powder (90 mm high; Whatman CC 31). Glass wool was used as the

stopper at the end of the column. This aliquot was forced through with air pressure of 10.0 psi. Ten milliliters of distilled water were then flowed through the cellulose column, in order to elute the yellow colored pigment from the column. A 10 ml aliquot of aqueous pyridine (40 ml of pyridine diluted to 200 ml with distilled water) was then forced through the column. Ten milliliters of this solution was collected in a 10 ml volumetric flask. The optical density measurement of this solution (red colored) at 532 nm was made against a blank solution which was obtained by the same procedure except no lipid had been added. The optical density was multiplied by a hundred and divided by the weight of sample lipid (O.D. x 100/gm) which is referred to as the modified TBA index (M-TBA Index).

Residual Oxygen Concentration of the Package

Residual oxygen concentration in the package was measured using the Oxygen Analyzer LC-700 F (Toray Engineering Co., Ltd., Tokyo). This detects the amount of oxygen in the sampled gas based on the electromotive force of the Zirconium solid cell (see Appendix 2). A 5 ml sample of gas was withdrawn from the package and injected into the sample loop of the Oxygen Analyzer. The oxygen concentration was recorded from the digital readout.

Sensory Evaluation

The flavor of each sample was observed throughout storage. A portion of each sample was stored at -20°C. After 3 months of storage, each sample was numbered at random and evaluated for flavor and color change. There were 14 different storage conditions having 4 sampling times including the initial sample, thus there were 57 different sample conditions, each having 2 sample pouches. 2 pouched samples were mixed and deposited into one numbered vial (1 to 57) with an airtight closure. Evaluation was conducted once a day over 3 days. This evaluation was performed by one researcher, so there was no statistical significance to the results. However, the results were used to show the general trends.

Oxygen Permeability of the Sample Films

The oxygen permeability of the sample films were measured using the Oxtran 100 Oxygen Permeability Tester (Modern Controls Instrument, Rochester, Minnesota). This instrument measures O_2 transmission by an isostatic method. The sensing device (coulometric) detects the amount of oxygen passing from the oxygen chamber through the film and into the nitrogen chamber. The O_2 is swept via a carrier gas to the detector. Gas flow rate (both N_2 and O_2) were maintained at 15 ml/min. Permeability measurement were performed at either 0% RH or 100% RH at 21°C. Relative

humidities at elevated temperatures (41°C, 65°C) were calculated using a mathematical relationship (see Appendix 4).

Scavenging Ability of the Oxygen Absorber

The oxygen absorber used in this study was Type LH-1000 made by Tōa Synthetic Chemical Industry Co., Ltd., Tokyo, Japan and consisted of a 4.8 gm mixture of iron powder, catalysts and water. To test its O_2 scavenging ability, 0.5, 1.0, 1.5, 2.0, and 2.5 gm weight of the mixed powders were put into the barrier package (PVDC coated PP/PE, 18 cm x 18 cm; length x width). The surface area of the package was 648 cm^2 with headspace volume adjusted to 500 ml of air by an airtight syringe. Water of which the weight was equal to 10% of each sample powder, was also injected into the package to create a condition of high relative humidity. The oxygen concentration inside the package was measured by the Oxygen Analyzer after 2 and 4 days at 21°C. The scavenging ability of the oxygen absorber was calculated by relating the amount of scavenged oxygen to the weight of the mixed powder. The amount of permeated oxygen was accounted for by this calculation, though it was almost negligible.

RESULTS AND DISCUSSION

Storage Study

The M-TBA index varied depending upon the oxygen concentration, which was affected by the initial oxygen concentration, oxygen permeability of the package and presence of oxygen absorber. M-TBA index of the original sample was 5.0 (O.D. x 100/gm). After one month, PE pouched samples with and without OA had approximately a tenfold increase in the M-TBA index as compared to the original sample, when they were stored at 41^{o}C, 40% RH (Figure 3). The M-TBA index for either sample condition did not increase further, however the TBA values were still high when compared to other sample conditions. Distribution of M-TBA indexes is shown in Table 3. The advantage of using OA was not significant, when analysis of variance (ANOVA) for two factors (time and sample condition) were applied to the result of M-TBA index (Table 7, 12). Sensory evaluation of these samples after one month also showed that they were extensively oxidized, resulting in very strong odors (Table 5). The use of OA did not prevent oxidation from occurring for the oat cereal in the PE

Figure 3. M-TBA index as a function of time for oat cereal packaged in PE, and stored at 41°C, 40% RH, under 21% initial headspace O_2.

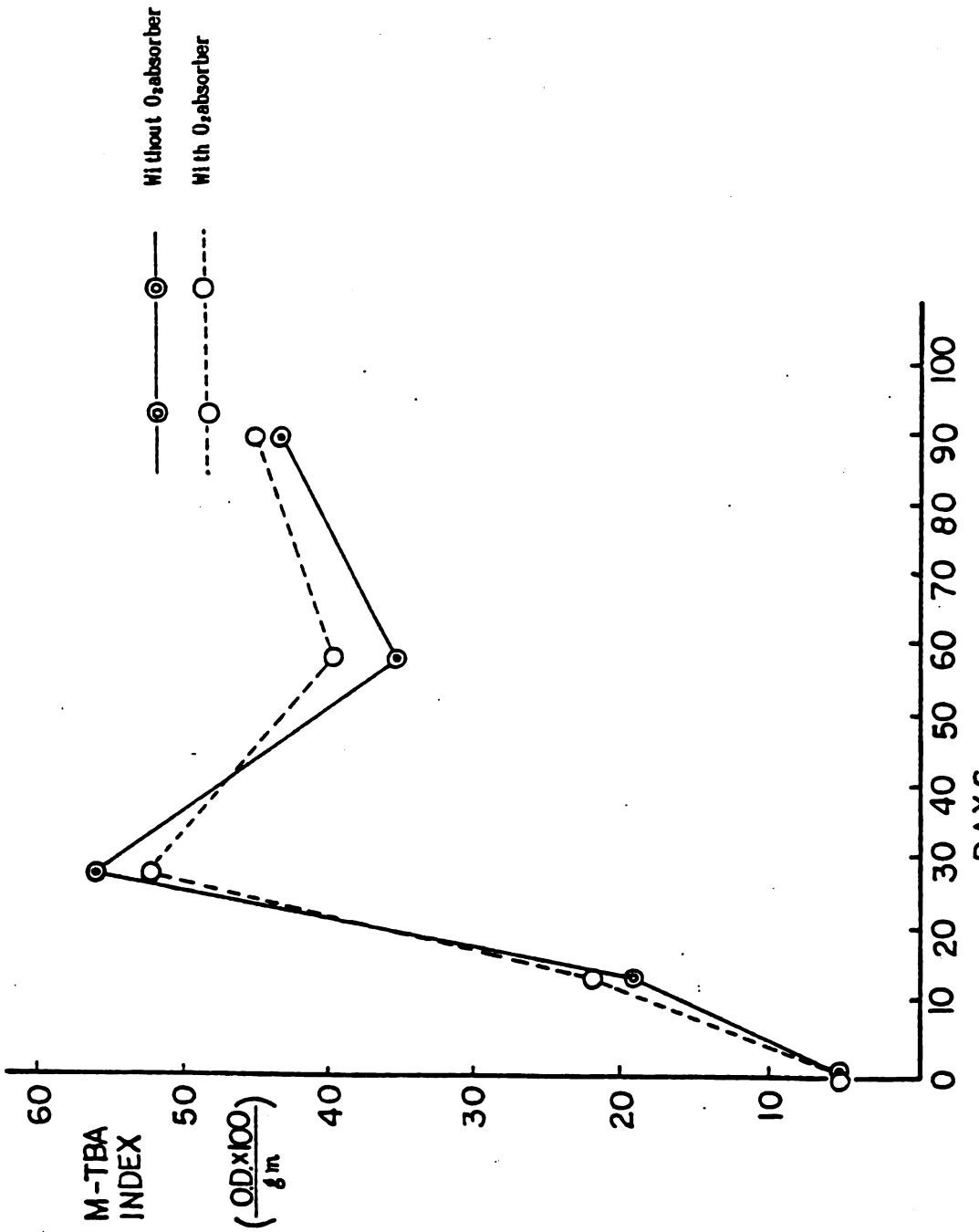

Without O₂absorber
With O₂absorber
M-TBA INDEX
(O.D.x100 / g m)
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
DAYS

Table 3. Change in the M-TBA index for M-TBA index.

No	Temp	R.H.	Material (package)	Light	OA	Initial O_2 conc	M-TBA index n = 4	O.D.* 100 / gm , ( ) : days , distribution of M-TBA index : s^2				
1	21 °C	45 %	PVDCcoated PP / PE	No	No	21 %	5.0 (0) s^2= 0.86	—	11.0 (21) s^2= 1.0	10.5 (35) s^2= 2.3	15.2 (61) s^2= 2.3	16.4 (96) s^2= 1.6
2	21 °C	45 %	PVDCcoated PP / PE	No	Yes	21 %	5.0 (0) s^2= 0.86	—	10.0 (21) s^2= 1.8	9.8 (35) s^2= 3.7	13.6 (61) s^2= 1.4	7.5 (96) s^2= 0.7
3	41 °C	40 %	PVDCcoated PP / PE	No	No	21 %	5.0 (0) s^2= 0.86	—	15.0 (15) s^2= 1.2	30.4 (28) s^2= 20.8	19.3 (59) s^2= 7.0	21.1 (90) s^2= 63.6
4	41 °C	40 %	PVDCcoated PP / PE	No	No	5 %	5.0 (0) s^2= 0.86	—	13.5 (15) s^2= 2.1	15.6 (28) s^2= 0.5	17.4 (59) s^2= 12.4	24.4 (90) s^2= 22.8
5	41 °C	40 %	PVDCcoated PP / PE	No	No	1 %	5.0 (0) s^2= 0.86	—	13.0 (15) s^2= 1.2	12.7 (28) s^2= 20.8	19.3 (59) s^2= 7.0	19.1 (90) s^2= 63.6
6	41 °C	40 %	PVDCcoated PP / PE	No	Yes	21 %	5.0 (0) s^2= 0.86	—	12.1 (15) s^2= 5.2	10.2 (28) s^2= 2.6	12.6 (59) s^2= 5.9	11.4 (90) s^2= 7.2
7	41 °C	40 %	PE	No	No	21 %	5.0 (0) s^2= 0.86	—	22.6 (14) s^2= 34.1	52.6 (28) s^2=141.3	39.6 (58) s^2= 80.6	46.3 (90) s^2= 94.8
8	41 °C	40 %	PE	No	Yes	21 %	5.0 (0) s^2= 0.86	—	19.5 (14) s^2= 8.2	56.3 (28) s^2= 69.7	35.2 (58) s^2= 44.5	43.1 (90) s^2=206.8
9	41 °C	40 %	PVDCcoated PP / PE	Yes	No	21 %	5.0 (0) s^2= 0.86	—	19.7 (18) s^2= 3.7	18.7 (31) s^2= 10.6	20.0 (61) s^2= 0.8	13.4 (90) s^2= 0.0
10	41 °C	40 %	PVDCcoated PP / PE	Yes	Yes	21 %	5.0 (0) s^2= 0.86	—	12.3 (18) s^2= 4.8	11.2 (31) s^2= 1.2	12.5 (61) s^2= 1.5	8.6 (90) s^2= 0.3
11	41 °C	80 %	PVDCcoated PP / PE	No	No	21 %	5.0 (0) s^2= 0.86	—	17.2 (18) s^2= 31.5	13.8 (31) s^2= 3.1	13.2 (61) s^2= 1.1	9.5 (95) s^2= 1.7
12	41 °C	80 %	PVDCcoated PP / PE	No	Yes	21 %	5.0 (0) s^2= 0.86	—	15.7 (18) s^2= 1.7	11.4 (31) s^2= 0.7	12.8 (61) s^2= 2.6	7.9 (95) s^2= 0.2
13	65 °C	45 %	PVDCcoated PP / PE	No	No	21 %	5.0 (0) s^2= 0.86	12.8 (4) s^2= 1.8	14.9 (11) s^2= 5.3	14.8 (24) s^2= 3.9	18.7 (66) s^2= 4.2	19.7 (94) s^2= 1.0
14	65 °C	45 %	PVDCcoated PP / PE	No	Yes	21 %	5.0 (0) s^2= 0.86	11.8 (4) s^2= 1.5	17.1 (11) s^2= 0.8	22.0 (24) s^2= 27.8	22.9 (66) s^2= 8.7	66.2 (94) s^2= 18.7

Table 7

ANOVA table for a p x q factorial experiment with r replicates

source	sum of squares	d.f.	mean square	F ratio
Factor A	$SS_A = qr\sum_{i=1}^{p}(y_i - y)^2$	p - 1	MS_A	$\frac{MS_A}{MSE}$
Factor B	$SS_B = pr\sum_{j=1}^{q}(y_j - y)^2$	q - 1	MS_B	$\frac{MS_B}{MSE}$
Inter-action A x B	$SS_{AB} = r\sum_{i=1}^{p}\sum_{j=1}^{q}(y_{ij} - y_i - y_j + y)^2$	(p - 1)(q - 1)	MS_{AB}	$\frac{MS_A}{MSE}$
Residual	$SSE = \sum_{i=1}^{p}\sum_{j=1}^{q}\sum_{k=1}^{r}(y_{ijk} - y_{ij})^2$	pq(r - 1)	MSE	
Total	$\sum_{i=1}^{p}\sum_{j=1}^{q}\sum_{k=1}^{r}(y_{ijk} - y)^2$	pqr - 1		

Here

$$MS_A = \frac{SS_A}{p - 1}$$

$$MS_B = \frac{SS_B}{q - 1}$$

$$MS_{AB} = \frac{SS_{AB}}{(p - 1)(q - 1)}$$

$$MSE = \frac{SSE}{pq(r - 1)}$$

Table 12

ANOVA for the Date of sampling x Packaged condition (41°C, 40%RH PE, 21% initial O_2 concentration , with and without O_2 absorber)

source	sum of squares	d.f.	mean square	F ratio	testing hypotheses
date (Factor A)	4669.2	3	1556.3	18.3	significant (99%)
packaged condition (Factor B)	14.0	1	14.0	0.2	
Inter-action A x B	77.0	3	25.7	0.3	
Residual	2040.1	24	85.0		
Total	6800.4	31			

Table 5. Results of the sensory evaluation.

Temp.	R.H.	Material of a package	Exposure to light	O_2 absorber	Initial O_2 conc.	Time (months)			
						0.5	1	2	3
21°C	45%	PVDCcoated PP/PE	No	No	21%	○	○	○	A little oxidized
〃	〃	〃	〃	Yes	〃	○	○	○	○
41°C	40%	〃	〃	No	〃	○	A little oxidized	Oxidized	Oxidized
〃	〃	〃	〃	〃	5%	○	○	Oxidized	Oxidized
〃	〃	〃	〃	〃	1%	○	○	Oxidized	Oxidized
〃	〃	〃	〃	Yes	21%	○	○	○	A little oxidized
〃	〃	PE	〃	No	〃	A little oxidized	Oxidized Stung smell	Oxidized Stung smell	Oxidized
〃	〃	〃	〃	Yes	〃	A little oxidized	Oxidized Stung smell	Oxidized Stung smell	Oxidized
〃	〃	PVDCcoated PP/PE	Yes	No	〃	Oxidized	Oxidized	Oxidized Sting smell	Oxidized Sting smell
〃	〃	〃	〃	Yes	〃	○	○	A little oxidized	Oxidized
〃	80%	〃	No	No	〃	○	○	A little oxidized	Oxidized
〃	〃	〃	〃	Yes	〃	○	○	Sweet smell	Sweet smell
65°C	45%	〃	〃	No	〃	Oxidized Sweet smell	Sweet smell	Burned smell	Burned smell
〃	〃	〃	〃	Yes	〃	Sweet smell	Sweet smell	Burned smell	Burned smell

package. Oxygen concentration in the PE packages were nearly zero (less than 0.01%) within one day (Table 4), however, after 3 days, O_2 concentration was the same as in the atmosphere (Figure 12). The OA used in this experiment has a capacity of 160 ml oxygen in ambient condition (see Figure 28, Table 17). The permeability of the PE film was 4100 ml/m^2/day at 41°C, 0% RH (Figure 26, Table 16) which corresponds to 220 ml/pouch/day. The head space of the sample pouch was 185 ml (Appendix 1), so 38.7 ml of oxygen (185 x 0.209) was the initial quantity of O_2 in the pouch. Therefore, the OA should lose its absorbing ability by 3 days, assuming the driving force was maintained at 0.209 atm.

1) $$\frac{(160 - 38.7)\ \text{ml/pouch}}{220\ \text{ml/pouch.day.atm} \times 0.209\ \text{atm}} = 2.6\ \text{day}$$

- 38.7 : initial amount of O_2 in the pouch (ml)
- 160: absorbing ability of OA (ml)
- 220: permeability of the PE film (ml/pouch.day)
- 0.209: pressure difference between outside and inside.

Assumptions

- OA initially absorbed the headspace O_2 completely within a few hours.
- OA absorbed all permeating O_2 immediately as it came through the package.

Table 4. Concentration change of headspace O_2.

Temp.	R.H.	Material (package)	Exposure to light	OA	Initial O_2 conc.	Concentration change of head space O_2 (%), ( ) : days							
21°C	45%	PVDC coated PP/PE	No	No	21%	20.9 (0)	17.5 (5)	—	17.3 (20)	13.5 (35)	11.6 (67)	3.2 (96)	0.02 (148)
〃	〃	〃	〃	Yes	〃	〃	0.01 (5)	0.01 (12)	0.01 (20)	0.01 (35)	0.02 (67)	0.01 (96)	—
41°C	40%	〃	〃	No	〃	〃	15.9 (5)	13.7 (12)	14.6 (14)	3.3 (28)	0.01 (59)	0.01 (90)	—
〃	〃	〃	〃	〃	5%	5.0 (0)	4.6 (1)	4.3 (5)	4.1 (12)	4.2 (14)	2.2 (28)	0.01 (59)	0.01 (89)
〃	〃	〃	〃	〃	1%	1.0 (0)	0.90 (1)	1.1 (5)	1.5 (13)	0.90 (28)	0.01 (59)	0.01 (89)	—
〃	〃	〃	〃	Yes	21%	20.9 (0)	0.01 (1)	0.01 (5)	0.15 (13)	0.02 (28)	0.10 (59)	1.5 (90)	—
〃	〃	PE	〃	No	〃	〃	20.8 (3)	20.8 (7)	20.6 (14)	18.6 (28)	20.6 (58)	20.8 (90)	—
〃	〃	〃	〃	Yes	〃	〃	0.01 (1)	17.7 (3)	20.6 (7)	20.6 (14)	18.7 (28)	20.4 (58)	20.6 (90)
〃	〃	PVDC coated PP/PE	Yes	No	〃	〃	15.4 (5)	9.2 (12)	4.7 (16)	3.7 (19)	0.01 (32)	0.01 (62)	0.01 (90)
〃	〃	〃	〃	Yes	〃	〃	0.01 (1)	0.01 (5)	0.02 (12)	0.02 (19)	0.01 (32)	0.01 (62)	0.01 (90)
〃	80%	〃	No	No	〃	〃	18.4 (5)	15.9 (12)	14.9 (16)	13.3 (19)	10.2 (32)	4.0 (62)	2.5 (90)
〃	〃	〃	〃	Yes	〃	〃	0.01 (1)	0.01 (5)	0.01 (12)	0.01 (19)	0.01 (32)	0.01 (62)	9.2 (90)
65°C	〃	〃	〃	No	〃	〃	6.6 (4)	5.0 (11)	6.0 (24)	—	2.3 (65)	11.6 (94)	—
〃	〃	〃	〃	Yes	〃	〃	0.01 (1)	0.01 (4)	0.01 (11)	0.01 (24)	0.01 (65)	0.01 (94) Vacuumed	—

Figure 12. Headspace O_2 concentration as a function of time for oat cereal packaged in PE under 21% initial headspace O_2 and stored at 41°C, 40% RH.

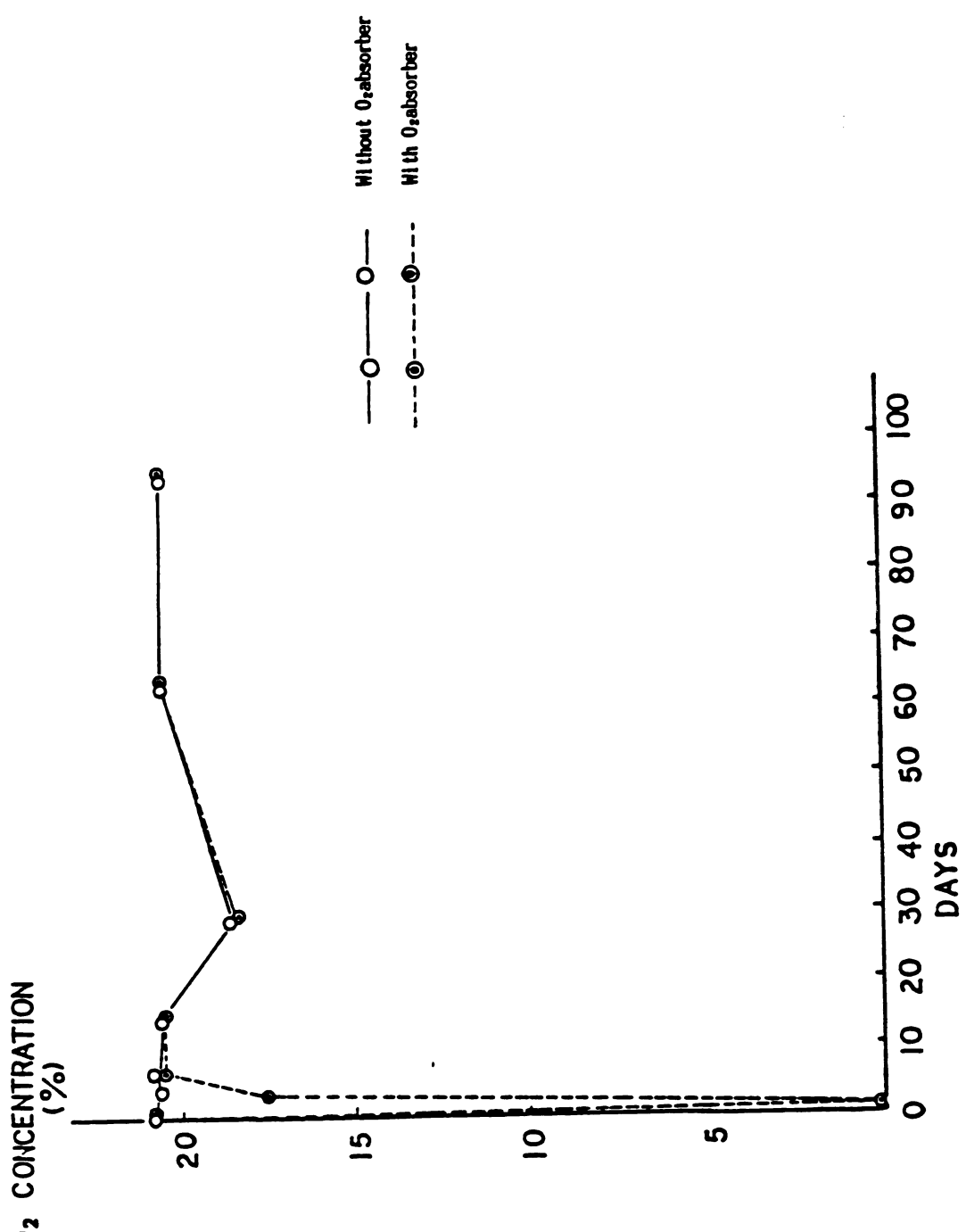

O2 CONCENTRATION (%)
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
DAYS
Without O2absorber
With O2absorber

Figure 28. Absorbing ability of the O_2 absorber as a function of weight at 21°C.

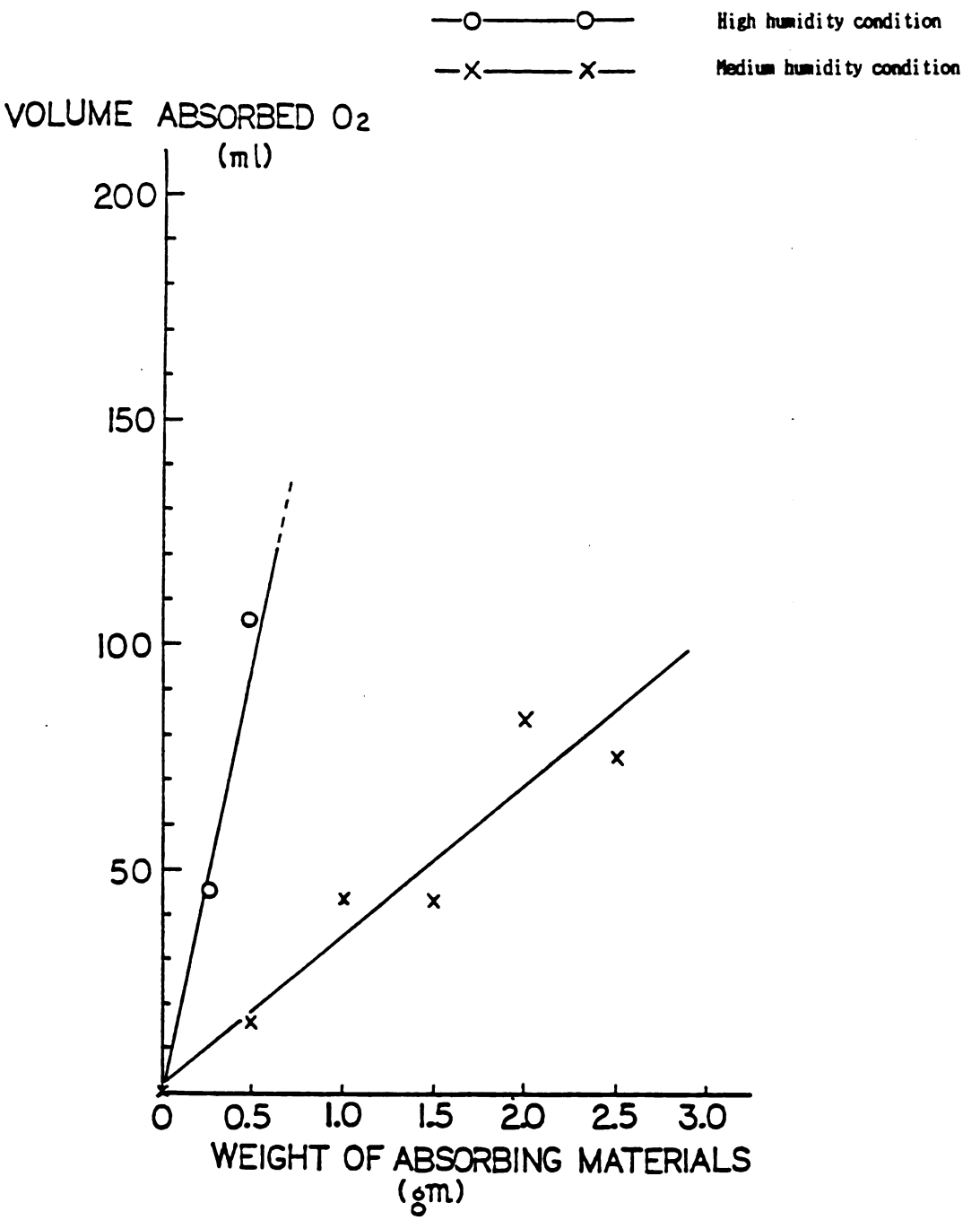

—O——O— High humidity condition
—X——X— Medium humidity condition
VOLUME ABSORBED O2
(ml)
200
150
100
50
0
0.5
1.0
1.5
2.0
2.5
3.0
WEIGHT OF ABSORBING MATERIALS
(gm.)

Table 17. Absorbing ability of the O_2 absorber.

Weight of absorbing materials (gm) X	O_2 concentration (%) 2 days	4 days	(20.9 O_2 conc)	O_2 Vol. (ml) Y
Moderate humidity condition (40%)				
0.5	17.7	17.7	(3.2)	16
1.0	12.2	12.1	(8.8)	44
1.5	12.7	12.3	(8.6)	43
2.0	4.5	4.1	(16.8)	84
2.5	6.2	5.8	(15.1)	76
High humidity condition (80%)				
0.25	12.2	11.8	(9.1)	45.5
0.50	1.0	0.01	(20.8)	104
0.75	<0.01	<0.01		>104
1.00	<0.01	<0.01		>104
1.25	<0.01	<0.01		>104

Y = 33X + 2.3 1 pouch contains 4.8 gm materials

Y = 160 ml/pouch

Y = 209X - 23 1 pouch contains 4.8 gm material

Y = 1000 ml/pouch

Figure 26. O_2 permeability of PE and PVDC coated PP/PE as a function of temperature.

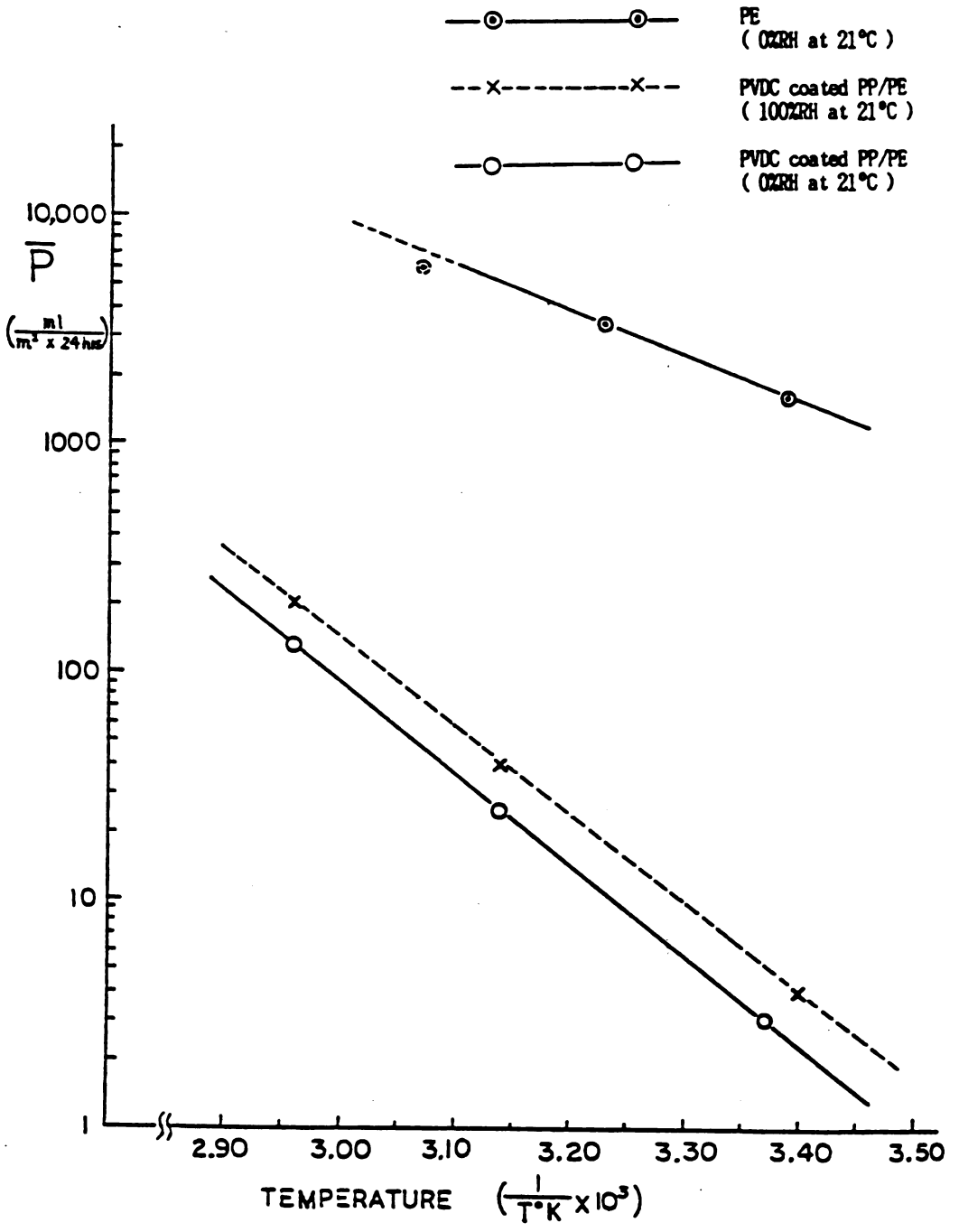

PE
(0%RH at 21°C)
PVDC coated PP/PE
(100%RH at 21°C)
PVDC coated PP/PE
(0%RH at 21°C)
10,000
$\overline{P}$
$\left(\frac{ml}{m^2 \times 24hr}\right)$
1000
100
10
1
2.90
3.00
3.10
3.20
3.30
3.40
3.50
TEMPERATURE $\left(\frac{1}{T°K} \times 10^3\right)$

Table 16. O_2 permeability of the sample films.

Film	Temperature °C	Temperature (1/°K) 10^3	Relative humidity % RH	Relative humidity (at 21°C)	Permeability constant ($\bar{P}$) $ml/m^2/day$
PE	22	3.39	0	(0)	1600
	37	3.23	0	(0)	3500
	53	3.07	0	(0)	>5900 (over the sensing capacity)
PVDC PP/PE	21	3.40	100	(100)	4.0
	45	3.14	32	(100)	41
	65	2.96	10	(100)	210
	24	3.37	0	(0)	3.1
	45	3.14	0	(0)	25
	65	2.96	0	(0)	130

After OA was no longer able to absorb O_2, accumulation occurred due to permeation from the outside. O_2 concentration in the pouch increased depending upon the permeability of the pouch material. The driving force would decrease, with increased O_2 concentration in the pouch. The amount of O_2 permeating through the package changed, according to the following relationship:

$$2)\quad An = \left(0.209 - \frac{Ao + A_1 + A_2 + \ldots + A_{n-1}}{185}\right) \times 9.17$$

An; Amount of O_2 permeated from outside from n-1 to n hours after OA lost its ability to absorb O_2 (ml)

9.17; Permeability constant of the PE film (ml/pouch. hour.atm)

185; Headspace volume of the pouch (ml)

$Ao = 0$

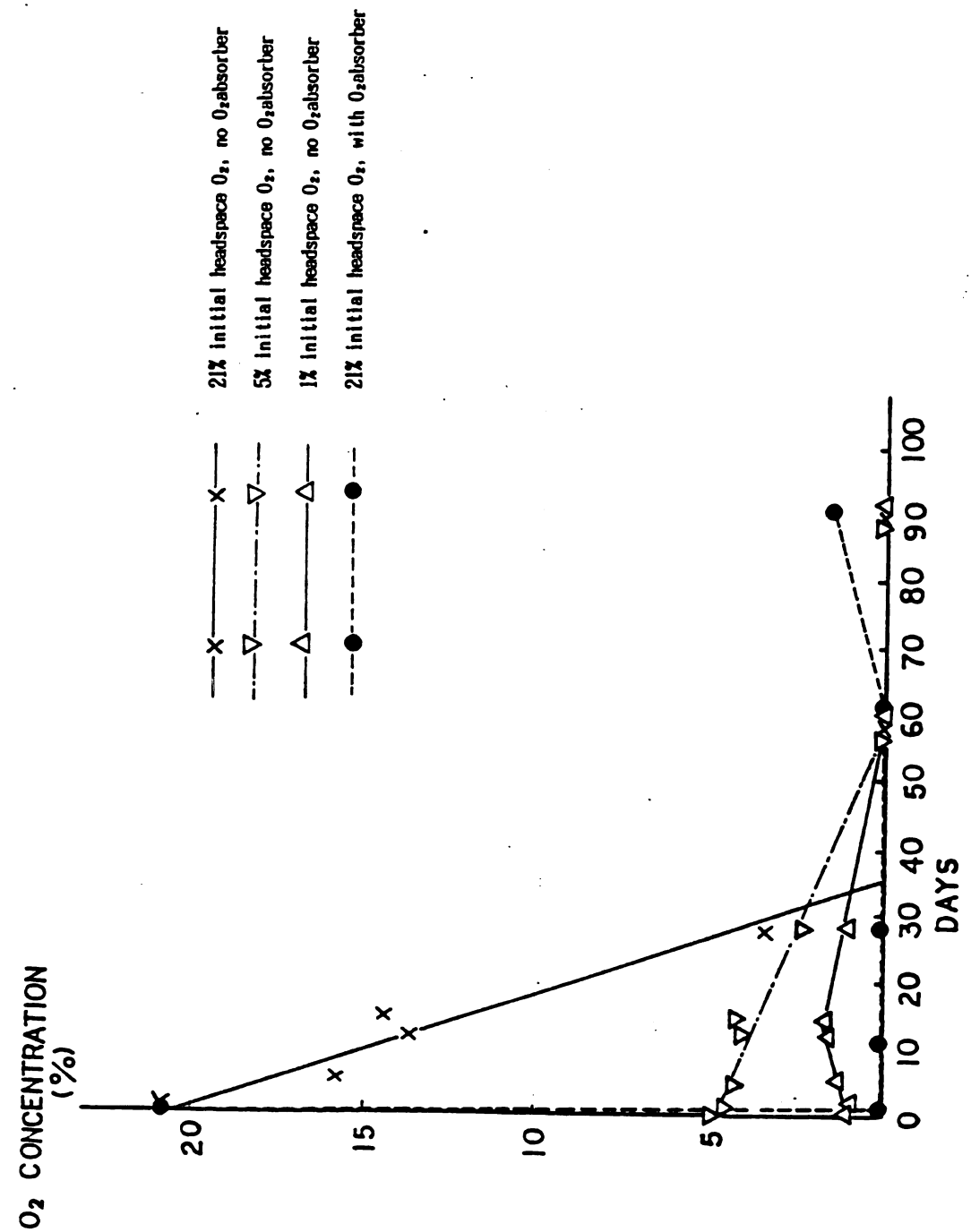
$\left(0.209 - \frac{Ao + A_1 + \ldots + A_{n-1}}{185}\right)$; Pressure difference after n hours. (atm·ml/ml)

The amount of $O_2 = A_0 + A_1 + A_2 \ldots + A_n$

Calculated results are shown in Appendix 6. These results show that, after 28 hours (which corresponds to 4.2 days from the time, OA was put into the pouch) that the headspace O_2 concentration was 17.8%.

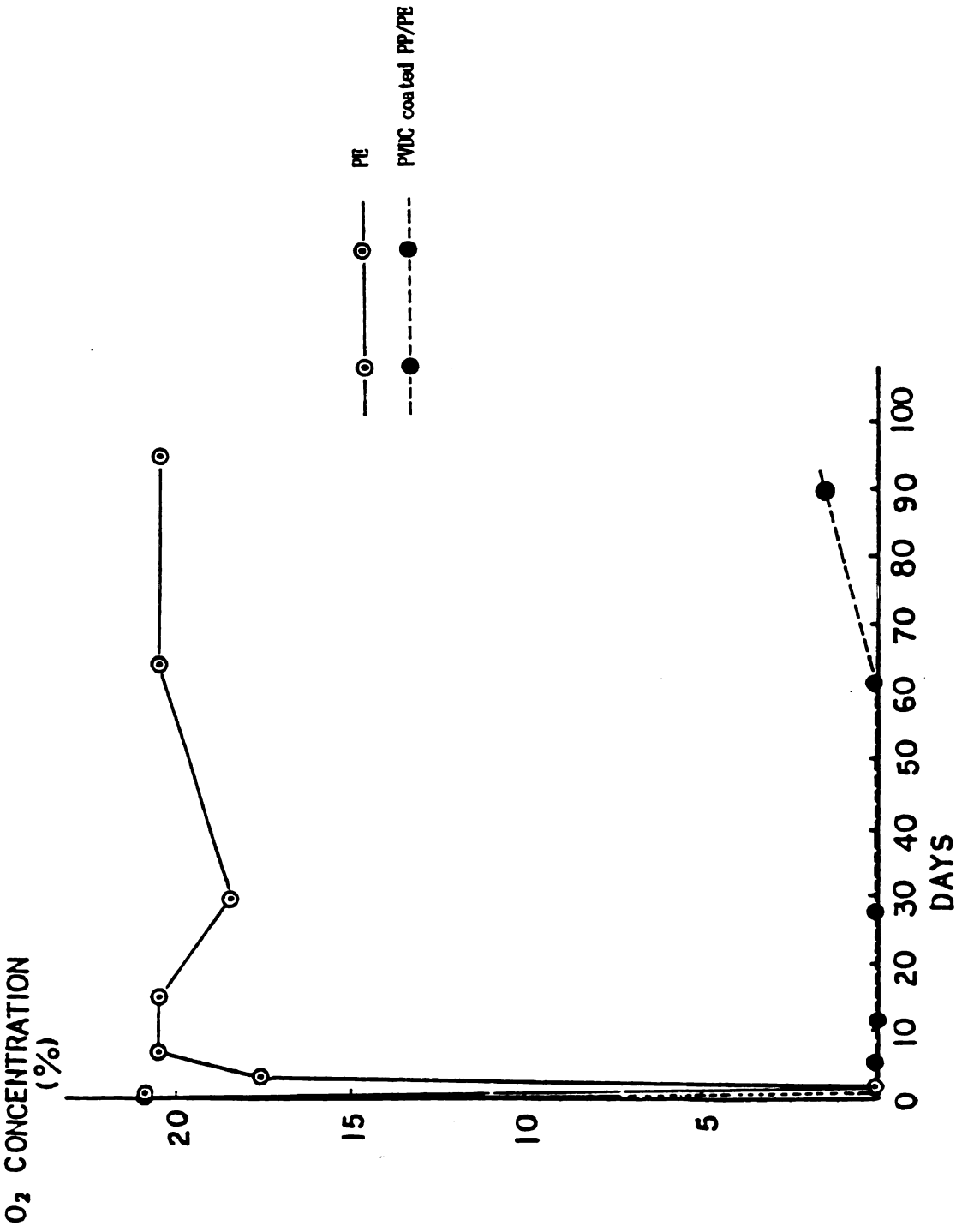
The headspace O_2 concentration in PVDC coated PP/PE, stored at 41°C. 40% RH changed dependent on the initial O_2 concentration and capacity of O_2 absorber (Figure 13).

Figure 13. Headspace O_2 concentration as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 41°C, and 40% RH.


O2 CONCENTRATION (%)
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
DAYS
21% initial headspace O2, no O2absorber
5% initial headspace O2, no O2absorber
1% initial headspace O2, no O2absorber
21% initial headspace O2, with O2absorber

Samples containing 21% initial headspace O_2 absorbed all O_2 in the package by 35 days. Least square regression analysis was used to treat the sample data. Packages (no OA) with initial headspace O_2 concentrations of 5% and 1% were reduced to zero by 60 days. Packages, packed with O_2 absorbers and an initial O_2 concentration of 21%, were reduced to zero within a few hours and maintained this condition until 60 days. A gradual increase was noted until at 90 days it was 1.7% (Figure 13). The headspace O_2 concentration of PE pouches changed much more rapidly compared to that of PVDC coated PP/PE pouches (41^{o}C, 40% RH). As mentioned previously, the headspace O_2 concentration for both packages dropped to nearly zero within a few hours, headspace O_2 concentration in PE pouches then increased to 20% by 6 days. O_2 concentration in PVDC coated PP/PE pouches was maintained at less than 0.01% until 60 days (Figure 14). High barrier package materials are important in order to prevent the O_2 absorber from being overwhelmed. From the headspace O_2 content, the amount of O_2 consumed an average O_2 consumption rate (AOR) were calculated. These directly relate to the oxidation of the oat cereal, and changed depending upon oxygen pressure, temperature, surface-to-volume ratio and extent of reaction. AOR is an index of O_2 consumed during a specific time interval. The time intervals were divided into 0 to 20 days, 20 to 50 days, and 50 to 90 days. In the fastest O_2 consumption condition (exposure to light,

Figure 14. Headspace O_2 concentration as a function of time for oat cereal packaged with O_2 absorber and stored at 41°C, 40% RH, 21% initial headspace O_2.


PE
PVDC coated PP/PE
O2 CONCENTRATION (%)
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
DAYS

41°C, 40% RH, PVDC coated PP/PE), the initial headspace O_2 (20.9%) was fully consumed within 23 days (Figure 15). Once the headspace O_2 was consumed, the consumption rate was limited by the permeability of the package material. The change in headspace O_2 concentration was a result of O_2 consumption by the cereal and permeated O_2 from the outside. The actual results were agreeable. The oxygen concentration of PE pouched sample with OA was 17.8% (Table 4) after 3 days. This indicates that the influence of OA in this package on lipid oxidation was very little. As shown, PE pouched product with and without OA had very similar M-TBA indexes and sensory scores. The TBA index for the oat cereal without OA was dependent on the initial head space O_2 concentration, permeability of the film, and storage conditions. After 1 month, the PE pouched sample, which had an initial head space O_2 concentration of 20.9%, had the largest increase in M-TBA index, followed by the PVDC coated PP/PE package (20.9% O_2 No - OA), the third was the 5% initial headspace O_2 PVDC coated PP/PE pouch. The sample with the smallest M-TBA index was the 1% initial headspace O_2. The M-TBA index of the PVDC coated PP/PE package packed with OA, an initial O_2 concentration of 20.9%, was lower than that of the same package having an initial O_2 concentration of 1% with no OA. This was significant at the 99% level (Table 8). After 2 months, the M-TBA index for

Figure 15. Headspace O_2 concentration as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 41°C.

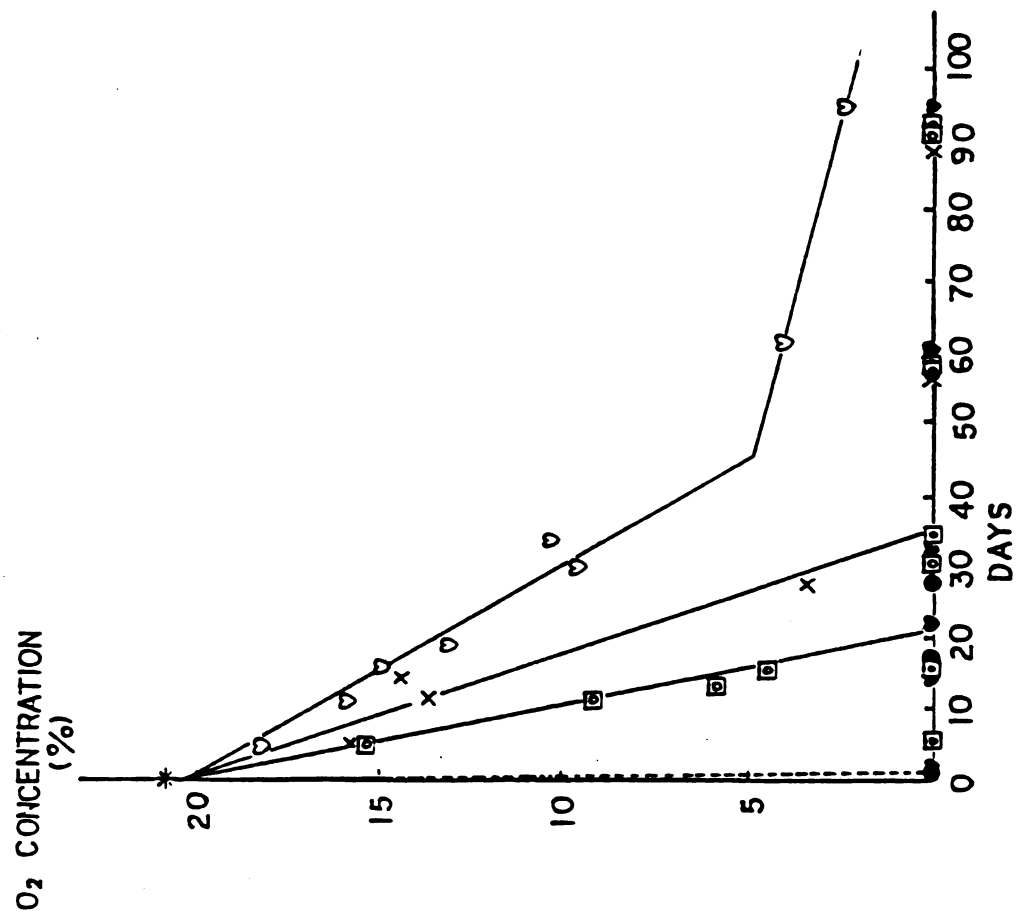

O2 CONCENTRATION (%)
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
DAYS
40ZAMI, no O2absorber
80ZAMI, no O2absorber
40ZAMI, exposure to light, no O2absorber
40ZAMI, with O2absorber
80ZAMI, with O2absorber
40ZAMI, exposure to light with O2absorber

Table 8

ANOVA for the Date of sampling x Packaged condition (41°C, 40%RH PVDC coated PP / PE, 21% initial O_2 concentration, with O_2 absorber vs 41°C, 40%RH, PVDC coated PP / PE,1% initial O_2 concentration no O_2 absorber)

ANOVA table for a 4 x 2 factorial experiment with 4 replicates

source	sum of squares	d.f.	mean square	F ratio	testing hypotheses
date (Factor A)	110.7	3	36.9	3.6	significant (95%)
packaged condition (Factor B)	154.4	1	154.4	15.0	significant (99%)
Inter-action A x B	63.3	3	21.1	2.1	
Residual	246.9	24	10.3		
Total	575.4	31			

Data of M-TBA index used for the ANOVA (41°C, 40%RH PVDC coated PP / PE, 21% initial O_2 concentration , with O_2 absorber vs 41°C, 40%RH, PVDC coated PP / PE,1% initial O_2 concentration no O_2 absorber)

Factor A		storage term (day)			
Factor B		15	28	59	90
21% initial O_2 conc. with absorber	1	14.1	12.1	13.7	14.6
	2	14.1	10.7	12.3	12.3
	3	10.6	9.6	15.1	10.5
	4	9.8	8.3	9.4	8.3
1% initial O_2 conc. no absorber	1	14.6	14.9	13.6	17.8
	2	11.2	11.1	18.1	20.0
	3	15.8	11.9	27.5	14.2
	4	10.4	12.7	17.8	24.2

high barrier packaged oat cereal (20.9%, 5% and 1% initial oxygen head space) was almost the same (20 O.D. x 100/gm) irrespective of initial O_2 concentration. This M-TBA index is twice as large as that of sample containing OA (10 O.D. x 100/gm) and four times as large as the original sample (5.0 O.D. x 100/gm) (Figure 4). The difference in the M-TBA index between 5% and 1% initial O_2 concentration was not significant (Table 9). The difference between 21% and 5% initial O_2 concentration was significant at the 95% level (Table 10) while the difference between 21% initial O_2 concentration with and without OA was significant at the 99% level (Table 12).

Change of headspace O_2 = O_2 permeated - O_2 consumed
= Total headspace (185 ml) * (final O_2 concentration - initial O_2 concentration) (1)

$$O_2 \text{ permeated} = \bar{P}\text{pouch} * \int_0^t P(t) * dt \quad (2)$$

Amount of O_2 consumed and AOR (t_x - t_y days) are shown by the formula (3) and (4).

$$O_2 \text{ consumed} = \bar{P}\text{pouch} * \int_0^t P(t) * dt - 185 * (O_2 \text{ conc. } (t) - O_2 \text{ conc. } (0)) \quad (3)$$

$$\text{AOR } (t_x - t_y \text{ days}) = \frac{(O_2 \text{ consumed})}{(t_y - t_x)} \Bigg|_{t_x}^{t_y} \quad (4)$$

Table 9

ANOVA for the Date of sampling x Packaged condition (41°C, 40%RH PVDC coated PP / PE, 5% initial O_2 concentration , no O_2 absorber vs 41°C, 40%RH, PVDC coated PP / PE,1% initial O_2 concentration, no O_2 absorber)

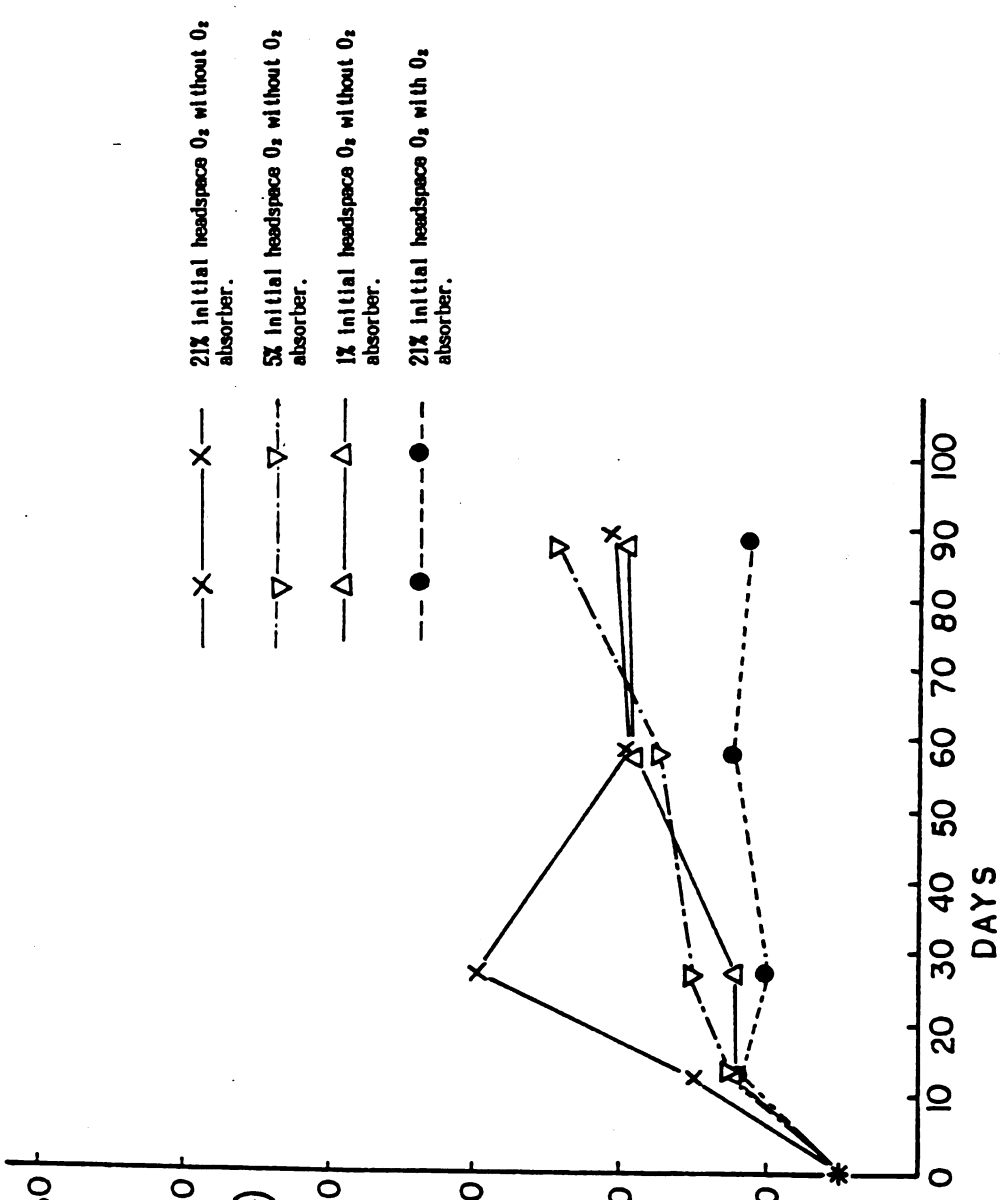
source	sum of squares	d.f.	mean square	F ratio	testing hypotheses
date (Factor A)	371.1	3	123.7	10.0	significant (99%)
packaged condition (Factor B)	23.5	1	23.5	1.9	
Inter-action A x B	58.3	3	19.4	1.6	
Residual	297.9	24	12.4		
Total	750.8	31			

Table 10

ANOVA for the Date of sampling x Packaged condition (41°C, 40%RH PVDC coated PP / PE, 21% initial O_2 concentration, no O_2 absorber vs 41°C, 40%RH, PVDC coated PP / PE,5% initial O_2 concentration, no O_2 absorber)

source	sum of squares	d.f.	mean square	F ratio	testing hypotheses
date (Factor A)	412.3	3	137.4	8.9	significant (99%)
packaged condition (Factor B)	111.4	1	111.4	7.2	significant (95%)
Inter-action A x B	363.5	3	121.1	7.8	significant (99%)
Residual	372.4	24	15.5		
Total	1259.6	31			

Figure 4. M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 41°C, 40% RH.


M-TBA INDEX
(OD x 100 / gm)
60
50
40
30
20
10
0
10 20 30 40 50 60 70 80 90 100
DAYS
21% initial headspace O2 without O2 absorber.
5% initial headspace O2 without O2 absorber.
1% initial headspace O2 without O2 absorber.
21% initial headspace O2 with O2 absorber.

$\bar{P}$pouch: permeability constant of the pouch (ml/pouch*day* atm)

P(t): Pressure difference between outisde and inside the package at 5 days (atm * ml/ml)

O_2 conc. (t): headspace O_2 concentration as a function of time (ml/ml) (final O_2 concentration)

O_2 conc. (0): initial headspace O_2 concentration (ml/ml)

(O_2 consumed) $^{ty}_{tx}$: amount O_2 consumed during certain time (from t_x to t_y days)

Here

$$P(t) = 0.209 - O_2 \text{ conc. } (t) \qquad (5)$$

0.209: Outside concentration of O_2 * 1 atm (atm * ml/ml)

O_2 conc. (t) can be assumed to be a combination of the serial straight lines. These lines are obtained as least square regression lines.

When

$$0 \leqq t \leqq t_1$$

$$O_2 \text{ conc. } (t) = a_1 t + O_2 \text{ conc. } (0) \qquad (6)$$

$$t_1 \leqq t \leqq t_2$$

$$O_2 \text{ conc. } (t) = a_2 (t - t_1) + O_2 \text{ conc. } (t_1) \qquad (7)$$

$$t_{n-1} \leqq t \leqq t_n$$

$$O_2 \text{ conc. } (t) = a_n (t - t_{n-1}) + O_2 \text{ conc. } (t_{n-1}) \quad (8)$$

Here t_1 is a day when first straight line connects to second line. As the same way t_n is a day when n - 1th line connects to n th line.

While

$$O_2 \text{ consumed} = \overline{P}\text{pouch} * \int_0^t P\ (t) * dt - 185 * (O_2 \text{ conc. } (t) - O_2 \text{ conc. } (0))$$

$$P\ (t) = 0.209 - O_2 \text{ conc. } (t) \quad \text{see (3)}$$

Calculate the amount of O_2 consumed in serial orders.

When

$$0 \leqq t \leqq t_1$$

$$\overline{P}\text{pouch} * \int_0^t P\ (t) * dt = \overline{P}\text{pouch} * \int_0^t (0.209 - O_2 \text{ conc. } (t)) * dt$$

$$= \overline{P}\text{pouch} * \int_0^t (0.209 - a_1 t - O_2 \text{ conc. } (0)) * dt$$

$$= \overline{P}\text{pouch} * \left(- \frac{a_1}{2} t^2 + (0.209 - O_2 \text{ conc. } (0)) * t \right) \quad (9)$$

$$185 * (O_2 \text{ conc. } (t) - O_2 \text{ conc. } (0)) = 185 *$$

$$(a_1 t + O_2 \text{ conc. } (0)) - O_2 \text{ conc. } (0)) = 185 * (a_1 t) \quad (10)$$

So

$$O_2 \text{ consumed} = \overline{P}\text{pouch} * \left(-\frac{a_1}{2} t^2 + (0.209 - O_2 \text{ conc. } (0)) * t\right) - 185 * (a_1 t) \quad (11)$$

When

$$t_1 \leq t \leq t_2$$

$$O_2 \text{ consumed} = (O_2 \text{ consumed})_{o}^{t_1} + (O_2 \text{ consumed})_{t_1}^{t} \qquad (12)$$

$$(O_2 \text{ consumed})_{t_1}^{t} = \bar{P}\text{pouch} * \int_{t_1}^{t} P(t) * dt - 185 * (O_2 \text{ conc. } (t) - O_2 \text{ conc. } (t_1)) \qquad (13)$$

$$\bar{P}\text{pouch} * \int_{t_1}^{t} P(t) * dt$$

$$= \bar{P}\text{pouch} * \int_{t_1}^{t} (0.209 - a_2 t + a_2 t_1 - O_2 \text{ conc. } (t_1)) * dt$$

$$= \bar{P}\text{pouch} * \left(-\frac{a_2}{2} t^2 + (0.209 + a_2 t_1 - O_2 \text{ conc. } (t_1)) * t\right)_{t_1}^{t} \qquad (14)$$

$$185 * (O_2 \text{ conc. } (t) - O_2 \text{ conc. } (t_1))$$

$$= 185 * (a_2 (t - t_1) + O_2 \text{ conc. } (t_1) - O_2 \text{ conc. } (t_1))$$

$$= 185 * (a_2 (t - t_1)) \qquad (15)$$

$(O_2 \text{ consumed})_{o}^{t_1}$ is calculated from the formula (11).

From (13), (14) and (15)

$$(O_2 \text{ consumed})_{t_1}^{t} = \bar{P}\text{pouch} * \left(-\frac{a_2}{2} t^2 + (0.209 + a_2 t_1 - O_2 \text{ conc. } (t_1)) * t\right)_{t_1}^{t} - 185 * (a_2(t-t_1)) \quad (16)$$

$$\left(-\frac{a_2}{2} t^2 + (0.209 + a_2 t_1 - O_2 \text{ conc. } (t_1)) * t\right)_{t_1}^{t}$$

$$= -\frac{a_2}{2} * (t^2 - t_1) + (0.209 + a_2 t_1 - O_2 \text{ conc. } (t_1)) * (t - t_1)$$

$$= -\frac{a_2}{2} * (t^2 - t_1) + a_2 t_1 * (t-t_1) + (0.209 - O_2 \text{ conc. } (t_1)) * (t-t_1)$$

$$= -\frac{a_2}{2} * (t-t_1)^2 + (0.209 - O_2 \text{ conc. } (t_1)) * (t-t_1) \quad (17)$$

So O_2 consumed

$$= \bar{P}\text{pouch} * \left(-\frac{a_2}{2} * (t-t_1)^2 + (0.209 - O_2 \text{ conc. } (t_1)) * (t-t_1)\right) - 185 * (a_2 (t-t_1)) + (O_2 \text{ consumed})_{0}^{t_1}$$

See (12), (16), and (17)

By the same way

$$t_n - 1 \leq t \leq t_n$$

$$O_2 \text{ consumed}$$

$$= \overline{P}\text{pouch} * \left(-\frac{a_n}{2} * (t - t_n\text{-}1)^2 + (0.209 - O_2 \text{ conc.}\right.$$

$$\left.(t_{n-1})) * (t-t_{n-1})) - 185 * (a_n(t-t_{n-1})) + (O_2\right.$$

$$\left.\text{consumed})\right)_0^{tn-1} \qquad (18)$$

The calculated results for O_2 consumed and AOR are shown in Figure 19-25, and Table 6. In Figure 19, the relation between the amount of O_2 consumed and M-TBA index as a function of time for oat cereal packed in PE and stored at 41°C, 40% RH, 21% initial headspace O_2 is shown. Headspace O_2 was consumed rapidly from 20 to 45 days. O_2 was still absorbed after 45 days, though the amount was relatively small. The M-TBA index generally behaved in the same manner. It increased for the first 30 days, and then leveled off, probably because malonaldehydes were being consumed by proteins.

The relation between the amount of O_2 consumed and the M-TBA index of pouched samples in PVDC coated PP/PE with different initial headspace O_2 levels and stored at 41°C, 40% RH are shown in Figures 20 and 21. Oat cereal packed in 21% initial headspace O_2 consumed more O_2 than samples containing 1% and 5% initial headspace O_2. The 1% and 5% samples consumed O_2 in a similar way. The sample packed in 1% initial headspace O_2 consumed 22 ml O_2 while the

Figure 19. O_2 consumed and M-TBA index as a function of time for oat cereal packaged in PE and stored at 41°C, 40% RH, 21% initial headspace O_2.

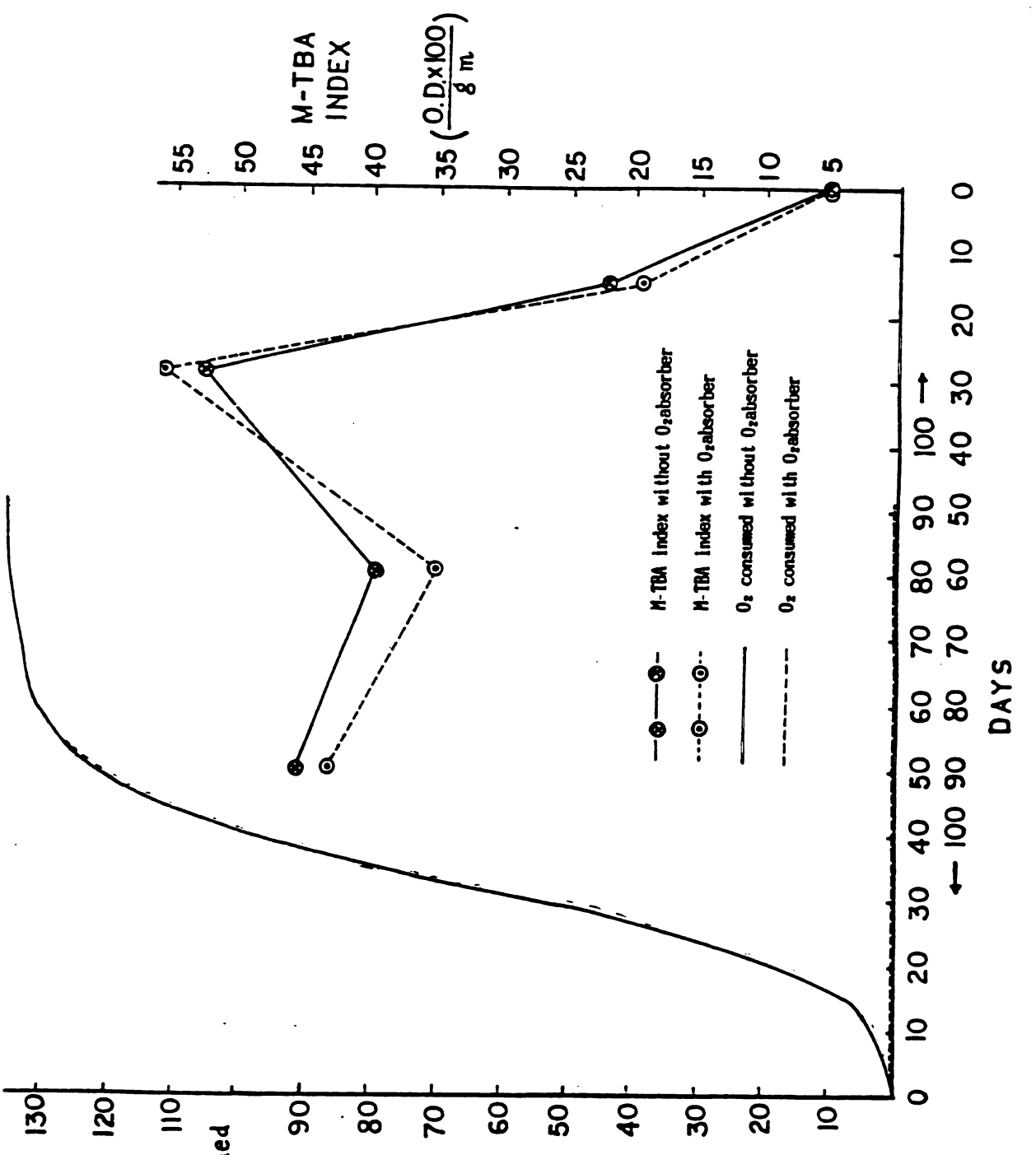

M-TBA INDEX
(O.D.x100 / g m)
O₂ Consumed (ml)
DAYS
M-TBA Index without O₂absorber
M-TBA Index with O₂absorber
O₂ consumed without O₂absorber
O₂ consumed with O₂absorber

Figure 20. O_2 consumed and M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 41°C, 40% RH, 21% initial headspace O_2.

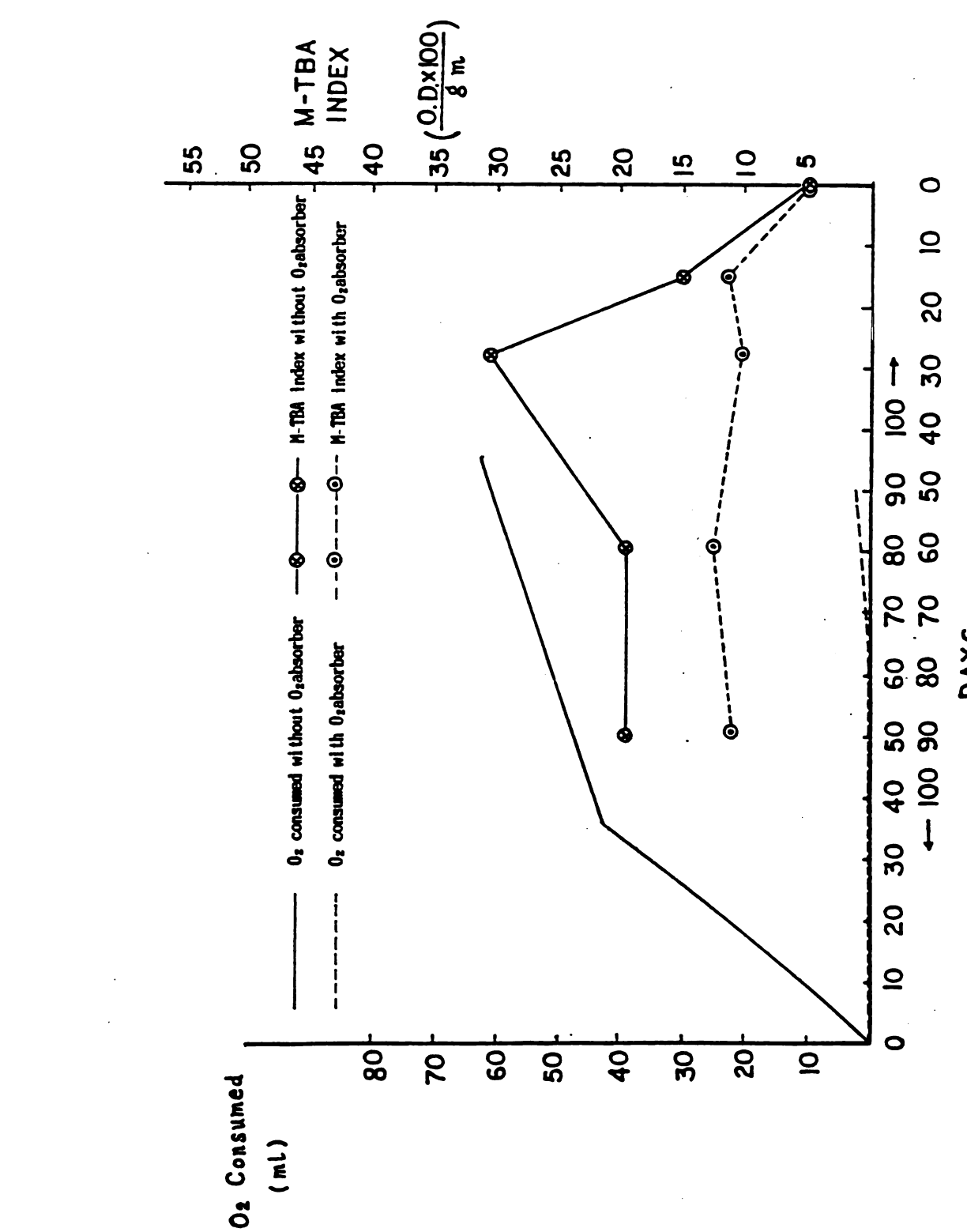

O₂ Consumed (ml)
M-TBA INDEX
$\left(\frac{O.D \times 100}{g\ m}\right)$
O₂ consumed without O₂absorber
O₂ consumed with O₂absorber
M-TBA index without O₂absorber
M-TBA index with O₂absorber
DAYS

Figure 21. O_2 consumed and M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 41°C, 40% RH.

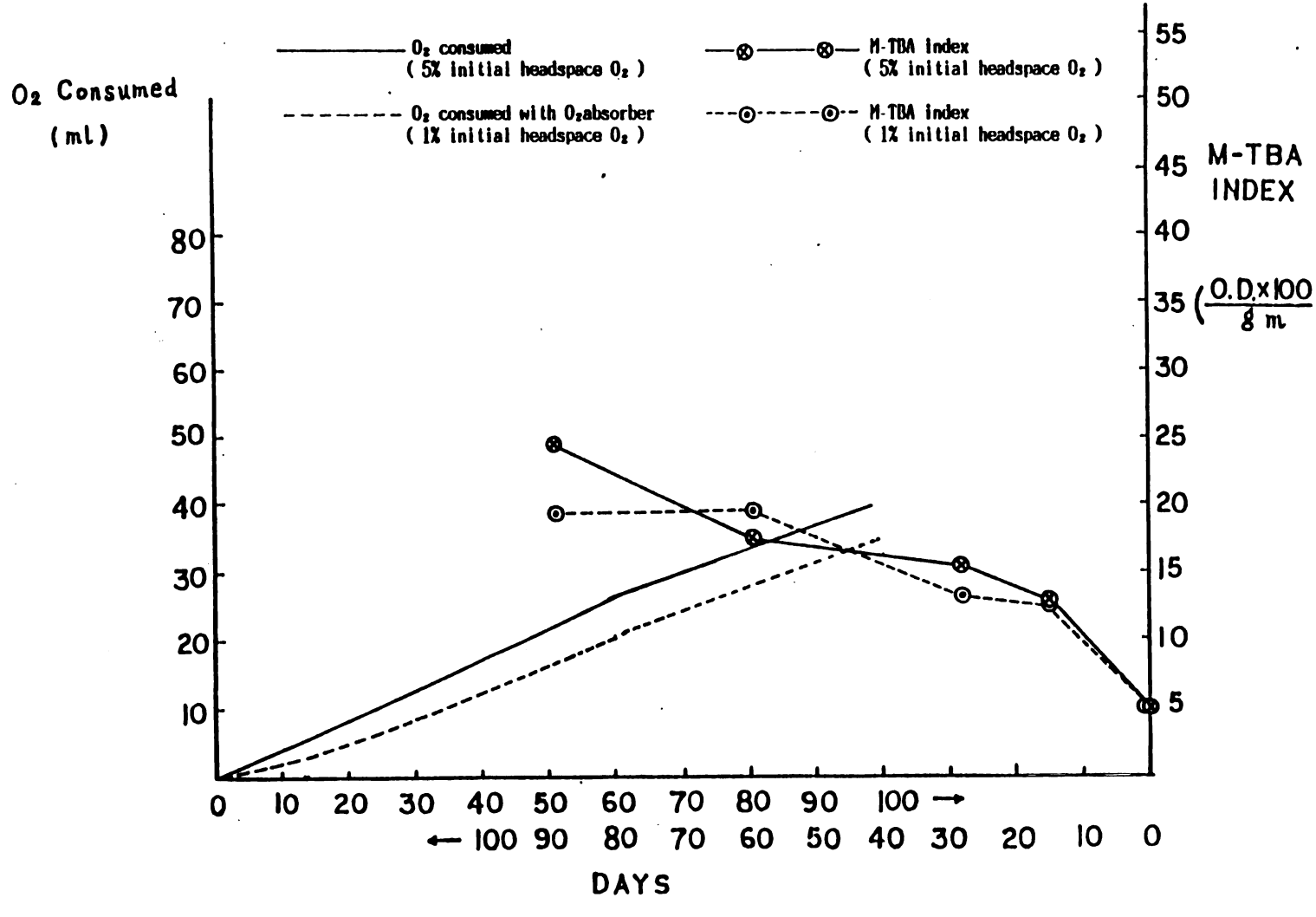

O₂ Consumed
(ml)
O₂ consumed
(5% initial headspace O₂)
O₂ consumed with O₂absorber
(1% initial headspace O₂)
M-TBA index
(5% initial headspace O₂)
M-TBA index
(1% initial headspace O₂)
M-TBA INDEX
(O.D.×100 / g m)
80
70
60
50
40
30
20
10
55
50
45
40
35
30
25
20
15
10
5
0 10 20 30 40 50 60 70 80 90 100 →
← 100 90 80 70 60 50 40 30 20 10 0
DAYS

Figure 22. O_2 consumed and M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 41°C, 80% RH, 21% initial headspace O_2.

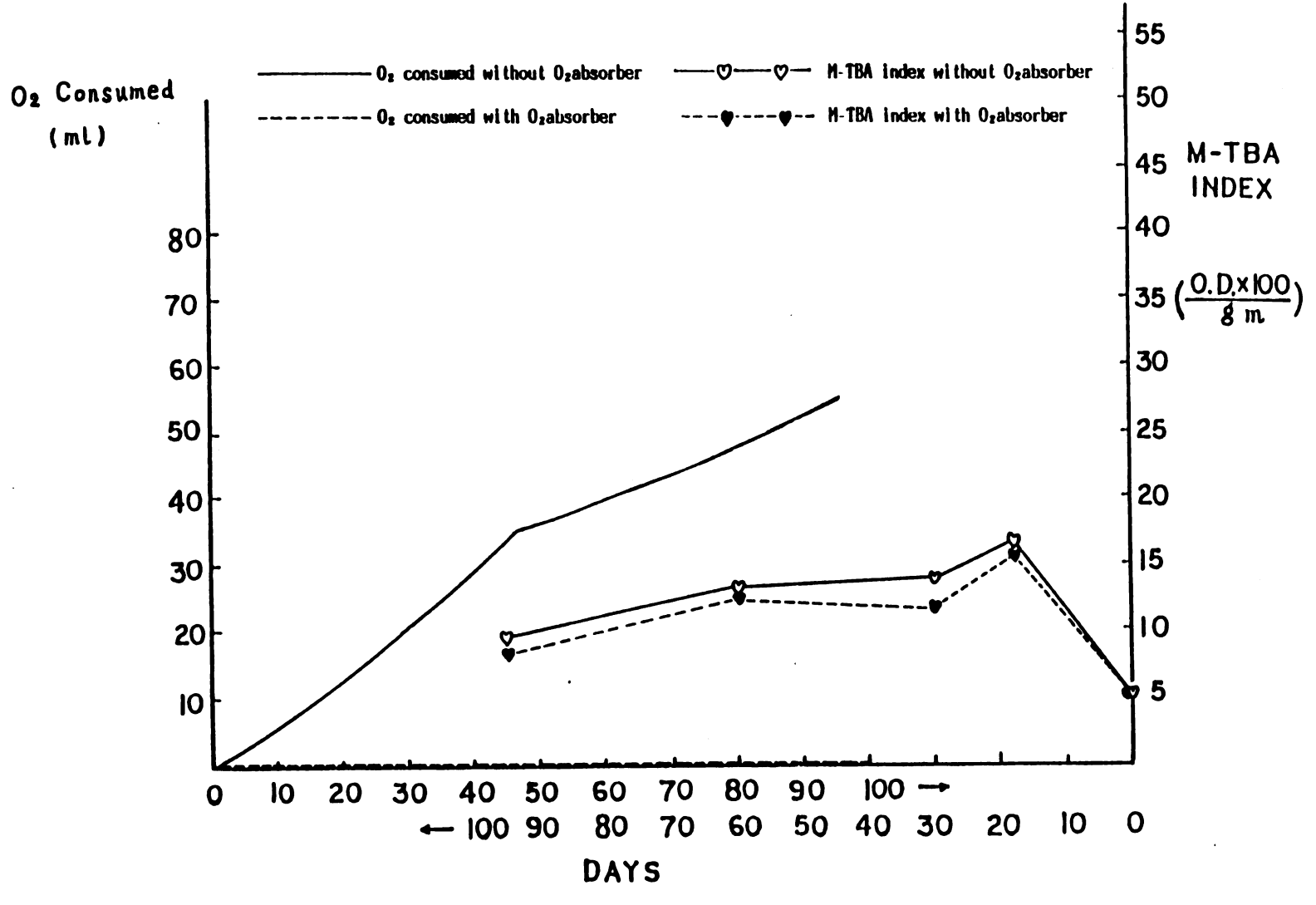

O₂ Consumed
(ml)
O₂ consumed without O₂absorber
O₂ consumed with O₂absorber
M-TBA index without O₂absorber
M-TBA index with O₂absorber
M-TBA INDEX
(O.D.x100 / g m)
80
70
60
50
40
30
20
10
55
50
45
40
35
30
25
20
15
10
5
0 10 20 30 40 50 60 70 80 90 100 →
← 100 90 80 70 60 50 40 30 20 10 0
DAYS

Figure 23. O_2 consumed and M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 21°C, 45% RH, 21% initial headspace O_2.

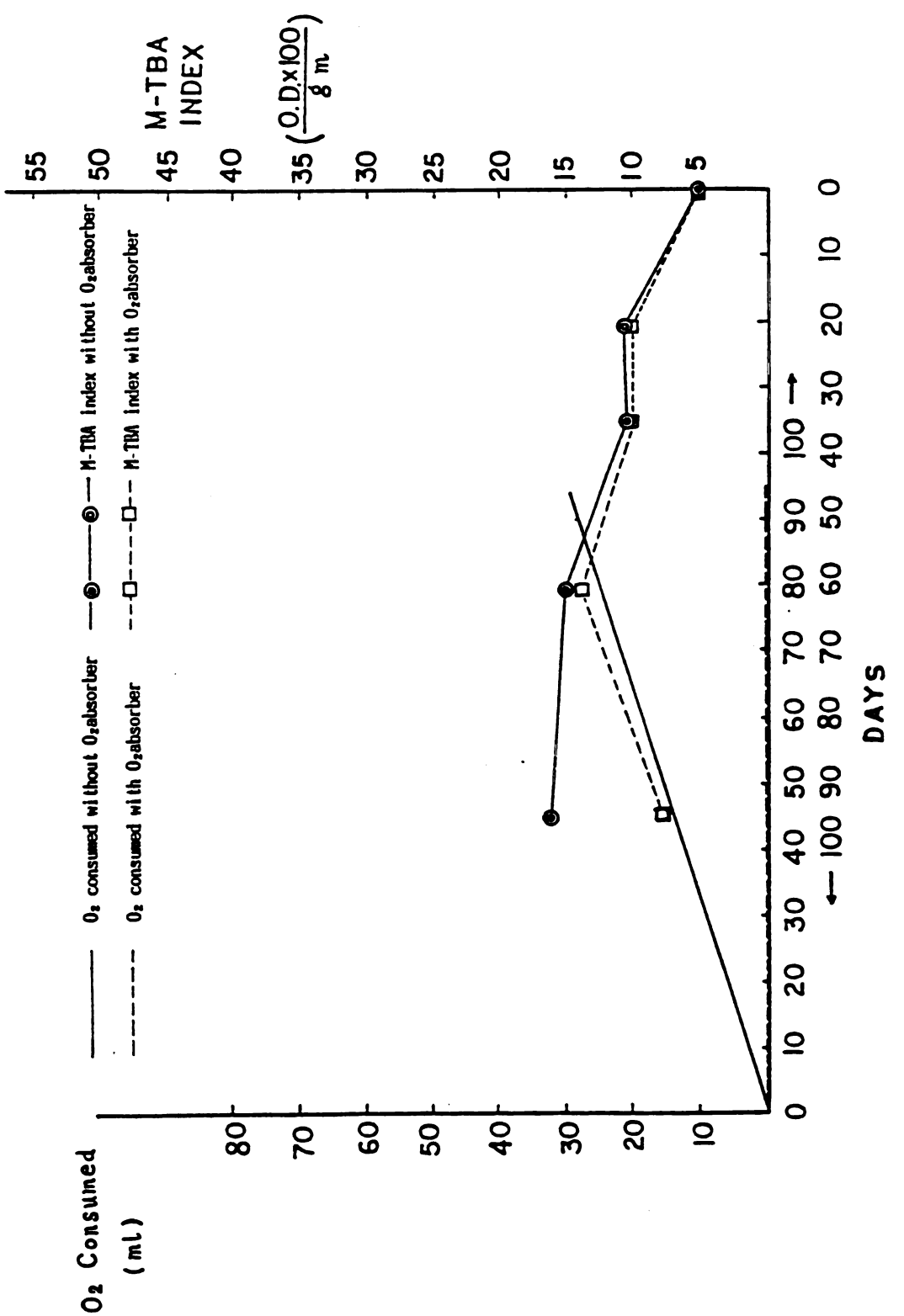

O2 Consumed (ml)
M-TBA INDEX
35 (O.D.x100 / g m)
O2 consumed without O2absorber
O2 consumed with O2absorber
M-TBA index without O2absorber
M-TBA index with O2absorber
DAYS

Figure 24. O_2 consumed and M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 65°C, 45% RH, 21% initial headspace O_2.

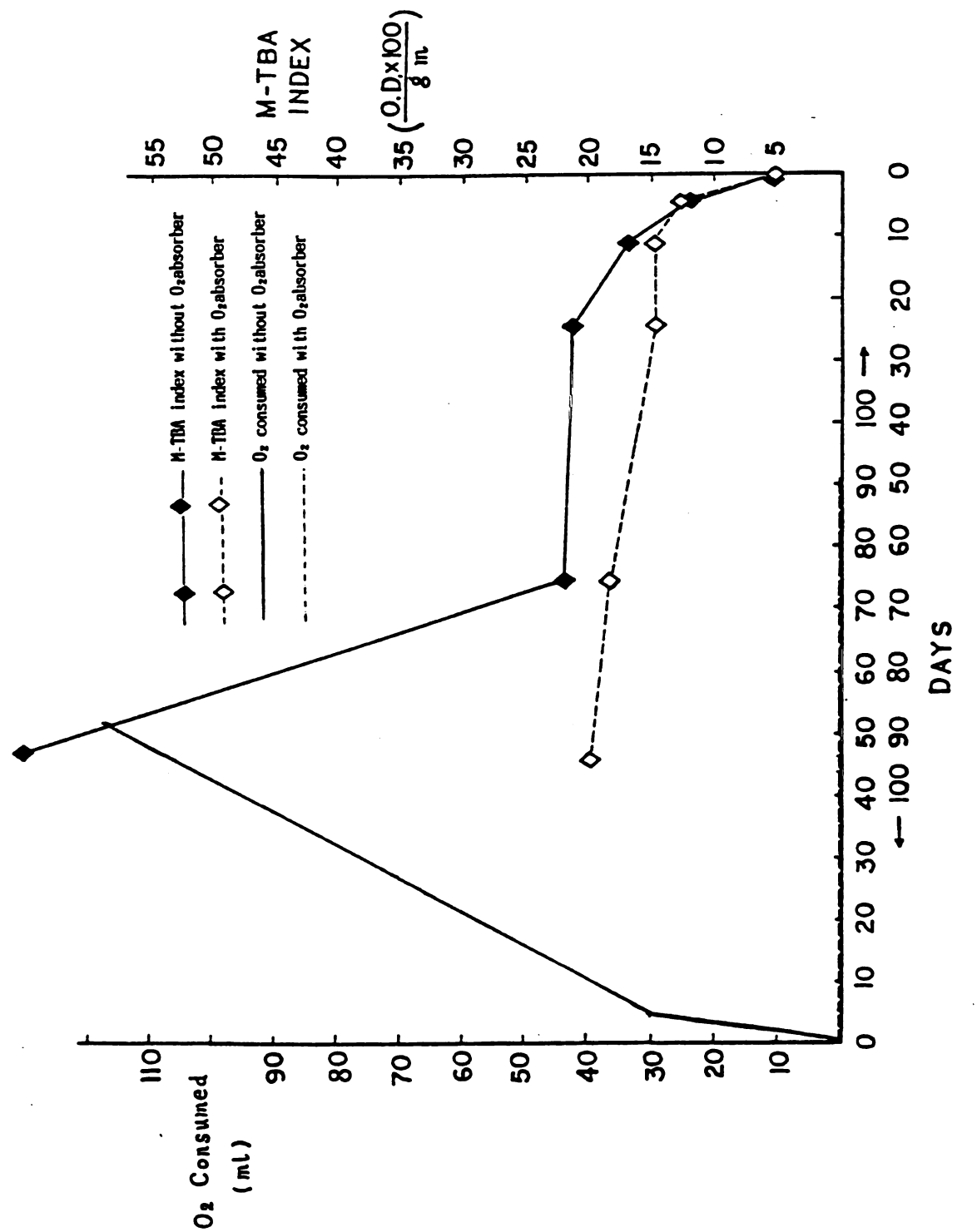

M-TBA Index without O₂absorber
M-TBA Index with O₂absorber
O₂ consumed without O₂absorber
O₂ consumed with O₂absorber
M-TBA INDEX
(O.D.x100 / g m)
O₂ Consumed (ml)
DAYS
110
90
80
70
60
50
40
30
20
10
55
50
45
40
35
30
25
20
15
10
5
0
100 90 80 70 60 50 40 30 20 10 0
0 10 20 30 40 50 60 70 80 90 100

Figure 25. O_2 consumed and M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE and stored under light at 41°C, 40% RH, 21% initial headspace O_2.

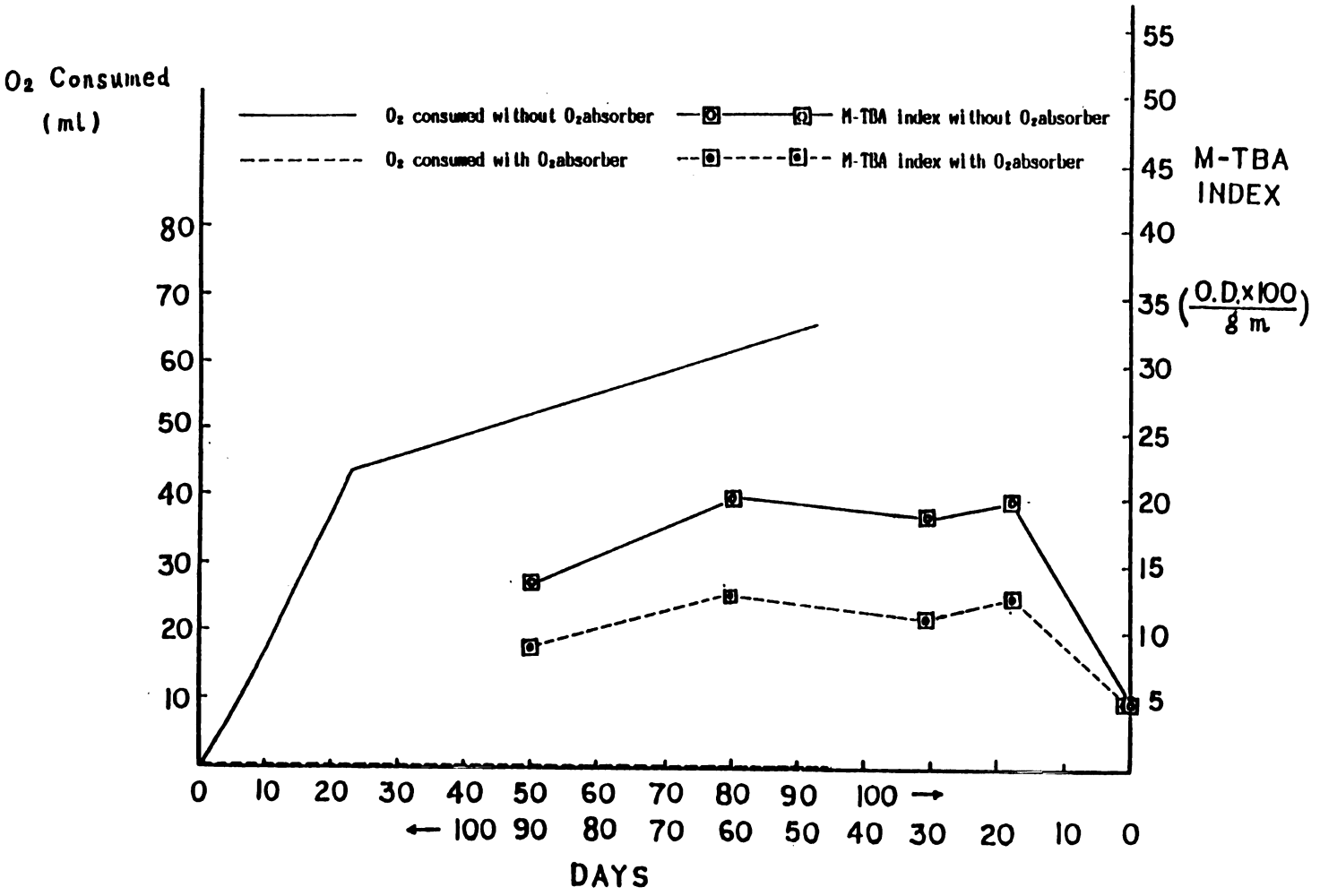

O₂ Consumed
(ml)
O₂ consumed without O₂absorber
M-TBA index without O₂absorber
O₂ consumed with O₂absorber
M-TBA index with O₂absorber
M-TBA INDEX
(O.D.x100 / g m)
80
70
60
50
40
30
20
10
55
50
45
40
35
30
25
20
15
10
5
0 10 20 30 40 50 60 70 80 90 100 →
← 100 90 80 70 60 50 40 30 20 10 0
DAYS

Table 6. Average O_2 consumption rate.

Temperature	RH	Material	Light	Initial O_2 conc.	AOR (t_1-t_2 days), ml/day		
					(0-20)	(20-50)	(50-90)
21°C	45%	PVDC coated PP/PE	No	21%	0.30	0.31	0.32
41°C	40%	PVDC coated PP/PE	No	21%	1.2	0.87	0.34
41°C	40%	PVDC coated PP/PE	No	5%	0.43	0.60	0.37
41°C	40%	PVDC coated PP/PE	No	1%	0.29	0.39	0.35
41°C	40%	PE	No	21%	0.82	3.5	0.34
41°C	40%	PVDC coated PP/PE	Yes	21%	1.9	0.45	0.34
41°C	80%	PVDC coated PP/PE	No	21%	0.66	0.73	0.38
65°C	45%	PVDC coated PP/PE	No	21%	2.9	2.9	1.9

sample packed in 5% absorbed 28 ml O_2 up to 60 days, when all headspace O_2 was consumed. After 60 days, both samples absorbed all O_2 permeating through the pouch. The difference of 6 ml did not cause any effect on the M-TBA index. The M-TBA index of both samples was very similar.

The OAR (0-20 days) for these samples (21% initial O_2 concentration packaged in PE with and without O_2 absorber, 21%, 5% and 1% initial O_2 concentration without O_2 absorber packaged in PVDC coated PP/PE) were respectively 0.82 ml/day, 1.2 ml/day, 0.43 ml/day and 0.30 ml/day. The PE pouched samples had a smaller AOR (0-20 days) than the PVDC coated PP/PE pouched samples (both 21% initial headspace O_2 concentration), however during the next period (20-50 days) PE samples had an AOR of 3.6 ml/day and PVDC coated PP/PE samples had an AOR of 0.87 ml/day. The comparison of M-TBA indexes for PE and PVDC coated PP/PE products containing absorbers is shown in Fig. 5. The statistical significance of these comparisons is shown in Table 11. The level of headspace O_2 was a very significant factor in lipid oxidation. The concentration of headspace O_2 in PE pouches was almost the same as the external environment, while PVDC coated PP/PE controlled the amount of O_2 in the headspace because of its barrier properties. With this package, zero O_2 concentration should continue for up to 358 days by calculation; however the actual O_2 concentration was 1.5% at 90 days. The oxygen absorber consisted of iron (Fe) and several catalysts, and was precisely prepared in order to absorb O_2 under a broad range of circumstances. The fundamental reaction involves the oxidation of iron. The

Figure 5. M-TBA index as a function of time for oat cereal packaged under 21% initial headspace O_2 with O_2 absorber and stored at 41°C, 40% RH.

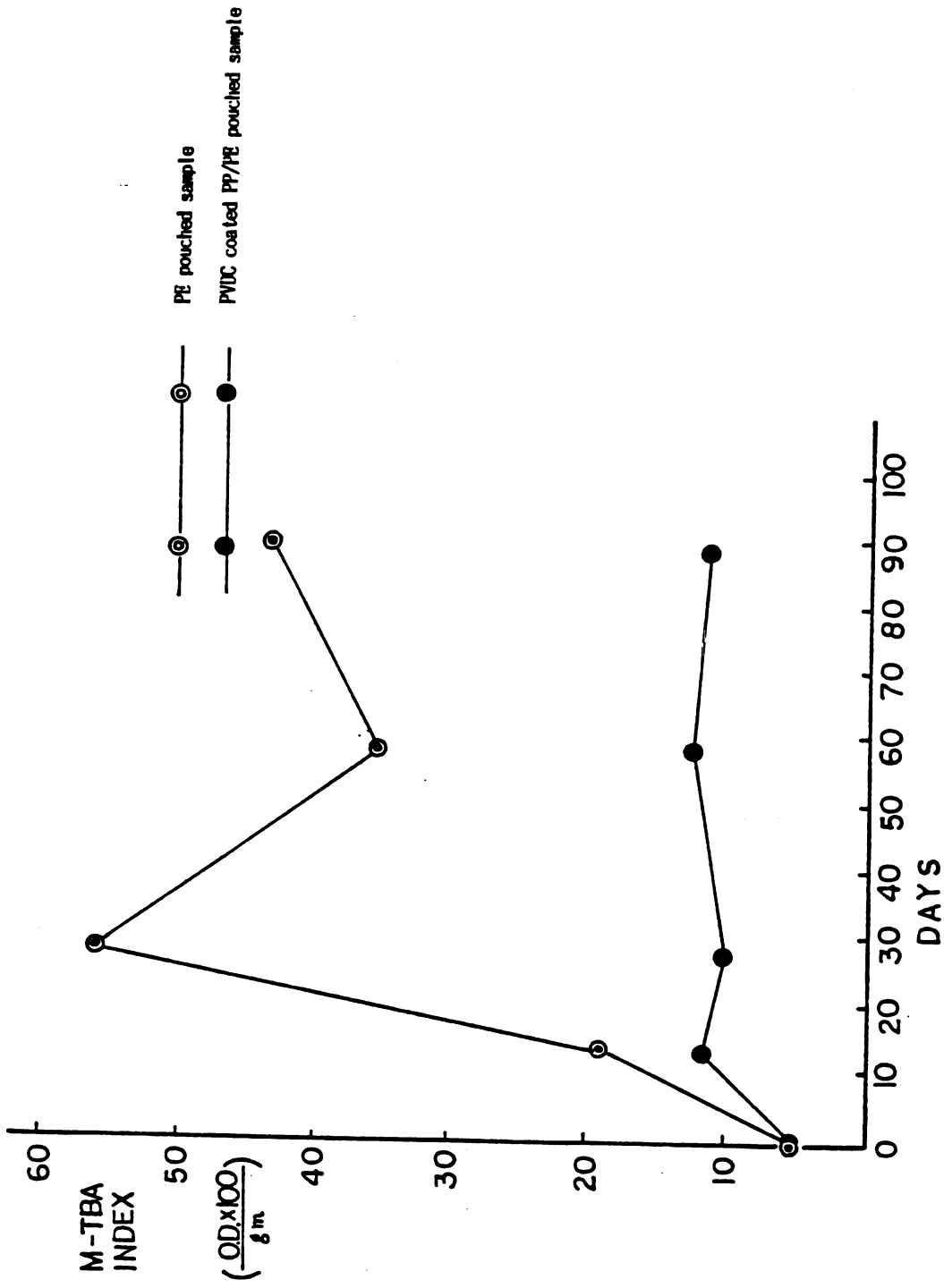

PE pouched sample
PVDC coated PP/PE pouched sample
M-TBA INDEX
(O.D.x100/gm)
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
DAYS

Table 11

ANOVA for the Date of sampling x Packaged condition (41°C, 40%RH PVDC coated PP / PE, 21% initial O_2 concentration, with and without O_2 absorber)

source	sum of squares	d.f.	mean square	F ratio	testing hypotheses
date (Factor A)	185.8	3	61.9	4.4	significant (95%)
packaged condition (Factor B)	784.0	1	784.1	55.3	significant (99%)
Inter-action A x B	334.1	3	111.4	7.9	significant (99%)
Residual	340.4	24	14.2		
Total	1644.4	31			

absorbing ability will decrease in low temperature, because the activation energy is not sufficient. The absorbing capacity will increase in high temperature, until the temperature reaches a point where the reaction will be suppressed. Because this is a reversible exothermic reaction, it will move in the reductive direction in extreme high temperature. This suppression did not occur at 41°C, as this temperature difference (21°, 41°C) is not sufficient to affect the chemical equilibrium.

Low levels of H_2O in the product package system may possibly explain the low absorbing ability. H_2O should permeate from the outside into the pouch at 41°C, 40% RH. Probably this RH was not high enough to allow the absorber to fully absorb O_2 at this temperature.

Sensory evaluation suggested that when the M-TBA index reached 20 (O.D. x 100/gm) oxidative change had taken place. Some oxidative aromas were noticed for samples after 3 months, with an M-TBA index of 10 (O.D. x 100/gm).

Storage in high relative humidity (41°C, 80% RH) resulted in different M-TBA index and oxygen uptake as compared to storage at medium RH (41°C, 40% RH in PVDC coated PP/PE). Headspace O_2 decreased more slowly at high humidity than at medium humidity (Figure 15). It did not reach zero even at 90 days storage. Samples with O_2 absorber maintained zero headspace O_2. At 90 days, one of the pouches had a headspace O_2 level of 20.9%, probably due

to a seal failure. At high humidity samples packaged in the PVDC coated PP/PE pouch with and without OA showed slight increase in the M-TBA index during the storage period (Figure 6). The M-TBA index was almost the same as the OA contained sample at the same temperature (41°C) and medium RH (40% RH). There was no statistical difference between the results for these two samples (Table 14). Samples surrounded by high RH absorbed more O_2 than samples surrounded by medium humidity (40%) (1% and 5% initial headspace O_2, PVDC coated PP/PE) (see Figure 21, 22), however M-TBA levels were not higher. AOR (0-20) for this sample condition (21% initial headspace O_2, PVDC coated PP/PE, 80% RH, 41°C) was 0.66 ml/pouch.day. Water is known to retard lipid oxidation in many dehydrated and low-moisture food products. Hydrogen bonding of hydroperoxides with water could occur (A_w) in a methyl linoleate model system (Aw 0.5) (Maloney et al., 1966). Quast and Karel (1972) showed that the oxidation rate of potato chips was lowest in 40% RH. At high RH (75% RH at 37°C), the rate increased considerably, possibly due to increased mobility of the reactants. Product kept at 75% RH also showed strong nonenzymatic browning. At high humidity (41°C, 80% RH) the M-TBA index and the AOR (0-20 days) were less than at lower RH. Oxidation was observed after 2 months by sensory evaluation for samples packed without OA. The oxygen consumption rate might be higher than the

Figure 6. M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE under 21% initial headspace O_2 and stored at 41°C.

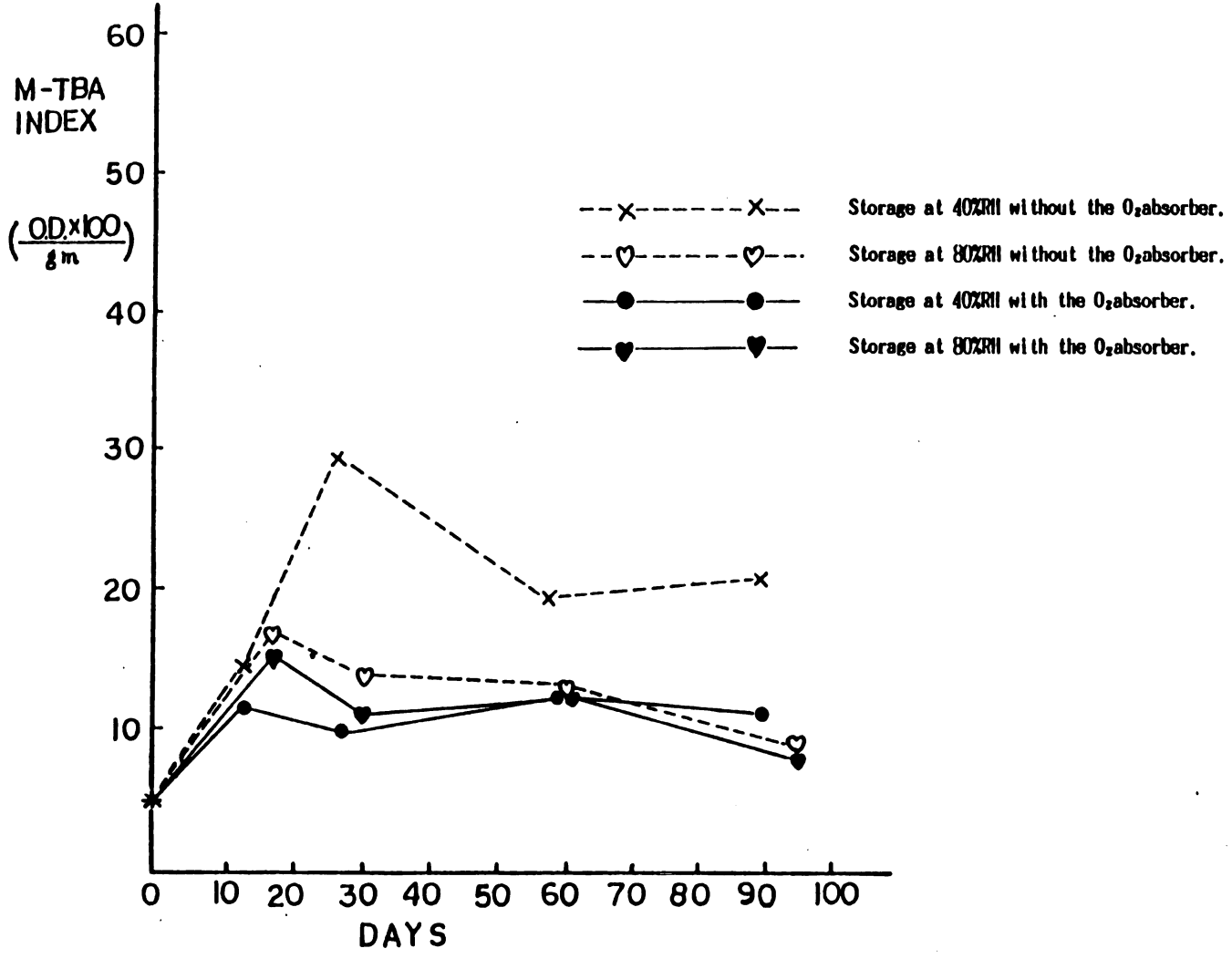

M-TBA INDEX
(O.D.x100 / gm)
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
DAYS
Storage at 40%RH without the O₂absorber.
Storage at 80%RH without the O₂absorber.
Storage at 40%RH with the O₂absorber.
Storage at 80%RH with the O₂absorber.

Table 14

ANOVA for the Date of sampling x Packaged condition (41°C, 80%RH, PVDC coated PP / PE, 21% initial O_2 concentration, with and without O_2 absorber)

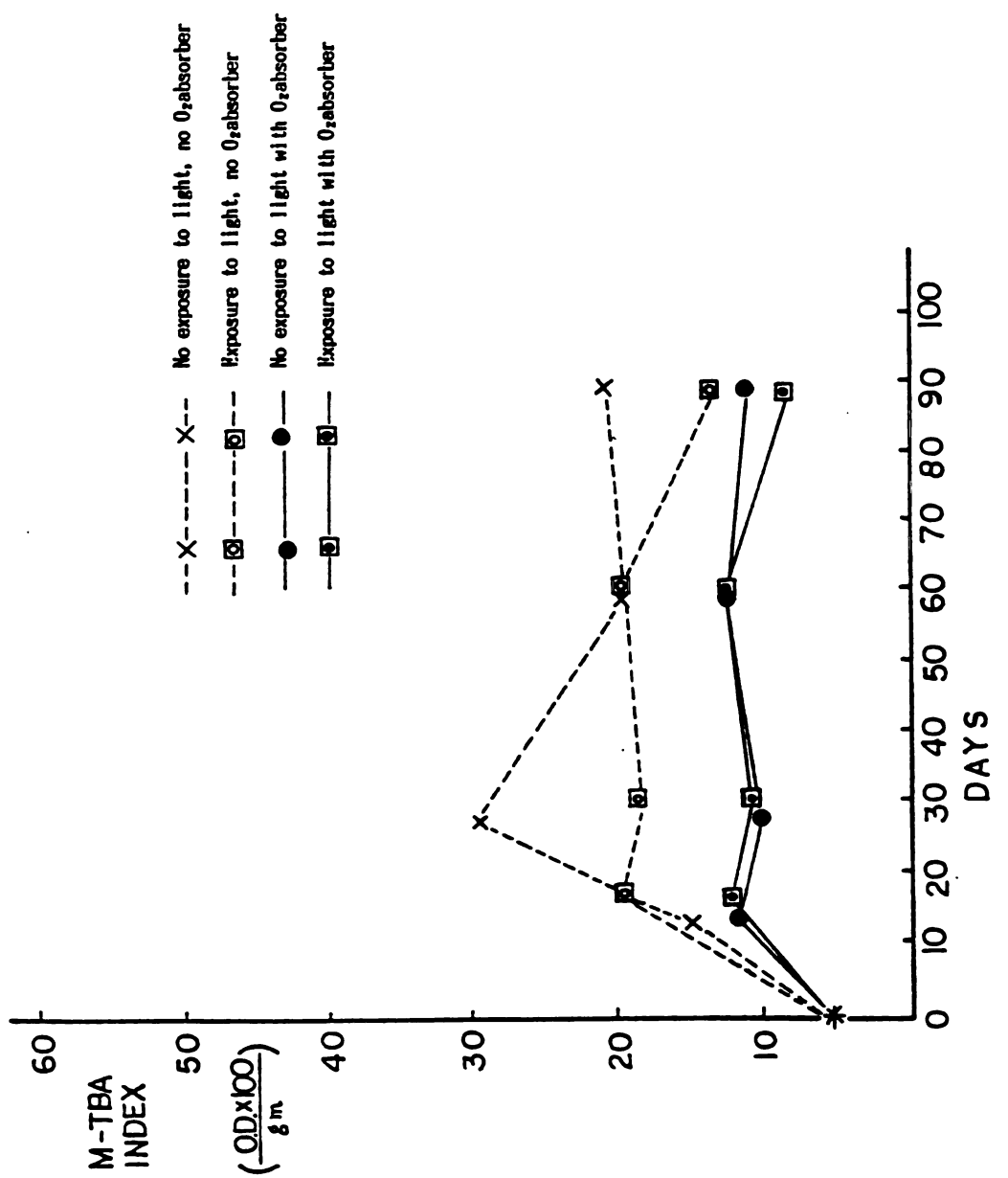
source	sum of squares	d.f.	mean square	F ratio	testing hypotheses
date (Factor A)	239.7	3	79.9	15.0	significant (99%)
packaged condition (Factor B)	18.0	1	18.0	3.4	
Inter-action A x B	4.0	3	1.3	0.3	
Residual	127.7	24	5.3		
Total	389.4	31			

calculated value (0.66 ml/pouch·day, 0-20 days) because the permeability of PVDC coated PP/PE film at high humidity could be larger than at medium humidity.

Exposure to light did not cause further increase in the M-TBA index compared to no light exposure (Figure 11), however it did affect the amount of O_2 consumed and the AOR when all headspace O_2 had been consumed by the cereal. The AOR (0-20 days) under light exposure was 1.9 ml/day·pouch, while the AOR (0-20 days) was 1.2 ml/day·pouch in the dark (Table 6). Figure 15 shows the influence of RH and light exposure on headspace O_2 content. Sensory evaluation of the samples indicated oxidized product even after 0.5 month.

Singh et al. (1974) showed that an increase in light exposure caused an increase in the rate of riboflavin degradation in whole milk and that oxygen uptake can be expressed as a function of light intensity. In this study, light intensity ranged from 40 to 90 foot candles (430 lux to 970 lux, Appendix 3). These intensities are approximately the same as display case lighting (500-1000 lux, Uematsu and Someya, 1978). Light exposure accelerated product deterioration even when packed with OA. This change was not detected by the M-TBA index, but by sensory evaluation after 2 months storage. Possibly competitive consumption of permeated O_2 by the OA or by the lipid in the oat cereal may have caused the difference. Under light exposure the

Figure 11. M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 41°C, 40% RH, 21% initial headspace O_2.


M-TBA INDEX
(O.D.X100/gm)
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
DAYS
No exposure to light, no O2absorber
Exposure to light, no O2absorber
No exposure to light with O2absorber
Exposure to light with O2absorber

difference between the M-TBA index with and without O_2 absorber was significant at 99% level (Table 13).

A temperature effect was also observed. At 21°C (21% initial O_2 concentration, 45% RH, PVDC coated PP/PE, no absorber) headspace O_2 decreased linearly throughout 100 days of storage. Headspace O_2 remained at zero with O_2 absorber (Figure 16). The amount of O_2 consumed (Figure 23) was relatively small compared to the sample stored at 41°C and 65°C (Figure 20-24). M-TBA index of the sample with and without O_2 absorber and stored at 21°C increased slightly. Headspace O_2 (21% initial O_2 concentration, 45% RH, PVDC coated PP/PE, no O_2 absorber storage 65°C) decreased quickly and thereafter remained about the same (2-6% O_2) followed by an increase to 12%. The O_2 concentration with absorber was maintained at zero for 90 days (Figure 17). The change in headspace O_2 for all 3 temperatures is shown in Figure 18. According to the permeability of PVDC coated PP/PE at 65°C (Table 6, Figure 26), the time span in which O_2 absorber could maintain zero O_2 concentration in this condition was:

$$\frac{160 - 38.7}{10.8 \times 0.209} = 54 \text{ (days)}$$

160: Absorbing ability of O_2 absorber at 21°C (ml)

38.7: Amount of headspace O_2 (ml)

10.8: Permeability constant of PVDC coated PP/PE at 65°C

0.209: Pressure difference (atm ml/ml)

Table 13

ANOVA for the Date of sampling x Packaged condition (41°C, 40%RH, PVDC coated PP / PE, 21% initial O_2 concentration, light exposure, with and without O_2 absorber)

source	sum of squares	d.f.	mean square	F ratio	testing hypotheses
date (Factor A)	143.1	3	47.7	16.6	significant (99%)
packaged condition (Factor B)	372.7	1	372.6	129.5	significant (99%)
Inter-action A x B	10.2	3	3.4	1.2	
Residual	69.1	24	2.9		
Total	595.0	31			

Figure 16. Headspace O_2 concentration as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 21°C, 45% RH.

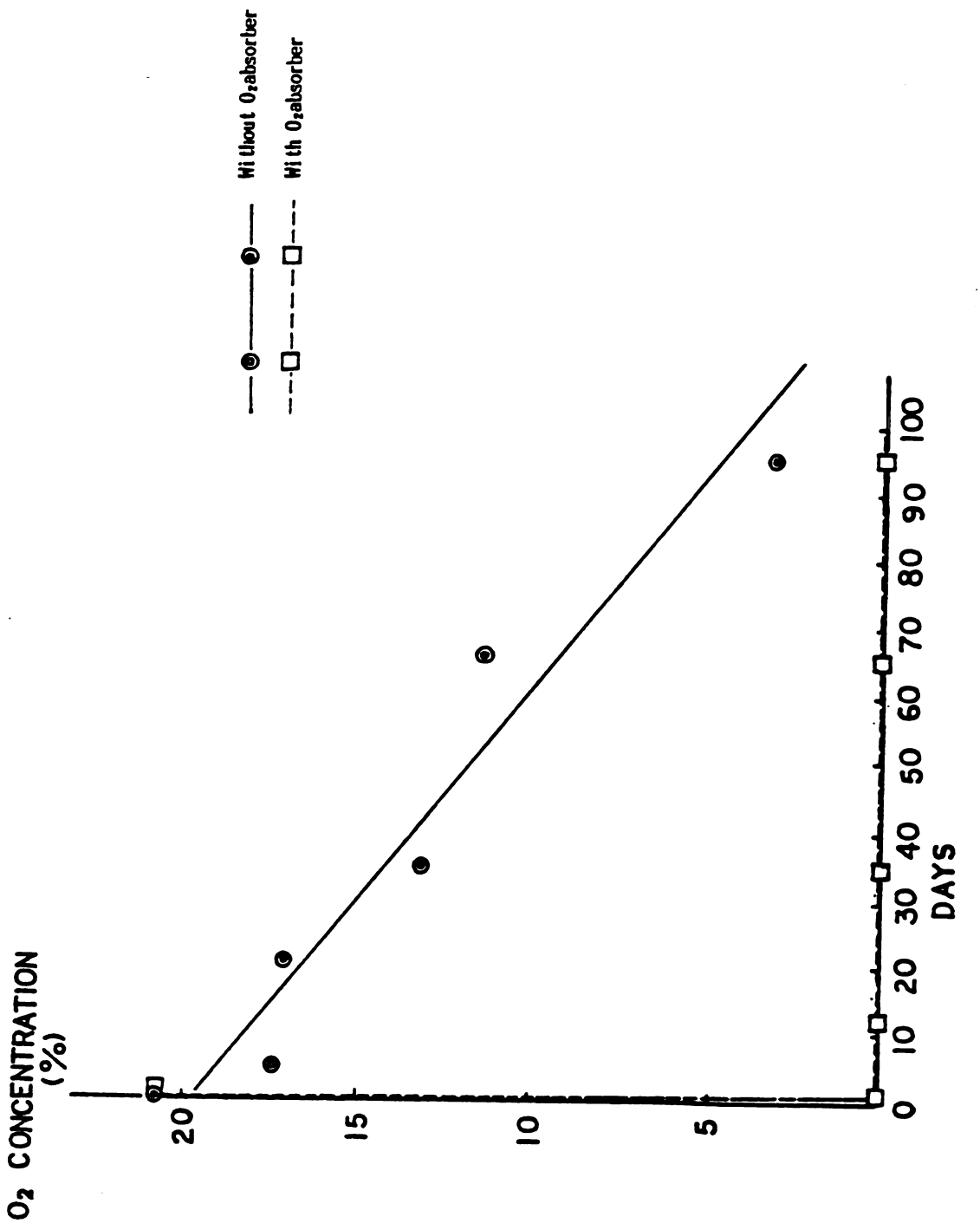

Without O2absorber
With O2absorber
O2 CONCENTRATION (%)
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
DAYS

Figure 17. Headspace O_2 concentration as a function of time for oat cereal packaged in PVDC coated PP/PE and stored at 65^{o}C, 45% RH.

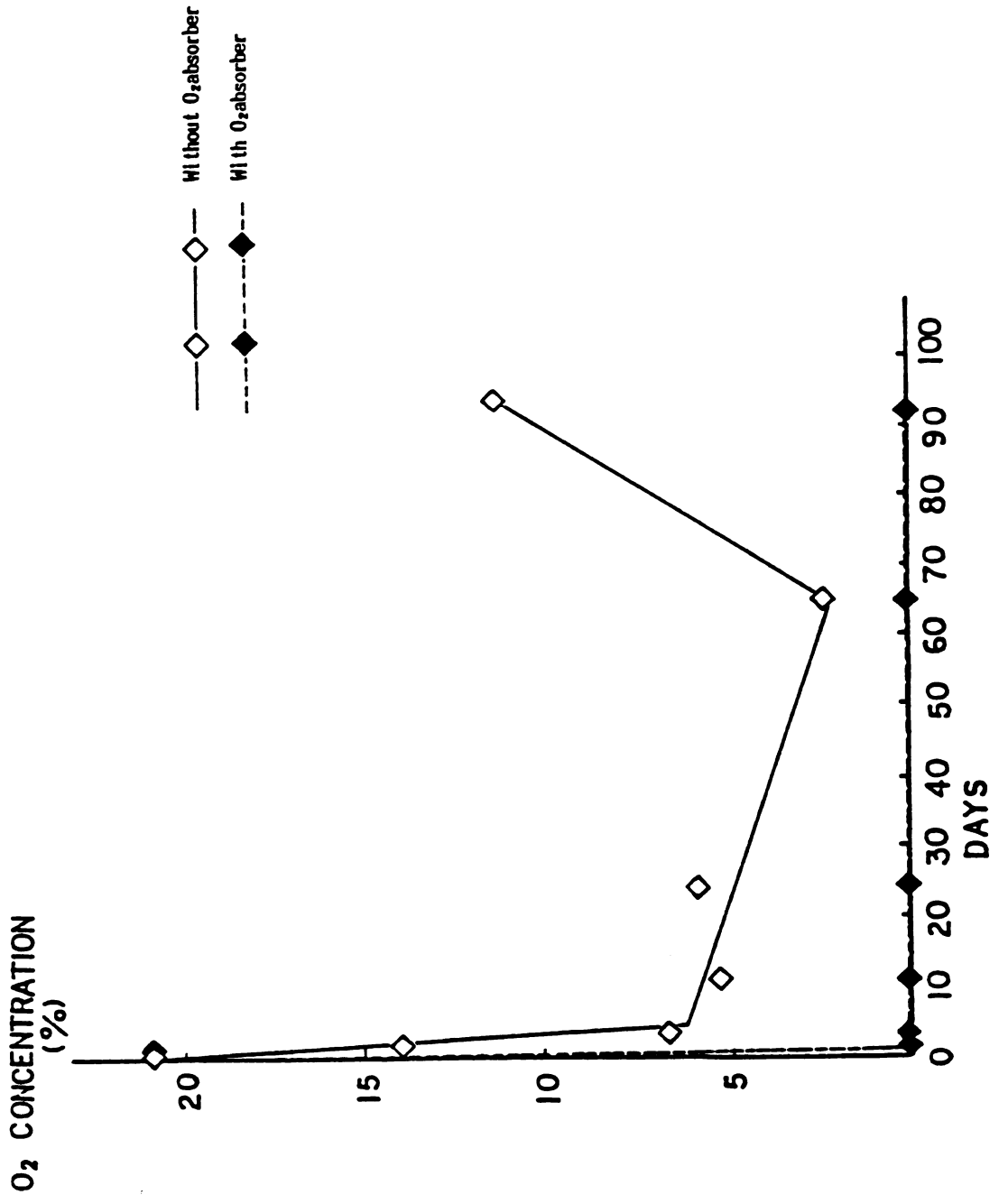
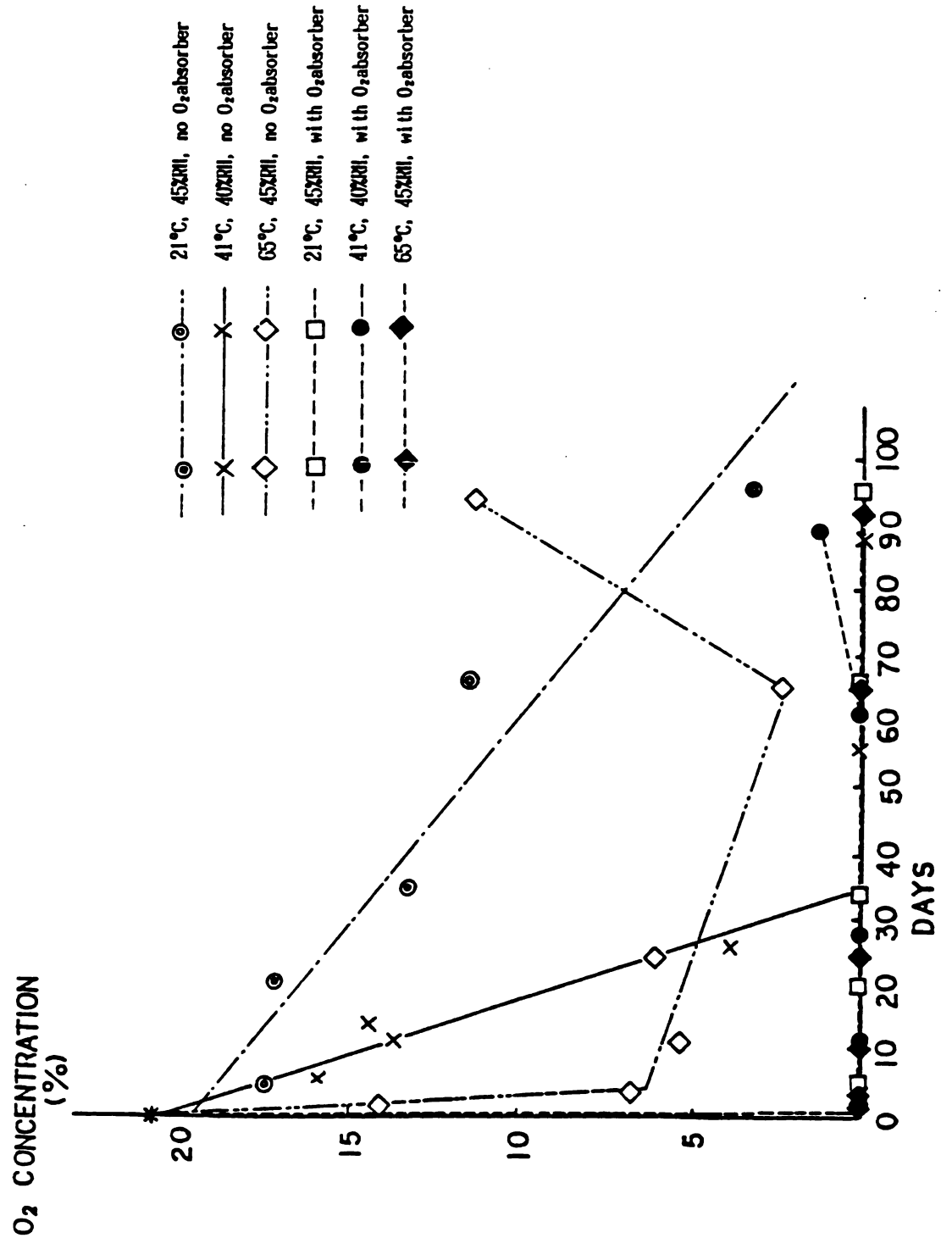

Without O2absorber
With O2absorber
O2 CONCENTRATION (%)
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
DAYS

Figure 18. Headspace O_2 concentration as a function of time for oat cereal packaged in PVDC coated PP/PE and stored either at 40 or 45% RH, 21% initial headspace O_2.


21°C, 45%RH, no O2absorber
41°C, 40%RH, no O2absorber
65°C, 45%RH, no O2absorber
21°C, 45%RH, with O2absorber
41°C, 40%RH, with O2absorber
65°C, 45%RH, with O2absorber
O2 CONCENTRATION (%)
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
DAYS

Even after 54 days, headspace O_2 remained zero. Oxidation should have occurred at this stage. The average O_2 consumption rate (0-20 days), was 0.29 ml/day at 21°C and 1.2 ml/day at 41°C and 1.9 ml/day at 65°C. The value at 65°C was derived from the permeability study of the PVDC coated PP/PE film, which utilized water saturated flow gas (N_2, O_2) at 21°C and an elevated temperature of 65°C. This corresponded to 10% RH at 65°C (Appendix 4). As RH of the storage condition (45% RH) was higher than this the actual consumption rate was probably higher than what was reported here.

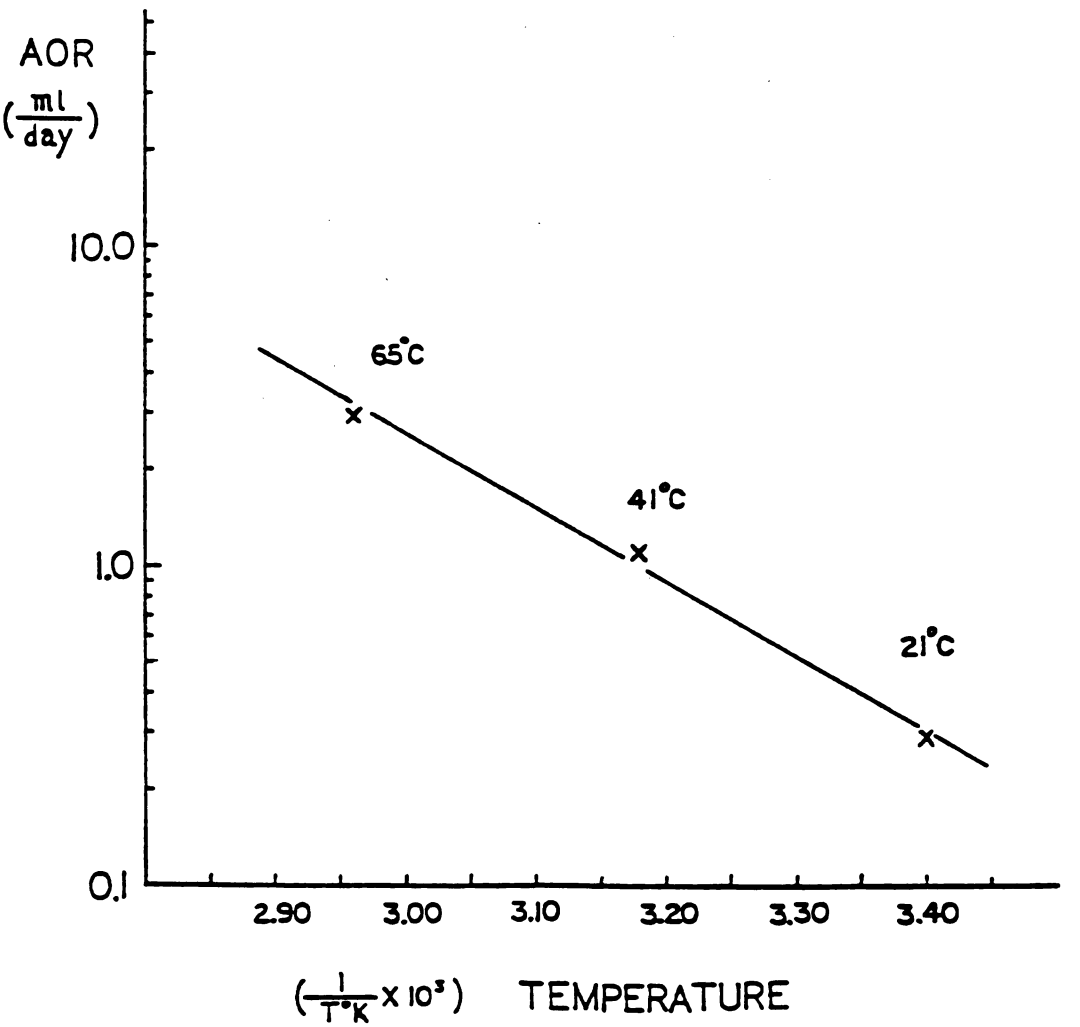
The generally accepted assumption with regard to temperature dependence of product deterioration is that it will follow the Arrhenius equation (Saguy and Karel, 1980)

$$K = K_o \exp(-E_A/RT) \qquad (19)$$

This formula is applicable to the data from the AOR (0-20 days). PVDC coated PP/PE packed without OA. The activation energy (E_A) calculated from formula (19) and Figure 27 was 10.1 Kcal/mol. The slope of the line (1/T°K Vs log AOC) was $-1/4.5 \times 10^{-4}$. Calculation was conducted as follows:

$$K = K_o \exp(-E_A/RT)$$
$$\ln K/K_o = -E_A/RT$$
$$\log K/K_o = -E_A/2.3 \cdot RT$$
$$\log K = \log K_o - (E_A/2.3\,R)\,1/T$$
$$\text{slope} = -(E_A/2.3R) = -1/(4.5 \times 10^{-4})$$

Figure 27. Average O_2 consumption rate (AOR, 0-20 days) as a function of temperature for oat cereal packaged in PVDC coated PP/PE and stored at medium humidity in the dark, 21% initial headspace O_2.


AOR
(ml/day)
10.0
1.0
0.1
65°C
41°C
21°C
2.90
3.00
3.10
3.20
3.30
3.40
(1/T°K x 10³) TEMPERATURE

$$R: 1.98 \times 10^{-3} \text{ Kcal}/^{o}\text{K}\cdot\text{mol}$$

$$E_A = 10.1 \text{ Kcal/mol}$$

This value was in the lower range of that reported by Labuza (1972) with regard to lipid oxidation (10-25 Kcal/mol). The M-TBA index was different for storage at 21°C and 41°C without OA (Figure 7-8). In Table 15 is shown the statistical significance for oat cereal packaged in PVDC coated PP/PE and stored at 21°C. The comparison of M-TBA index for all three temperatures is shown in Figure 10. At 65°C M-TBA index increased to 20 (O.D. x 100/gm) with and without OA after 1-2 months (Figure 9). At 65°C obvious browning occurred (visual only) after 1-2 months with and without OA. Very severe off odors were noticeable. The amount of O_2 consumed correlated well with the results of sensory evaluation (Table 5). Oxidation was observed when the amount of O_2 consumed reached 30 ml. The exception was one sample packed at 80% RH (41°C, 21% initial headspace O_2). The M-TBA index was in general agreement with sensory evaluation when it was applied to less than extreme conditions. In normal conditions, oxidized change was observed over 20 (O.D. x 100/gm) by sensory evaluation. In extreme conditions, high RH (80% RH, 41°) and high temperature (65°C, 45% RH), the M-TBA index did not correlate with sensory evaluation. For samples stored at high RH (41°C, 80% RH) without OA, the M-TBA index gave low values even though oxidized odors were observed by sensory evaluation. At 65°C, an increase in the M-TBA index (O.D. x 100/gm) occurred with and without OA after 12 months. Both samples had very severe off odors. The factors which

Figure 7. M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE under 21% initial headspace O_2 and stored at 21°C, 45% RH.

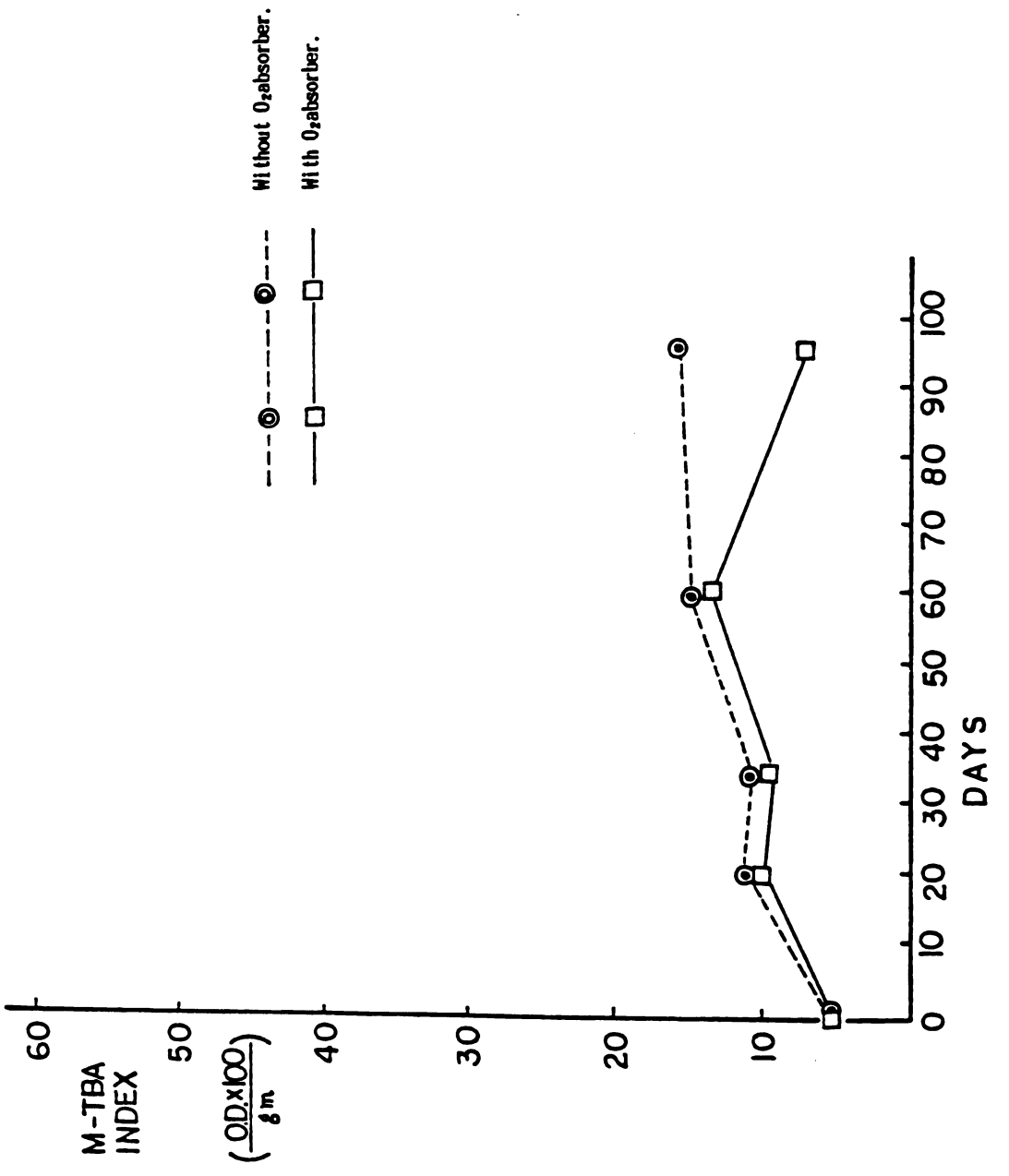

M-TBA INDEX
(OD x 100 / gm)
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
DAYS
Without O2absorber.
With O2absorber.

Figure 8. M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE under 21% initial headspace O_2 and stored at 41°C, 40% RH.

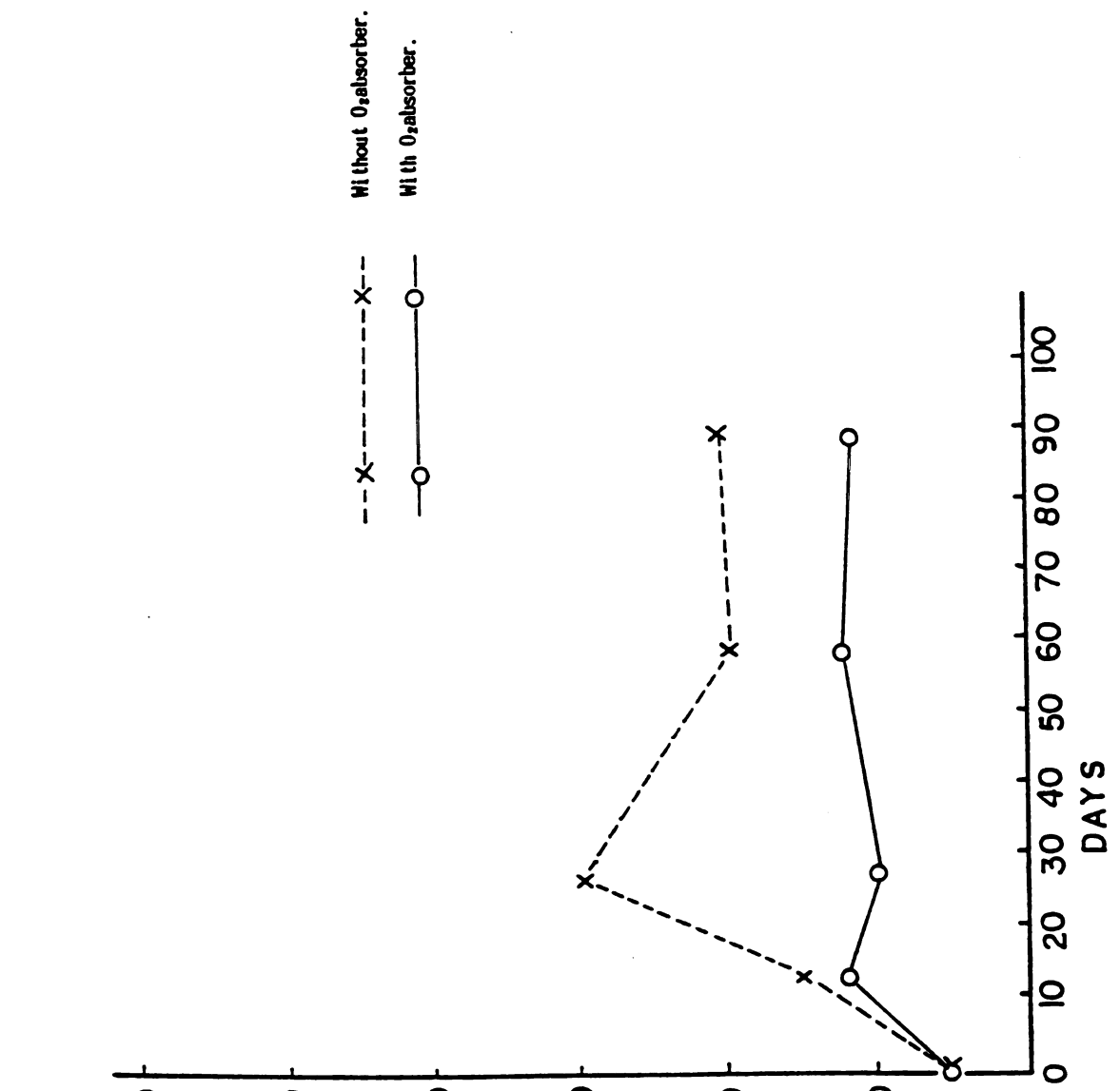

M-TBA INDEX
(OD×100/gm)
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
DAYS
Without O2absorber.
With O2absorber.

Table 15

ANOVA for the Date of sampling x Packaged condition (21°C, 45%RH, PVDC coated PP / PE, 21% initial O_2 concentration, with and without O_2 absorber)

source	sum of squares	d.f.	mean square	F ratio	testing hypotheses
date (Factor A)	90.7	3	30.2	16.3	significant (99%)
packaged condition (Factor B)	73.5	1	73.5	39.7	significant (99%)
Inter-action A x B	91.2	3	30.4	16.4	significant (99%)
Residual	44.4	24	1.9		
Total	299.8	31			

Figure 9. M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE under 21% initial headspace O_2 and stored at 65°C, 45% RH.

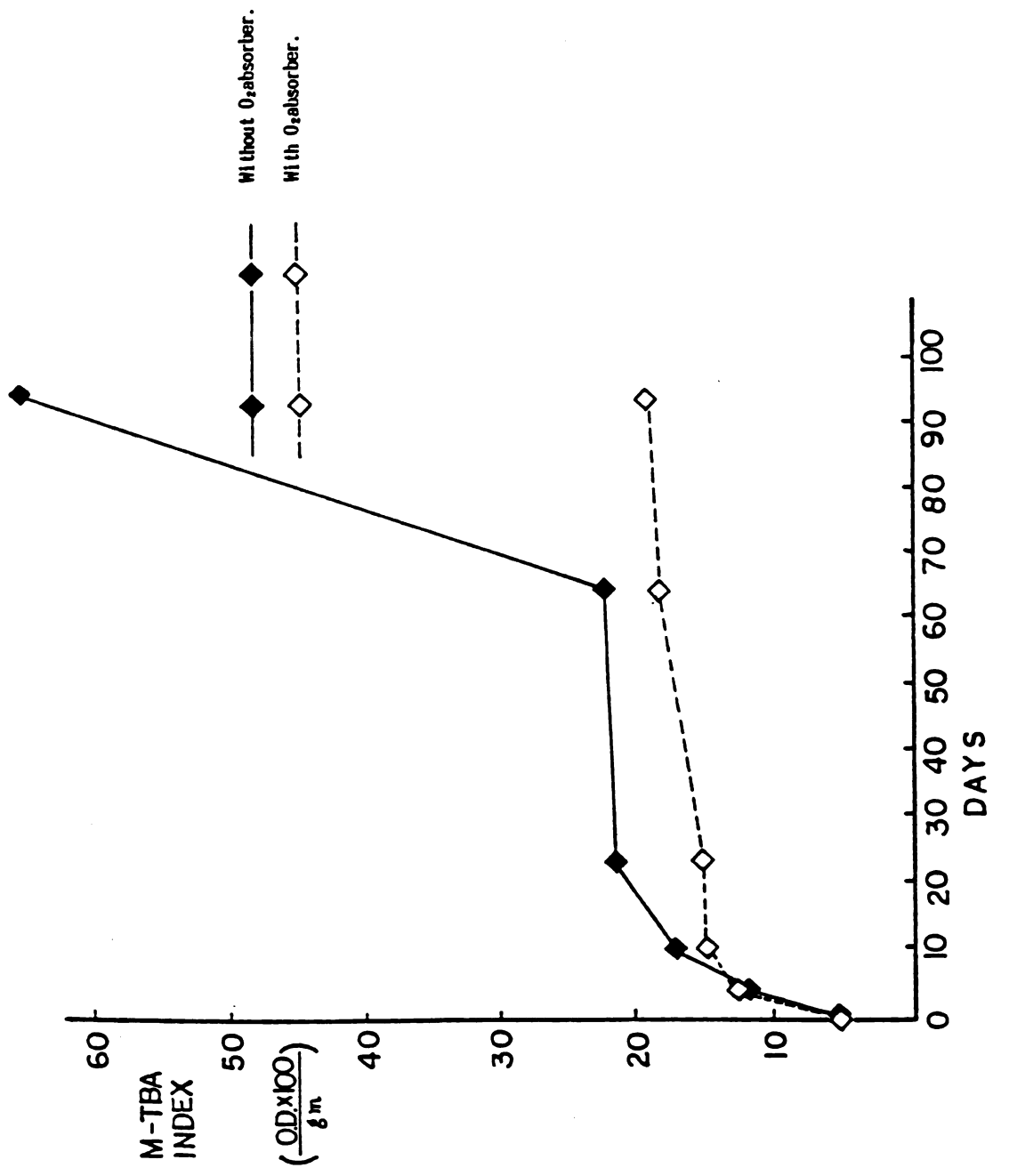
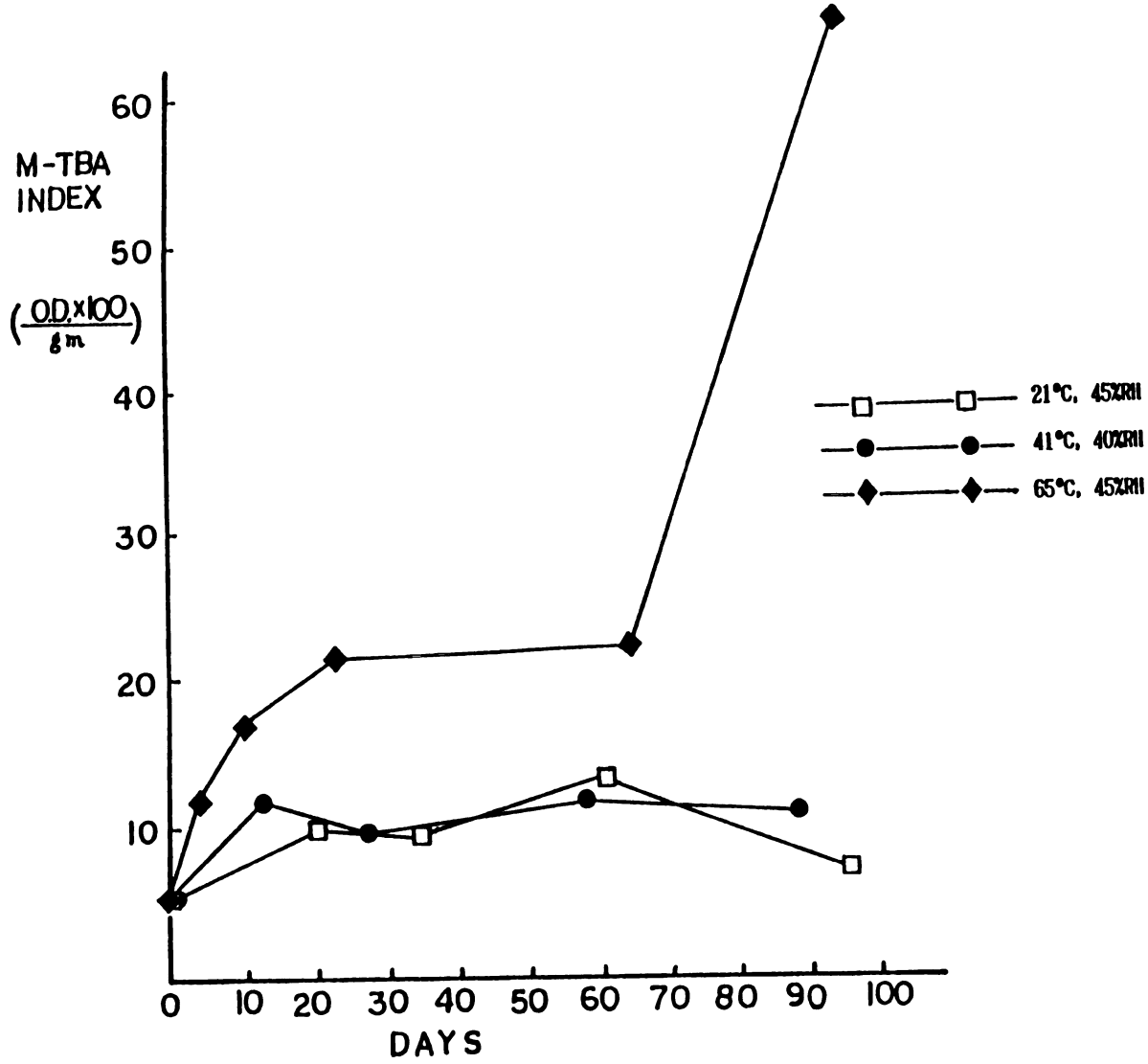

Without O₂absorber.
With O₂absorber.
M-TBA INDEX
(OD.x100/g m)
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
DAYS

Figure 10. M-TBA index as a function of time for oat cereal packaged in PVDC coated PP/PE with O_2 absorber, 21% initial headspace O_2.


M-TBA
INDEX
(O.D.×100/gm)
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
DAYS
21°C, 45%RH
41°C, 40%RH
65°C, 45%RH

influenced the TBA test were debated by several persons (Dugan, 1955; Buttkus and Rose, 1972; Baumgartner, 1975). Certain amines from protein degradation can condensate with malonaldehyde, which can interfere with the TBA reaction. At high temperature (65^{o}C, 45% RH) and at high humidity (41^{o}C, 80% RH) browning related reactions can occur and produce amines which consume malonaldehyde.

Oat lipids usually have only 0.5-5.0% double bonded fatty acids (Hammond, 1983), which can form the condensation product (pigment) with malonaldehyde, however, application of the M-TBA test to determine the oxidation of oat cereal was in general agreement with sensory evaluation and amount of O_2 consumed at ambient condition. The M-TBA index for products packed with OA in PVDC coated PP/PE was less than 15 (O.D. x 100/gm) in most conditions during the whole storage period except at 65^{o}C. The O_2 concentration in the headspace of packages packed with OA was maintained at a minimal level for up to 2 months in most cases. The use of OA in delaying lipid oxidation was supported by the M-TBA index at 41^{o}C, 40% RH and sensory evaluation.

Absorbing Ability of the OA

The absorbing capacity of the OA was 160 ml/pouch in ambient condition (Table 7, Figure 1), however, the water activity inside the container influenced the absorbing ability. Temperature could also affect absorbing ability.

When the water content inside the container is high, it could absorb approximately 1000 ml/pouch. The OA consists of iron powder, water, and catalysts. The exact reaction with oxygen is not certain, however, the basic mechanism of the reaction involves oxidation of the iron powder. When there is an infinite supply of O_2 and enough H_2O, iron powder (Fe) is oxidized to Fe^{3+}. In this situation, one mole Fe can theoretically absorb 3/4 mole O_2 (Formula 8).

$$Fe + 3/4\ O_2 + 3/2\ H_2O \longrightarrow Fe\ (OH)_3 \longrightarrow$$

$$Fe_2O_3 \cdot 3H_2O \qquad (19)$$

$$Fe + 1/2\ O_2 + H_2O \longrightarrow Fe\ (OH)_2 \longrightarrow$$

$$Fe\ (OH)_2 + 1/4\ O_2 + 1/2\ H_2O \longrightarrow Fe\ (OH)_3 \longrightarrow$$

$$Fe_2O_3 \cdot 3H_2O$$

One gram iron is equivalent to 1/26 mole (molecular weight of Fe = 26). At 21°C, volume of 1 mole gas is 22.4×10^3 (ml) x 294/273. Therefore absorbed O_2 by 1 gm Fe (at 27°C) =

$$\frac{22.4 \times 10^3 \times 294 \times 3}{273 \times 4 \times 26} = 696\ (ml).$$

In actual use, the absorbing ability of the OA in ambient condition (21°C, 45% RH) was 33 ml per 1 gm absorbing powder. This value was much smaller than its theoretical value. Commercial OA is manufactured to carefully regulate

its reaction speed without generating heat and hydrogen during reaction. In ambient conditions, absorbing capacity of the Fe powder was only partially used.

SUMMARY

The storage stability of a flaked oat cereal product packed in Polyethylene (PE) and Polyvinylidene chloride (PVDC) coated polypropylene (PP)/polyethylene (PE) with and without oxygen absorber (OA) was evaluated.

OA reduced the oxidative deterioration in moderate environments. The increase of the M-TBA index with OA was smaller than that without OA; however, in extreme conditions of high temperature (65^{o}C, 45% RH) and high relative humidity (80% RH, 41^{o}C OA could not control deterioration. When OA was packed with product in low barrier material (PE), it also was unable to prevent oxidation. A reasonable nitrogen gas flush sample (1% initial headspace O_2 concentration) showed deterioration after one month, while OA sample prevented oxidative changes for up to three months.

Increased temperature and oxygen concentration, and exposure to light accelerated the oxidative deterioration for samples packed without OA as detected by headspace O_2 change and sensory evaluation. This accelerating effect of temperature and light was also observed with OA, however this effect was reduced with OA. M-TBA index was generally in good agreement with sensory evaluation and amount of O_2 consumed except in extreme conditions.

The following conclusions are therefore, made:

1. Oxygen absorber (OA) reduces the oxidative deterioration in moderate circumstances. The increase of the M-TBA index with OA was smaller than that without OA.
2. In extreme conditions; high temperature (65^{o}C, 45% RH) or high humidity (41^{o}C, 80% RH), the OA loses its ability to retain the deterioration.
3. In this experiment, a reasonable gas flushed sample (1% initial headspace O_2 concentration) showed deterioration after 1 month, while the OA sample showed deterioration after 3 months by sensory evaluation. This difference of M-TBA index was significant at 99% level by analysis of variance.
4. M-TBA index was in general, good agreement with sensory evaluation and amount of O_2 consumed except in extreme conditions. Oxidative deterioration can occur when the headspace O_2 level is minimum (0.01%). Permeating oxygen is competitively utilized by lipids and OA.
5. High barrier package is necessary to utilize the ability of OA.
6. Light accelerates the oxidation of oat cereal with and without OA, observed by O_2 amount of O_2 consumed and sensory evaluation.

APPENDICES

APPENDIX 1

DETERMINATION OF THE HEAD SPACE VOLUME OF SAMPLE PACKAGES

Methodology

Head space volume of the package is measured by the following procedures:

1. Deposit the 50 g oat cereal into the plastic package. Flush N_2 into the package and regulate the total inner volume to 255 ml by the same manner as for the storage samples.
2. After, mix the pouch hard, measure the residual oxygen concentration of the flushed package (Co) by the oxygen analyzer. Sampling volume is 5 ml (Vs). Sampling times are twice (n).
3. Insert 10 ml air (Va) into the package by an airtight syringe.
4. After, blend the pouch vigorously, measure the new head space oxygen concentration by the oxygen analyzer (C_1).
5. Head space volume (V) is calculated by following formula.

$$C_1 = \frac{C_o\ (V - nVs) + Va \times 0.209}{(V - nVs) + Va}$$

$$V = \frac{Va\ (0.209 - C_1) + nVs\ (C_1 - C_o)}{C_1 - C_o}$$

V = origianl head space volume (ml)

Va = volume of added air (ml)

C_o = residual O_2 concentration (V_{O2}/V_{total})

C_1 = final O_2 concentration (V_{O2}/V_{total})

Vs = sampling volume for measurement for initial residual oxygen (ml)

n = sampling time of Vs

0.209 = O_2 concentration in the air

Results

$C_o(V_{O2}/V_{total})$	$C_1(V_{o2}/V_{total})$	V (ml)
0.0115	0.0222	185
0.0150	0.0251	192
0.0104	0.0213	181
0.0113	0.0225	176
0.0196	0.0295	191
		Ave. 185

Head space volume of sample: 185 ml

Air composition (Tamamushi B, 1981)

	Volume %	Weight %
O_2	20.93	23.01
N_2	78.10	75.51
Ar	0.9325	1.286
CO_2	0.03	0.04
Ne	0.0018	0.0012
He	0.0005	0.00007
Kripton	0.0001	0.0001
Xenon	0.000009	0.000009

APPENDIX 2

OXYGEN ANALYZER LC-700 F(O) MANUFACTURED BY TORAY ENGINEERING CO. LTD.

Principle of the Measurement

Zirconium solid electrolyte shows the O^{2-} ion conductivity in high temperature. A solid electrolyte oxygen concentration cell can be formed, when the electrodes are fabricated in both sides of this electrolyte.

This cell produces a electromotive force, when the O_2 partial pressure of each side is different. The electromotive force and ratio of oxygen pressure difference has a relation called Nernst formula. When one side is utilized as reference (air: 20.9% oxygen concentration), sample gas concentration can be measured.

High O_2 concentration side (reference)

$$O_2 + 4e \longrightarrow 2O^{2-}$$

Low O_2 concentration side (sample)

$$2O^{2-} \longrightarrow O_2 + 4e$$

Nernst formula

$$En = \frac{RT}{nF} \ln \frac{Pr}{Ps}$$

En: electromotive force (V)

F: Faraday constant 96500 (J/V)

F: Gas constant 8.314 (J/mol·deg)

T: Absolute temperature (^{o}K)

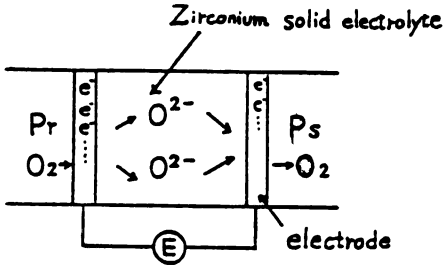
Pr: Partial pressure of reference gas (atm)

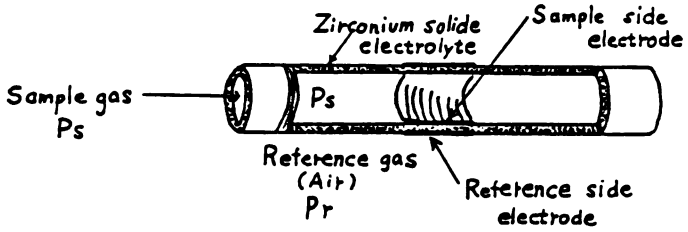
Ps: Partial pressure of sample gas (atm)

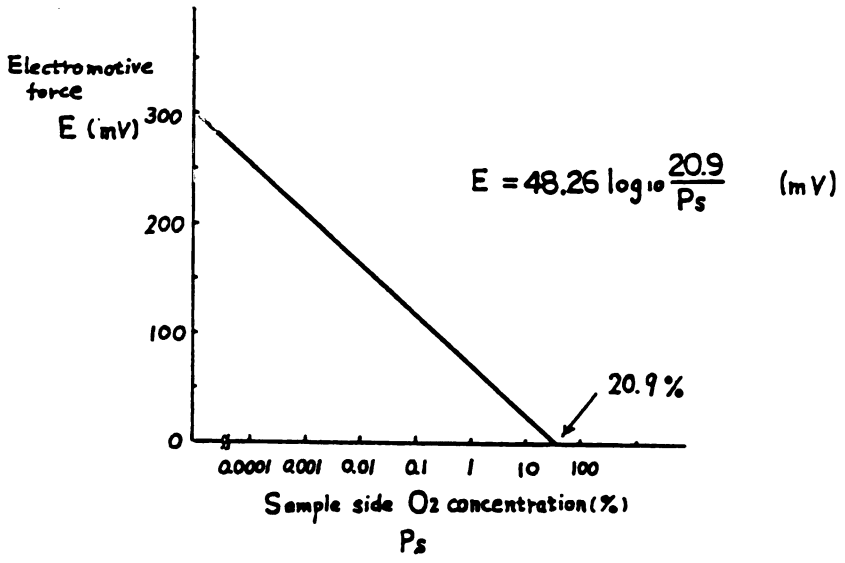
n: Charge numbers for ionization 4

When T = 700^{o}C (973^{o}K), Reference gas is air (Pr = 20.9)

$$E = 48.26 \log_{10} (20.9/Ps) \text{ (mV)}$$


Zirconium solid electrolyte
Pr
O2
e⁻
O2-
O2-
Ps
O2
electrode
E


Zirconium solide electrolyte
Sample side electrode
Sample gas
Ps
Ps
Reference gas
(Air)
Pr
Reference side electrode


Electromotive force
E (mV)
300
200
100
0
20.9%
0.0001
0.001
0.01
0.1
1
10
100
Sample side O2 concentration(%)
Ps
E = 48.26 log10 20.9/Ps (mV)

APPENDIX 3

MEASUREMENT OF THE LIGHT INTENSITY IN THE EXPOSURE BOX

Methodology

Exposure box is fabricated using corrugate board, and the size is 80 cm x 60 cm x 30 cm (L x W x H). Underneath the top flap, a 15 W fluorescent light is attached. Light intensity is measured by Gossen Pan Lux - Light meter. The sensing device,which can be removed from the main body of the light meter, is placed on the bottom of several different points. Light intensity is directly measured by an analog meter.

Results

Samples are placed inside the dotted line area (Figure 13) where light intensity ranged from 40 to 90 foot candles. Samples are replaced and turned over each month in order to average the effect of light exposure (conversion factor to international unit):

10.764 lux = 1 foot candle

APPENDIX 4

CALCULATION OF PERCENT RELATIVE HUMIDITY AT ELEVATED TEMPERATURES

Assume bubbler tubes produce gas at 100 percent relative humidity at bubbler temperature (i.e., room temperature).

W_b = saturation vapour density in bubbler tube at bubbler temperature.

W_c = vapour density of diffuser cell calculated from equation 1 below.

T_b = temperature of bubbler tubes (^oK)

T_c = temperature of diffuser cell (^oK)

W_s = saturation vapour density at diffusion cell temperature.

$$W_c = W_b \times (T_b/T_c) \qquad \text{(Equation 1)}$$

$$\text{Percent Relative Humidity} = W_c/W_s \times 100 \qquad \text{(Equation 2)}$$

Calculation

1. $T_b = 21^oC = 294^oK$

   $W_b = 18.5$ gm/m^3 at T_b

   $T_c = 41^oC = 314^oK$

   $W_s = 54.1$ gm/m^3 at T_c

   $W_c = 18.5 \times (294/314) = 17.3$ gm/m^3

   Relative humidity = $(17.3/54.1) \times 100 = 32\%$

   32% RH at 41^oC

2. $T_b = 21^oC = 294^oK$

   $W_b = 18.5$ gm/m^3 at T_b

   $T_c = 65^oC = 338^oK$

   $W_s = 161.3$ gm/m^3 at T_c

   $W_c = 18.5 \times (294/338) = 16.1$ gm/m^3

   Relative humidity = $(16.1/161.3) \times 100 = 10\%$

   10% RH at 65^oC

APPENDIX 5

Calculation of the amount of O_2 consumed and Average O_2 consumption Rate (AOR, from t_x to t_y days) at each condition

Calculation method

Change of headspace O_2 concentration was a result of O_2 consumption by the cereal and permeated O_2 from the outside.

$$\text{Change of headspace } O_2 = O_2 \text{ permeated} - O_2 \text{ consumed}$$

$$= \text{Total headspace (185 ml)} * \text{(final } O_2 \text{ concentration - initial } O_2 \text{ concentration)} \quad (1)$$

$$O_2 \text{ permeated} = \overline{P}_{pouch} * \int_0^t P(t) * dt \quad (2)$$

Amount of O_2 consumed and AOR (t_x -t_y days) are showed by the formula (3) and (4).

$$O_2 \text{ consumed} = \overline{P}_{pouch} * \int_0^t P(t) * dt - 185 * (O_2 \text{ conc.}(t) - O_2 \text{ conc.}(0)) \quad (3)$$

$$\text{AOR (} t_x - t_y \text{ days)} = \frac{\left[O_2 \text{ consumed} \right]_{tx}^{ty}}{(t_y - t_x)} \quad (4)$$

$\bar{P}_{pouch}$: permeability constant of the pouch (ml/pouch*day*atm)
P (t) : Pressure difference between outside and inside the package at t days (atm * ml/ml)
O_2 conc.(t) : headspace O_2 concentration as a function of time (ml/ml) (final O_2 concentration)
O_2 conc.(0) : initial headspace O_2 concentration (ml/ml)
$\left[O_2 \text{ consumed} \right]_{tx}^{ty}$: amount O_2 consumed during certain time (from t_x to t_y days)

Here

$$P(t) = 0.209 - O_2 \text{ conc.}(t) \qquad (5)$$

0.209 : Outside concentration of O_2 * 1 atm (atm * ml/ml)

O_2 conc.(t) can be assumed to be a combination of the serial straight lines. These lines are obtained as least squars regression lines.

When

$0 \leqq t \leqq t_1$

$$O_2 \text{ conc.}(t) = a_1 t + O_2 \text{ conc.}(0) \qquad (6)$$

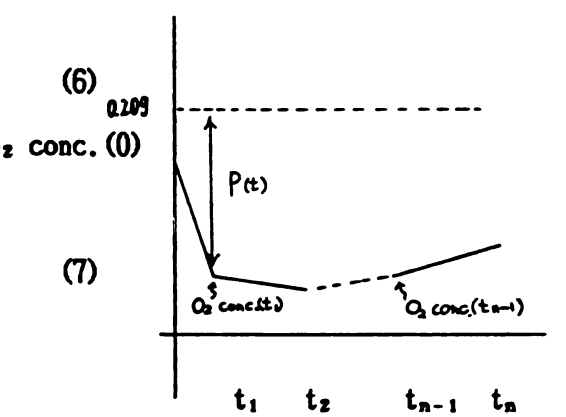
$t_1 \leqq t \leqq t_2$

$$O_2 \text{ conc.}(t) = a_2(t - t_1) + O_2 \text{ conc.}(t_1) \qquad (7)$$

|

$t_{n-1} \leqq t \leqq t_n$

$$O_2 \text{ conc.}(t) = a_n(t - t_{n-1}) + O_2 \text{ conc.}(t_{n-1}) \qquad (8)$$



Here t_1 is a day when first straight line connects to second line. As the same way t_n is a day when n-1th line connects to n th line.

While

$$O_2 \text{ consumed} = \bar{P}_{pouch} * \int_0^t P(t) * dt - 185 * (O_2 \text{ conc.}(t) - O_2 \text{ conc.}(0))$$

$$P(t) = 0.209 - O_2 \text{ conc.}(t) \qquad \text{see (3)}$$

Calculate the amount of O_2 consumed in serial orders.

When

$$0 \leq t \leq t_1$$

$$\overline{P}_{pouch} * \int_0^t P(t) * dt = \overline{P}_{pouch} * \int_0^t (0.209 - O_2 \text{ conc.}(t)) * dt$$

$$= \overline{P}_{pouch} * \int_0^t (0.209 - a_1 t - O_2 \text{ conc.}(0)) * dt$$

$$= \overline{P}_{pouch} * \left[- \frac{a_1}{2} t^2 + (0.209 - O_2 \text{ conc.}(0)) * t \right] \qquad (9)$$

$$185 * (O_2 \text{ conc.}(t) - O_2 \text{ conc.}(0)) = 185 * (a_1 t + O_2 \text{ conc.}(0) - O_2 \text{ conc.}(0))$$

$$= 185 * (a_1 t) \qquad (10)$$

So

$$O_2 \text{ consumed} = \overline{P}_{pouch} * \left[- \frac{a_1}{2} t^2 + (0.209 - O_2 \text{ conc.}(0)) * t \right] - 185 * (a_1 t) \qquad (11)$$

When

$$t_1 \leq t \leq t_2$$

$$O_2 \text{ consumed} = [O_2 \text{ consumed}]_0^{t_1} + [O_2 \text{ consumed}]_{t_1}^{t} \qquad (12)$$

$$[O_2 \text{ consumed}]_{t_1}^{t} = \overline{P}_{pouch} * \int_{t_1}^{t} P(t) * dt - 185 * (O_2 \text{ conc.}(t) - O_2 \text{ conc.}(t_1)) \qquad (13)$$

$$\overline{P}_{pouch} * \int_{t_1}^{t} P(t) * dt$$

$$= \overline{P}_{pouch} * \int_{t_1}^{t} (0.209 - a_2 t + a_2 t_1 - O_2 \text{ conc.}(t_1)) * dt$$

$$= \overline{P}_{pouch} * \left[- \frac{a_2}{2} t^2 + (0.209 + a_2 t_1 - O_2 \text{ conc.}(t_1)) * t \right]_{t_1}^{t} \qquad (14)$$

$185 * (O_2 \text{ conc.}(t) - O_2 \text{ conc.}(t_1))$

$= 185 * (a_2(t - t_1) + O_2 \text{ conc.}(t_1) - O_2 \text{ conc.}(t_1))$

$= 185 * (a_2(t - t_1))$ (15)

$[O_2 \text{ consumed }]_0^{t_1}$ is calculated from the formula (11).

From (13), (14), and (15)

$$[O_2 \text{ consumed }]_{t_1}^{t} = \overline{P}_{pouch} * [- \frac{a_2}{2} t^2 + (0.209 + a_2 t_1 - O_2 \text{ conc.}(t_1)) * t]_{t_1}^{t} - 185 * (a_2(t - t_1)) \quad (16)$$

$$[- \frac{a_2}{2} t^2 + (0.209 + a_2 t_1 - O_2 \text{ conc.}(t_1)) * t]_{t_1}^{t}$$

$$= - \frac{a_2}{2} * (t^2 - t_1) + (0.209 + a_2 t_1 - O_2 \text{ conc.}(t_1)) * (t - t_1)$$

$$= - \frac{a_2}{2} * (t^2 - t_1) + a_2 t_1 * (t - t_1) + (0.209 - O_2 \text{ conc.}(t_1)) * (t - t_1)$$

$$= - \frac{a_2}{2} * (t - t_1)^2 + (0.209 - O_2 \text{ conc.}(t_1)) * (t - t_1) \quad (17)$$

So O_2 consumed

$$= \overline{P}_{pouch} * [- \frac{a_2}{2} * (t - t_1)^2 + (0.209 - O_2 \text{ conc.}(t_1)) * (t - t_1)] - 185 * (a_2(t - t_1)) + [O_2 \text{ consumed }]_0^{t_1}$$

See (12), (16), and (17)

By the same way

$t_{n-1} \leqq t \leqq t_n$

O_2 consumed

$$= \overline{P}_{pouch} * [- \frac{a_n}{2} * (t - t_{n-1})^2 + (0.209 - O_2 \text{ conc.}(t_{n-1})) * (t - t_{n-1})] - 185 * (a_n(t - t_{n-1})) + [O_2 \text{ consumed }]_0^{t_{n-1}}$$

Calculation of each condition

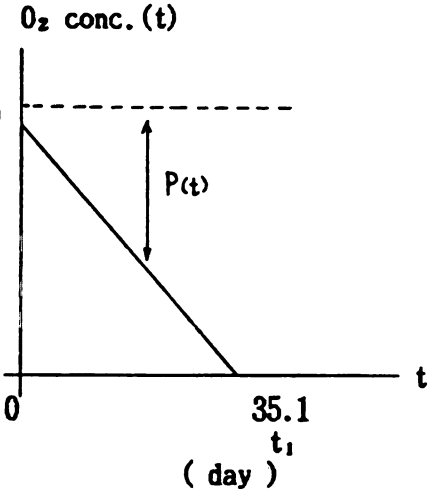
1. 41°C, 40%RH, no O_2absorber, PVDC coated PP / PE, 21% initial headspace O_2concentration

$$O_2 \text{ consumed} = \bar{P}_{pouch} * \int_0^t P(t) * dt - 185 * (O_2 \text{ conc.}(t) - O_2 \text{ conc.}(0))$$

$$AOR\ (t_x - t_y \text{ days}) = \frac{[\ O_2 \text{ consumed}\ ]_{tx}^{ty}}{(t_y - t_x)}$$

$$O_2 \text{ consumed} = \bar{P}_{pouch} * \left[-\frac{a_1}{2} t^2 + (0.209 - O_2 \text{ conc.}(0)) * t \right] - 185 * (a_1 t)$$

$\bar{P}_{pouch} = 1.62$ (ml / pouch * day * atm)



$0 \leqq t \leqq 35.1$

$a_1 = -0.00588$

$O_2 \text{ conc.}(t) = -0.00588t + 0.206$ (atm * ml / ml)

$$O_2 \text{ consumed} = 1.62 * \left(\frac{0.00588}{2} t^2 + 0.003t \right) + 185 * 0.00588 * t$$

$$= 0.0047t^2 + 1.09t \quad (\text{ml})$$

When	O_2 consumed (ml)
$t = 10$	$0.47 + 10.9 = 11.4$
$t = 20$	$1.88 + 21.2 = 23.1$
$t = 35.1$	$5.79 + 38.3 = 44.1$

$35.1 \leqq t$

$O_2 \text{ conc.}(t) = 0$

O_2 consumed

$$= \bar{P}_{pouch} * \left[-\frac{a_2}{2} * (t - t_1)^2 + (0.209 - O_2 \text{ conc.}(t_1)) * (t - t_1) \right] - 185 * (a_2(t - t_1)) + [\ O_2 \text{ consumed}\ ]_0^{t_1}$$

$a_2 = 0$, $O_2 \text{ conc.}(t_1) = 0$, $t_1 = 35.1$

So

O_2 consumed

$= 1.62 * 0.209 * (t - 35.1) + [O_2 \text{ consumed}]_0^{35.1}$

$= 0.339 * (t - 35.1) + 44.0$

When O_2 consumed

$t = 50$ $\quad 5.1 + 44.0 = 49.1$

$t = 90$ $\quad 18.6 + 44.0 = 62.6$

$$\text{AOR} (t_x - t_y \text{ days}) = \frac{[O_2 \text{ consumed}]_{tx}^{ty}}{(t_y - t_x)} \quad (\text{ml / day})$$

$$\text{AOR} (0 - 20 \text{ days}) = \frac{23.1}{20} = 1.2$$

$$\text{AOR} (20 - 50 \text{ days}) = \frac{49.1-23.1}{30} = 0.87$$

$$\text{AOR} (50 - 90 \text{ days}) = \frac{62.6-49.1}{40} = 0.34$$

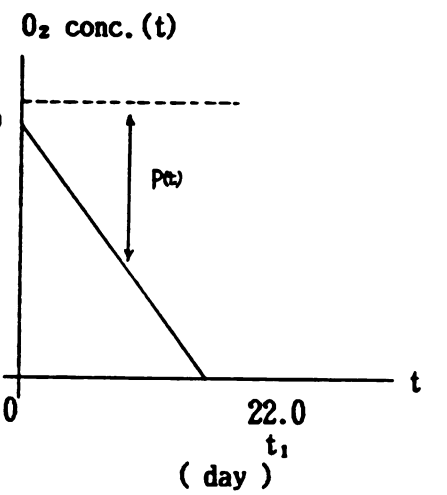
2. 41°C, 40%RH, no O_2absorber, PVDC coated PP / PE, light exposure, 21% initial headspace O_2 concentration

$\overline{P}_{pouch} = 1.62 (\text{ml / pouch * day * atm})$

$0 \leq t \leq 22.0$

$a_1 = 0.00928$

$O_2 \text{ conc.}(t) = - 0.00928t + 0.204 (\text{atm * ml / ml})$



$$O_2 \text{ consumed} = 1.62 * (\frac{0.00928}{2} t^2 + 0.005t) + 185 * 0.00928 * t$$

$= 0.00752t^2 + 1.73t$

When O_2 consumed

t = 5 0.19 + 8.65 = 8.84

t = 10 0.75 + 17.3 = 18.1

t = 20 3.0 + 34.6 = 37.6

t = 22 3.6 + 38.0 = 41.6

$22.0 \leqq t$

O_2 consumed

$= 1.62 * 0.209 * (t - 22.0) + [O_2 \text{ consumed}]_0^{22.0}$

$= 0.339 * (t - 22.0) + 41.6$

When O_2 consumed

t = 50 9.5 + 41.6 = 51.1

t = 90 23.1 + 41.6 = 64.7

$$\text{AOR} (0 - 20 \text{ days}) = \frac{37.6}{20} = 1.9$$

$$\text{AOR} (20 - 50 \text{ days}) = \frac{51.1-37.6}{30} = 0.45$$

$$\text{AOR} (50 - 90 \text{ days}) = \frac{64.7-51.1}{40} = 0.34$$

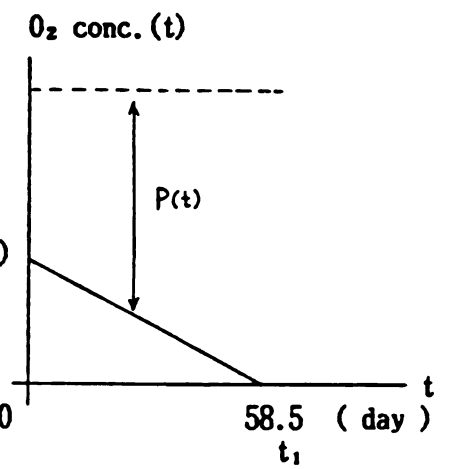
3. 41°C, 40%RH, no O_2absorber, PVDC coated PP / PE, 5% initial headspace O_2 concentration

$\bar{P}_{pouch} = 1.62$ (ml / pouch * day * atm)

$0 \leqq t \leqq 58.5$

$a_1 = 0.00084$

O_2 conc.(t) = - 0.00084t + 0.049 (atm * ml / ml)



$$O_2 \text{ consumed} = 1.62 * \left(\frac{0.00084}{2} t^2 + 0.16t \right)$$

$$+ 185 * 0.00084 * t$$

$$= 0.00068t^2 + 0.414t$$

When O_2 consumed

t = 10 0.68 + 4.14 = 4.21

t = 20 0.27 + 8.28 = 8.55

t = 50 1.7 + 20.7 = 22.4

t = 58.5 2.3 + 24.2 = 26.5

$58.5 \leqq t$

O_2 consumed

$$= 1.62 * 0.209 * (t - 58.5) + [O_2 \text{ consumed}]_0^{58.5}$$

$$= 0.339 * (t - 58.5) + 26.5$$

When O_2 consumed

t = 90 10.6 + 26.5 = 37.1

$$\text{AOR} (0 - 20 \text{ days}) = \frac{37.6}{20} = 1.9$$

$$\text{AOR} (20 - 50 \text{ days}) = \frac{51.1-37.6}{30} = 0.45$$

$$\text{AOR} (50 - 90 \text{ days}) = \frac{64.7-51.1}{40} = 0.34$$

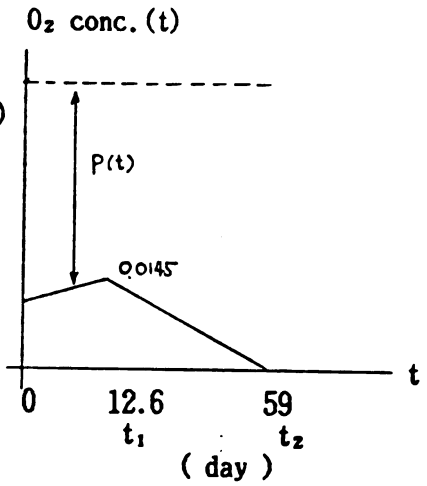
4. 41°C, 40%RH, no O_2absorber, PVDC coated PP / PE, 1% initial headspace O_2concentration

$$O_2 \text{ consumed} = \overline{P}_{pouch} * \left[- \frac{a_1}{2} t^2 + (0.209 - O_2 \text{ conc.}(0)) * t \right]$$

$$- 185 * (a_1 t)$$

$\overline{P}_{pouch}$ = 1.62 (ml / pouch * day * atm)

$0 \leq t \leq 12.6$



$a_1 = 0.00043$

O_2 conc. $(t) = -0.00043t + 0.009$ (atm * ml / ml)

$$O_2 \text{ consumed} = 1.62 * \left(-\frac{0.00043}{2} t^2 + 0.20t \right) - 185 * 0.00043 * t$$

$$= -0.00035t^2 + 0.244t$$

When O_2 consumed

$t = 10$ $\quad -0.04 + 2.44 = 2.40$

$t = 12.6$ $\quad -0.06 + 3.07 = 3.01$

$12.6 \leq t \leq 59$

$a_2 = -0.000318$, O_2 conc. $(t_1) = 0.0145$

$t_1 = 12.6$

O_2 conc. $(t) = a_2 * (t - t_1) + O_2$ conc. (t_1)

O_2 consumed

$$= \bar{P}_{pouch} * \left[-\frac{a_2}{2} * (t - t_1)^2 + (0.209 - O_2 \text{ conc.}(t_1)) * (t - t_1) \right] - 185 * (a_2(t - t_1)) + [O_2 \text{ consumed}]_0^{t_1}$$

$$= 1.62 * \left[\frac{0.000318}{2} * (t - 12.6)^2 + (0.209 - 0.0145) * (t - 12.6) \right] + 185 * 0.000318 * (t - 12.6) + [O_2 \text{ consumed}]_0^{12.6}$$

$$= 1.62 * \left[\frac{0.000318}{2} * (t - 12.6)^2 + 0.195 * (t - 12.6) \right] + 0.0588 * (t - 12.6) + 3.01$$

When O_2 consumed

$t = 20$ $\quad 5.80$

$t = 50$ $\quad 17.4$

$t = 59$ $\quad 20.8$

$59 \leq t$

O_2 consumed

$= 1.62 * 0.209 * (t - 59) + [O_2 \text{ consumed }]_0^{59}$

$= 0.339 * (t - 59) + 20.8$

When O_2 consumed

$t = 90$ $10.5 + 20.8 = 31.3$

$$\text{AOR } (0 - 20 \text{ days }) = \frac{5.8}{20} = 0.29$$

$$\text{AOR } (20 - 50 \text{ days }) = \frac{17.4-5.8}{30} = 0.39$$

$$\text{AOR } (50 - 90 \text{ days }) = \frac{31.3-17.4}{40} = 0.35$$

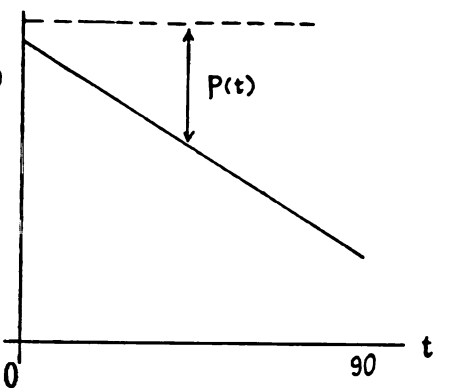
5. 21°C, 45%RH, no O_2absorber, PVDC coated PP / PE
21% initial headspace O_2 concentration

$\bar{P}_{pouch} = 0.189$ (ml / pouch * day * atm)

$0 \leq t$

$a_1 = - 0.0016$

O_2 conc. (t) $= - 0.0016t + 0.200$ (atm * ml / ml)



$$O_2 \text{ consumed} = 0.189 * \left(\frac{0.0016}{2} t^2 + 0.009t \right)$$

$+ 185 * 0.0016 * t$

$= 0.000151t^2 + 0.298t$

When	O_2 consumed	When	O_2 consumed
t = 10	3.0	t = 50	12.2
t = 20	6.0	t = 60	15.3
t = 40	12.2	t = 90	28.0

$$AOR\ (\ 0 - 20\ days\ ) = \frac{6.0}{20} = 0.30$$

$$AOR\ (\ 20 - 50\ days\ ) = \frac{15.3-6.0}{30} = 0.31$$

$$AOR\ (\ 50 - 90\ days\ ) = \frac{28.0-15.3}{40} = 0.32$$

6. 41°C, 80%RH, no O_2absorber, PVDC coated PP / PE, 21% initial headspace O_2concentration

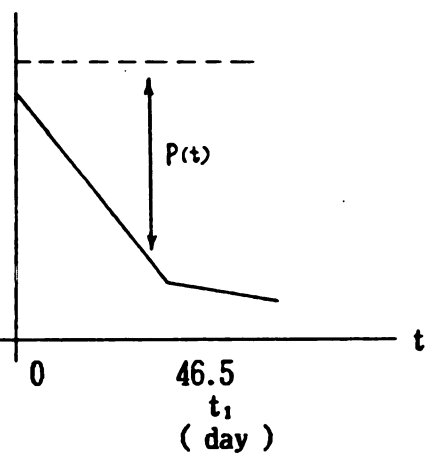
$$O_2\ consumed = \bar{P}_{pouch} * \left[- \frac{a_1}{2} t^2 + (0.209 - O_2\ conc.(0)) * t \right] - 185 * (a_1 t)$$

$$\bar{P}_{pouch} = 1.62\ (ml / pouch * day * atm)$$

$$0 \leqq t \leqq 46.5$$

$$a_1 = - 0.00331$$

$$O_2\ conc.(t) = - 0.00331t + 0.202\ (atm * ml / ml)$$



$$O_2\ consumed = 1.62 * \left(- \frac{0.00331}{2} t^2 + 0.007t \right) + 185 * 0.00331 * t$$

$$= 0.00268t^2 + 0.605t$$

When	O_2 consumed	When	O_2 consumed
t = 10	6.3	t = 40	28.5
t = 20	13.2	t = 46.5	33.9

$46.5 \leqq t$

$a_2 = -0.000536$, O_2 conc.$(t_1) = 0.048$

$t_1 = 46.5$

O_2 conc.$(t) = a_2 * (t - t_1) + O_2$ conc.(t_1)

O_2 consumed

$$= \bar{P}_{pouch} * \left[- \frac{a_2}{2} * (t - t_1)^2 + (0.209 - O_2 \text{ conc.}(t_1)) * (t - t_1) \right]$$

$$- 185 * (a_2 (t - t_1)) + [O_2 \text{ consumed }]_0^{t_1}$$

$$= 1.62 * \left[\frac{0.000536}{2} * (t - 46.5)^2 + (0.209 - 0.048) * (t - 46.5) \right]$$

$$+ 185 * 0.000536 * (t - 46.5) + [O_2 \text{ consumed }]_0^{46.5}$$

$$= 1.62 * \left[\frac{0.000536}{2} * (t - 46.5)^2 + 0.161 * (t - 46.5) \right]$$

$$+ 0.0992 * (t - 12.6) + 33.9$$

When	O_2 consumed
$t = 50$	35.2
$t = 67$	41.3
$t = 90$	50.4

$$\text{AOR (0 - 20 days)} = \frac{13.2}{20} = 0.66$$

$$\text{AOR (20 - 50 days)} = \frac{35.2 - 13.2}{30} = 0.73$$

$$\text{AOR (50 - 90 days)} = \frac{50.4 - 35.2}{40} = 0.35$$

7. 65°C, 45%RH, no O_2absorber, PVDC coated PP / PE, 21% initial headspace O_2 concentration

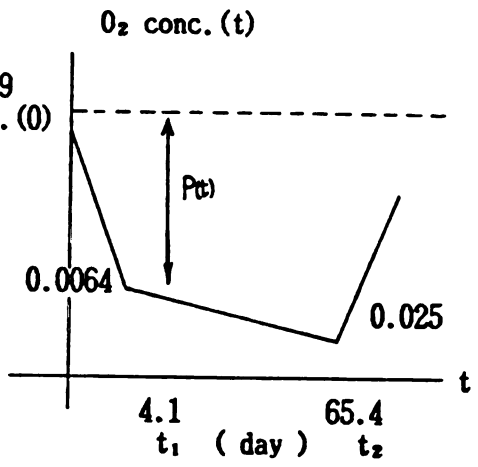
$$O_2 \text{ consumed} = \bar{P}_{pouch} * \left[- \frac{a_1}{2} t^2 + (0.209 - O_2 \text{ conc.}(0)) * t \right] - 185 * (a_1 t)$$

$$\bar{P}_{pouch} = 10.8 \text{ (ml / pouch * day * atm)}$$

$0 \leqq t \leqq 4.1$

$a_1 = - 0.0358$

O_2 conc.(t) = $- 0.0358t + 0.209$ (atm * ml / ml)



$$O_2 \text{ consumed} = 10.8 * \left(- \frac{0.0358}{2} t^2 \right) + 185 * 0.0358 * t$$

$$= 0.191t^2 + 6.62t$$

When	O_2 consumed
t = 2.0	0.76 + 13.2 = 14.0
t = 4.1	3.2 + 27.1 = 30.4

$4.1 \leqq t \leqq 65.4$

$a_2 = - 0.00064$, O_2 conc.(t_1) = 0.064

$t_1 = 4.1$

$$O_2 \text{ consumed} = 10.8 * \left[\frac{0.00064}{2} * (t - 4.1)^2 + (0.209 - 0.064) * (t - 4.1) \right] + 185 * 0.00064 * (t - 4.1) + \left[O_2 \text{ consumed} \right]_0^{4.1}$$

$$= 10.8 * \left[\frac{0.00064}{2} * (t - 4.1)^2 + 0.145 * (t - 4.1) \right] + 0.118 * (t - 4.1) + 30.4$$

When	O_2 consumed	When	O_2 consumed
t = 20	58.0	t = 65.4	146
t = 50	115	t = 44	103

$65.4 \leqq t$

$a_3 = 0.00321$, O_2 conc.$(t_2) = 0.025$

$t_2 = 65.4$

O_2 consumed

$$= 10.8 * \left[- \frac{0.00321}{2} * (t - 65.4)^2 + (0.209 - 0.025) * (t - 65.4) \right.$$

$$\left. - 185 * 0.00321 * (t - 65.4) + \left[O_2 \text{ consumed} \right]_0^{65.4} \right]$$

$$= 10.8 * \left[- \frac{0.00321}{2} * (t - 65.4)^2 + 0.206 * (t - 65.4) \right]$$

$$+ 0.594 * (t - 65.4) + 146$$

When	O_2 consumed	When	O_2 consumed
$t = 75$	161	$t = 90$	176
$t = 85$	172		

$$\text{AOR} (0 - 20 \text{ days}) = \frac{58.0}{20} = 2.9$$

$$\text{AOR} (20 - 50 \text{ days}) = \frac{115 - 58}{30} = 2.9$$

$$\text{AOR} (50 - 90 \text{ days}) = \frac{176 - 115}{30} = 1.9$$

8. 45°C, 40%RH, no O_2absorber, PE, 21% initial headspace O_2 concentration

$$O_2 \text{ consumed} = \overline{P}_{\text{pouch}} * \left[- \frac{a_1}{2} t^2 + (0.209 - O_2 \text{ conc.}(0)) * t \right]$$

$$- 185 * (a_1 t)$$

$\overline{P}_{\text{pouch}} = 220$ (ml / pouch * day * atm)

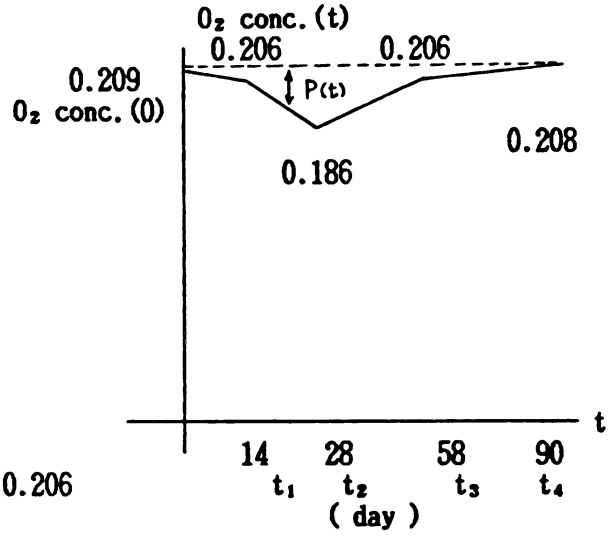
$0 \leqq t \leqq 14.0$

$a_1 = - 0.00021$

O_2 conc.(t) = - 0.00021t + 0.209 (atm * ml / ml)

$$O_2 \text{ consumed} = 220 * \left(- \frac{0.00021}{2} t^2 \right) + 185 * 0.00021 * t$$

$$= 0.023t^2 + 0.039t$$



When	O_2 consumed
t = 14	5.1

$14 \leqq t \leqq 28$

$a_2 = - 0.00143$, O_2 conc.$(t_1) = 0.206$

$t_1 = 14$

$$O_2 \text{ consumed} = 220 * \left[\frac{0.00143}{2} * (t - 14)^2 + (0.209 - 0.206) * (t - 14) \right] + 185 * 0.00143 * (t - 14) + \left[O_2 \text{ consumed} \right]_0^{14}$$

$$= 220 * \left[\frac{0.00143}{2} * (t - 14)^2 + 0.003 * (t - 14) \right] + 0.265 * (t - 14) + 5.1$$

When	O_2 consumed
t = 20	16.3
t = 28	48.9

$28 \leqq t \leqq 58$

$a_3 = 0.00067$, O_2 conc.$(t_2) = 48.9$

$t_2 = 28$

$$O_2 \text{ consumed} = 220 * \left[- \frac{0.00067}{2} * (t - 28)^2 + (0.209 - 0.186) * (t - 28) \right] - 185 * 0.00067 * (t - 28) + \left[O_2 \text{ consumed} \right]_0^{28}$$

$$= 220 * \left[- \frac{0.00067}{2} * (t - 28)^2 + 0.023 * (t - 28) \right]$$

$$- 0.124 * (t - 28) + 48.9$$

When	O_2 consumed	When	O_2 consumed
t = 38	106	t = 58	131
t = 50	122		

$58 \leqq t \leqq 90$

$a_4 = - 0.000067$, O_2 conc. $(t_3) = 131$

$t_3 = 58$

O_2 consumed

$$= 220 * \left[\frac{0.000067}{2} * (t - 58)^2 + (0.209 - 0.206) * (t - 58) \right.$$

$$\left. + 185 * 0.000067 * (t - 58) + [O_2 \text{ consumed}]_0^{58} \right.$$

$$= 220 * \left[- \frac{0.000067}{2} * (t - 58)^2 + 0.003 * (t - 58) \right]$$

$$+ 0.0124 * (t - 58) + 131$$

When	O_2 consumed
t = 90	135

$$\text{AOR} (0 - 20 \text{ days}) = \frac{16.3}{20} = 0.82$$

$$\text{AOR} (20 - 50 \text{ days}) = \frac{122 - 16.3}{30} = 3.5$$

$$\text{AOR} (50 - 90 \text{ days}) = \frac{135 - 122}{30} = 0.34$$

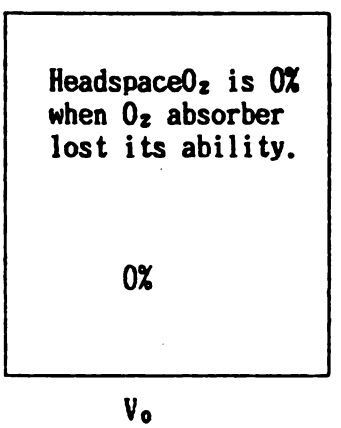
APPENDIX 6

Calculation of the amount of permeated O_2 by iterative way

Calculation method

Amount of permeated O_2 changes depending upon the pressure difference between outside and inside the package. This pressure difference is influenced by the package headspace, time, and permeability of the package material. In this calculation, O_2 absobed by the packaged product is ignored, however this calculation is only used at the time when the product is assumed to consume little amount of O_2.

Pressure difference is assumed not to change during 1 hour. Calculation is iterated in one hour.



First 1 hour

$$A_1 = 0.209 * \overline{P}_{pouch}$$

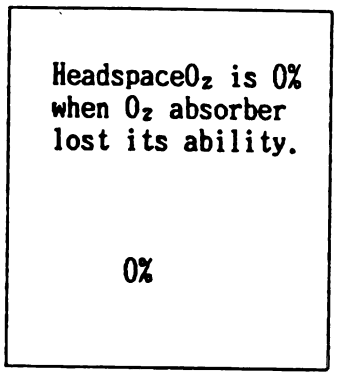
Second 1 hour

$$A_2 = \left(0.209 - \frac{A_1}{V_0} \right) * \overline{P}_{pouch}$$

Third 1 hour

$$A_3 = \left(0.209 - \frac{A_1 + A_2}{V_0} \right) * \overline{P}_{pouch}$$

0.209 (atm * ml / ml)



V_0

N th 1 hour

$$A_n = \left(0.209 - \frac{A_1 + A_2 + - - - A_{n-1}}{V_0} \right) * \overline{P}_{pouch}$$

So the amount of O_2 permeated during N hours is

$$\Sigma A_n$$

O_2 percentage inside the pouch at N hours later

$$\frac{\Sigma A_n}{V_0}$$

V_0 ; headspace (ml)

$\overline{P}_{pouch}$; permeability of the pouch (ml / pouch * hour * atm)

A_n ; amount of O_2 permeated from N-1 to N hours (ml)

0.209 ; outside O_2 partial pressure (atm * ml / ml)

Calculation for permeated O_2 amount of PE pouched sample after O_2 absorber lost its ability (41°C, 40%RH, PE, 21% initial headspace O_2)

Here $V_0 = 185$ (ml)

$\overline{P}_{pouch} = 9.17$ (ml / pouch * hour * atm)

hours	$\frac{A_1 + A_2 + - - + A_{n-1}}{V_0}$	$A_n = \left(0.209 - \frac{A_1 + A_2 + - + A_{n-1}}{V_0} \right) * \overline{P}_{pouch}$
1	0	1.92
2	0.0104	1.82
3	0.0202	1.73
4	0.0296	1.65
5	0.0385	1.57
6	0.0470	1.49
7	0.0550	1.41
8	0.0626	1.34
9	0.0699	1.28
10	0.0718	1.21

hours	$\frac{A_1 + A_2 + - - + A_{n-1}}{V_0}$	$A_n = (0.209 - \frac{A_1 + A_2 + - + A_{n-1}}{V_0}) * \overline{P}_{pouch}$
11	0.0833	1.15
12	0.0895	1.10
13	0.0918	1.07
14	0.0976	1.02
15	0.103	0.971
16	0.108	0.924
17	0.113	0.880
18	0.118	0.837
19	0.123	0.793
20	0.127	0.749
21	0.131	0.715
22	0.135	0.680
23	0.139	0.645
24	0.142	0.610
25	0.145	0.584
26	0.148	0.558
27	0.151	0.532
28	0.154	0.505
29	0.157	0.479
30	0.160	0.453
31	0.162	0.427
32	0.164	0.410
33	0.166	0.392
34	0.168	0.375
35	-	-
36	-	-
37	-	-

ΣA_{28} (hours) ; 29.1 ml ——— 15.7% headspace O_2

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