CLIN 0014 Data Item

"Thermal In-Pouch Microwave Sterilization" Contract No. W911QY-09-C-0205

Data Item A0002 Contract No. W911QY-09-C-0205

Final Scientific Report

Printpack, Inc. Atlanta, GA

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*: 09-01-2012

2. REPORT TYPE: Final

3. DATES COVERED *(From - To)*: 26 Sept 2009 - 06 Jan 2012

4. TITLE AND SUBTITLE

Thermal In-Pouch Microwave Sterilization

5a. CONTRACT NUMBER: W911QY-09-C-0205

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Minkow, Linda, E.

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Printpack, Inc.
2800 Overlook Parkway
Atlanta, GA 30339

8. PERFORMING ORGANIZATION REPORT NUMBER

55155

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Natick Contracting Division
ATTN: AMSRD-ACC-N Building 1
Kansas St.
Natick, MA 01760-5011

10. SPONSOR/MONITOR'S ACRONYM(S)

NSRDEC

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

20120305090

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

Polymeric flexible pouch laminations with high oxygen and water vapor barrier (OTR and WVTR, respectively) were optimized to better meet the US Army specification for WVTR. The optimized structure was evaluated for light barrier and found to protect food simulants from photo-oxidation. The selected optimized structure was used to process chicken and dumplings entrée items by Microwave Assisted Thermal Sterilization (MATS), and validation studies were performed per FDA and USDA filing requirements. Additionally, Time-Temperature Indicator (TTI) ink was developed and applied on the pouch to demonstrate that the sterilization temperature was maintained for sufficient time through the process. Modeling software was utilized, using known inputs for single materials and complete laminations, to dynamically model the shelf life of the packaged entrée items through temperature and humidity changes typically seen throughout the extended shelf life of the items.

15. SUBJECT TERMS

Oxygen barrier, moisture barrier, light barrier, microwave sterilization, MRE entrée, polymeric laminations, time-temperature indicator, shelf-life modeling, photo-oxidation

16. SECURITY CLASSIFICATION OF: U			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
U	U	U	U		

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

REPORT DOCUMENTATION PAGE (5F298)
(Continuation 5heet)

5ubmissions or publications under Natick sponsorship during this Contract

Thomas J. Dunn, 2010; *Non-Foil High Barrier Laminations FlexPackCon 21-24 Feb 2010*, Society of Plastics Engineers, 5outh Texas 5ection, Houston, TX, 8 pp. (Based on FY08 results, see DOD Contract W911QY-08-C-0132)

Thomas J. Dunn, 2010; *Non-Foil High Barrier Laminations for Advanced Food Processing*; Research and Development Association; Fall meeting, Lake Tahoe, NV, 8 pp. (Based on FY08 results, see DOD Contract W911QY-08-C-0132)

5upported Personnel Metrics for this Reporting Period (1 5ept 2009- 31 Dec 2011)

Name	% supported	%Full Time Equivalent (FTE)
Thomas J. Dunn	50	100
Amy Whiteman-5herrill	15	100
Linda Minkow	35	100

Expenditures for this Contract (1 5ept 2009- 31 Dec 2011)

CATEGORY	TOTAL CONTRACT	6 JAN 2012
Direct Labor	$232,930	$108,189.04
Tax & Benefits	$84,511	$38,948.05
Overhead	$135,996	$62,749.64
Labor Total#	$453,437	$209,886.73
Consulting	$544,500	$587,353.27
Materials	$70,850	$327,651.27
Travel	$24,530	$19,759.50
Other Direct*	$160,760	$97,748.00
Total	$1,254,077	$1,242,398.77
10% Fee	$125,409	$124,239.88
Grand Total	$1,379,486	$1,366,638.65

Much of the in-plant budgeted labor included in Materials' total

* Equipment at Printpack Analytical Services Lab.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Equipment Purchased with Government Funds

ITEM	MODEL	VENDOR	PRICE
Oxygen Transmission Test Module + Env. Chamber + Operating System	OXTRAN® 2/21 SL	Mocon, Minneapolis, MN 55428	$61,641
Leap Autosampler System	LEAP Combi PAL	Quantum Analytics, Foster City, CA 944049-1135	$36,107
		TOTAL	$97,748

All items are in the Printpack Analytical Services Lab, 5 Barber Industrial Ct., Villa Rica, GA 30180.

Thermal In-Pouch Microwave Sterilization

Preface

This report comprises an overview of the Objective, Background, Methods, Results, and Conclusions of this contract. These are then followed by six (6) detailed reports on its specific research activities. Future work is planned to evaluate the polymeric barrier material for quality, physical and barrier properties over accelerated shelf-life testing using traditional and novel food processing technologies.

1. Executive Summary

Several goals motivate the US Army Natick Soldier Research, Development, and Engineering Center (NSRDEC) to develop non-foil alternatives for the packaging materials now used to package various field ration items. In doing so, the protection afforded the rations from environmental oxygen, water vapor, and light by foil must be replaced by alternate materials. This study optimized polymeric laminations to provide oxygen and light barrier at levels measured in field-worn ration packaging; while they do not reach desired moisture barrier levels, the optimization process has brought them closer to desired levels. Packages of an entrée item, chicken and dumplings, were processed and incubated to produce a validation report in the method of an FDA filing. Shelf-life modeling software was utilized to evaluate the materials over standard as well as extreme conditions of temperature and humidity that the MRE items could experience over its shelf-life. Additionally, Time-Temperature Indicator (TTI) ink technology was developed and applied on-pouch as a sensor to indicate that package had seen the proper processing conditions.

2. Objective

The technical objective of this contract is to research and develop "Packaging technology based on non-foil high barrier polymeric material…needed to ensure protection against oxygen, moisture vapor, microbial, and insect penetrants to maintain integrity throughout the military logistics system, and to provide rations with a minimum three year shelf life." "Technology is needed to develop advanced materials/films/coatings for flexible, semi-rigid and rigid polymeric containers that provide physical and chemical protection comparable to traditional aluminum foil-based high barrier polymeric materials. Determine compatibility of non-foil high barrier polymeric material for both thermoprocessing and novel thermal/nonthermal processing, e.g. microwave or high pressure processing." Additionally, "Technology is needed to develop a model that will predict the barrier performance of film structures incorporating multiple high barrier technologies, while taking into account environmental variables such as temperature and relative humidity, as well as the packaged product" (NSRDEC, 2009). This report compiles the work done by Printpack Inc. under the subject contract to address these needs. Specifically, the following goals were addressed by the research:

1. To optimize the polymeric barrier packaging materials to better meet moisture barrier levels necessary for the 3 year shelf-life.
2. To evaluate the optimized structure with regards to oxygen, moisture and light barrier as well as physical properties to ensure it will maintain structural integrity through processing, handling and storage.
3. To process entrées with Microwave Assisted Thermal Sterilization (MATS) and successfully validate the processing technology through FDA filings.
4. To model standard and extreme shelf-life scenarios using novel modeling software.
5. To develop and evaluate an on-pouch time-temperature indicator (TTI) to assist with process quality control.

3. Background

The cited "physical and chemical protection" comparable to traditional aluminum foil-based combat ration packaging material is, for the present time, only qualitatively understood. The Army NSRDEC requires three-year shelf life for rations stored at 27°C (80°F) or six months at 38°C (100°F). At present, trained taste panels determine if packaged rations stored at indicated temperatures remain acceptable for warfighter consumption (Ratto et al, 2006). Empirical determination of the actual oxygen and water vapor barrier of current foil laminations damaged by normal storage and transport abuse indicate these specifications for a packaging material:

- OTR $\leq$0.06 cc/m^2/day
- WVTR $\leq$0.01 g/m^2/day

(DOD Specification Mil.-PRF-44073F)

Optimization was performed using data and materials identified during previous research done under contract W911QY-08-C-0132 in order to meet the WVTR requirements (OTR requirements were achieved previously). The optimized structure was evaluated for light barrier and found to protect food simulants from photo-oxidation. The selected optimized structure was then used to process chicken and dumplings MRE entrée items by Microwave Assisted Thermal Sterilization (MATS), and validation studies were performed per FDA filing requirements. Additionally, Time-Temperature Indicator (TTI) ink was developed and applied on the pouch to demonstrate that the sterilization temperature was maintained for sufficient time through the process. Modeling software was utilized, using known inputs for single materials and complete laminations, to dynamically model the shelf life of the packaged entrée items through temperature and humidity changes typically seen throughout the extended shelf life of the items.

This final report summarizes previous reports addressing the above-mentioned five goals and incorporates them as annexes here.

1. Methods

1. *Quantification of Hexanal in Yogurt and Extra Virgin Olive Oil as an indicator of Photo Oxidation*: An automated headspace SPME-GC-MS (solid phase micoextraction-gas chromatography-mass spectrophotometery) method was developed to quantify the ability of 10 polymeric packaging material variables to protect food products (specifically yogurt and extra virgin olive oil) from light-catalyzed degradation of linoleic acid to hexanal. Several alternative opacifying tactics were evaluated to assess their effectiveness compared to current opaque aluminum foil laminations.

2. *Physical Properties Report*: The Printpack research team created 10 polymeric packaging material variables, taking into consideration different approaches to light barrier, structural and barrier integrity through the retort process, and cost. Physical and barrier properties were measured at Printpack Analytical Services

Lab. Dielectric constant and loss factor were measured at Washington State University.

3. *Microwave Sterilization Validation Report*: Chicken pieces were identified as receiving the lowest thermal lethality using the chemical-marker based computer-vision method. Ellab sensors were used to measure the temperatures profiles to locate the cold spot. Heat penetration (HP) tests were conducted to achieve a target F_0 of 6.0 minutes inside the chicken piece placed at the cold spot in chicken-dumpling pouches at the end of complete thermal process. PA 3679 # 308 *Clostridium sporogenes* spore crop was used to calculate average D-values for the different temperatures and determine the z-value of PA 3679 spores in chicken breast. Process schedules and inoculation levels were determined for the inoculated pack studies. The pouches were processed, incubated and observed every day for the first 5 days and every 5 days thereafter for 3 months.

4. *Development of Time/temperature Indicator Labels for Microwave Sterilization Process*: Co-topo-polymeric indicator compositions have been adapted as an ink medium suitable for confirming the exposure of a printed label on a flexible pouch to a target temperature for an indicated interval. The ink was printed onto heat resistant pressure sensitive-coated film and adhered to the outer surface (oriented polyester) of polymeric laminated pouches and processed in a microwave sterilization process.

5. *Shelf Life Modeling Report – Standard and Extreme Scenarios*: Various model inputs about the packaging materials with known O_2TR values for base and coated films were used to dynamically model the shelf life of MRE Chicken & Dumpling entrée, peanut butter dessert bar, and mango peach applesauce combat rations with M-RULE® modeling software under standard and extreme temperature and humidity conditions.

6. *Development of On-Pack Time-Temperature Indicator Ink for Microwave Sterilization*: The ink developed in Task 4 was reverse-printed onto the outer surface (oriented polyester) of polymeric laminated pouches and backed with a retort-grade white ink for visualization. Some samples were laminated without white ink to determine effects of adhesive chemistry and pigmentation on the color development of the TTI ink.

4. Results

Individual reports for each of the six tasks are included as annexes 1-6. Following are summaries of key findings by task:

1. *Quantification of Hexanal in Yogurt and Extra Virgin Olive Oil as an indicator of Photo Oxidation*: The SPME-GC-MS protocols for yogurt and extra-virgin olive

oil were able to measure hexanal in the 0.1 ppm range. All ten light-barrier polymeric samples demonstrated very good opacity to 200-400 nm ultraviolet light. Appropriate controls and calibration indicate that this UV barrier protects these food systems from lipid photooxidation.

2. *Physical Properties Report*: As in previous work (Dunn, 2009) on non-foil barrier laminations, these laminations are able to meet the DOD target for oxygen barrier, but fall short of the water vapor target. Structure 6 (with the sub-retort grade Al_2O_3-coated OPET) in flat, protected form, did demonstrate improved moisture barrier compared to Structure 5 (with the retort grade Al_2O_3-coated OPET), but the advantage was not maintained after the gelbo flexing abuse. Physical properties for stiffness and unit weight confirmed previous research findings that polymeric pouches are comparable to or better than foil laminations in these matters. Dielectric properties of the polymeric laminations followed expected patterns. Light barrier levels needed for protecting package contents from photodegradation effects can be provided without impairing the efficiency of the MATS process.

3. *Microwave Sterilization Validation Report*: Results showed that the developed MW sterilization processing delivered expected lethality to *C. sporogenes* PA 3679 spores. Forty chicken-dumpling pouches processed in MW for F_0=6.2 min and 40 pouches processed in hot water for F_0=6 min were shipped to Natick for shelf-life testing.

4. *Development of Time/temperature Indicator Labels for Microwave Sterilization Process*: Co-topo-polymeric compositions can be developed and adapted for the time and temperature process conditions present during microwave sterilization. A bench top procedure for screening and evaluation of compositions satisfactorily predicts behavior of the label in the MATS structure.

5. *Shelf Life Modeling Report – Standard and Extreme* Scenarios: The M-RULE® Container Performance Model for Foods has clearly been shown to validate various model inputs for base and coated films with known O_2TR and MVTR values as well as composite foil and non-foil structures. These inputs have subsequently been used in modeling the anticipated shelf-life of representative combat ration items (an entrée, a fruit sauce and a dessert) over varying storage conditions in the foil and non-foil packages. The results have clarified the progress made in the oxygen and moisture barriers of the non-foil film while pinpointing areas for improvement in future research.

6. *Development of On-Pack Time-Temperature Indicator Ink for Microwave Sterilization*: The Time-Temperature Indicator ink technology is effective when printed on an orange background, as perfomed under laboratory conditions, but final color referencing is difficult to achieve compared with printing the TTI with a white backing and knockout reference color. Ideally for production articles, the TTI ink should not be in direct contact with the laminating adhesive.

References

NSRDEC, 2009; *Broad Agency Announcement "Solicitation Number "09 - 11 Natick BAA"*; Natick, (Ma); pp40-44.

Ratto, Jo Ann, J. Lucciarini, C. Thellen, D. Froio, and N. A. D'Souza, 2006, *The reduction of Solid Waste Associated with Military Ration Packaging* , US Army Soldier System Center, Technical Report, Natick (Ma) TR-06/023. 75pp.

Specification "Mil.-PRF-44073F", 4 September 2001; Requirements 3.1.1.2 and 3.1.1.3 using ASTM D3985 and F372 respectively

Project Expenses as of 6 Jan, 2012

Direct Labor	**108,189.04**
Tax & Benefits	**38,948.05**
Overhead	**62,749.64**
Labor Total	**$209,886.73**
Travel	**19,759.50**
Consulting: & Services	**587,353.27**
Materials & Plant Costs	**327,651.27**
Other Direct Costs	**97,748.00**
Total	**$1,242,398.77**
10% Fee	**$124,239.88**
Grand Total	**$1,366,638.65**

Equipment Purchased with Government Funds

ITEM	MODEL	VENDOR	PRICE
Oxygen Transmission Test Module + Env. Chamber + Operating System	OXTRAN® 2/21 SL	Mocon, Minneapolis, MN 55428	$61,641
Leap Autosampler System	LEAP Combi PAL	Quantum Analytics, Foster City, CA 944049-1135	$36,107
		TOTAL	$97,748

All items are in the Printpack Analytical Services Lab, 5 Barber Industrial Ct., Villa Rica, GA 30180.

Exhibit B for CLIN 0015

CONTRACT DATA REQUIREMENTS LIST
(2 Data Items)

Form Approved
OMB No. 0704-0188

A. CONTRACT LINE ITEM NO.	B. EXHIBIT	C. CATEGORY
0015	B	● TDP ○ TM ○ Other

D. SYSTEM / ITEM	E. CONTRACT / PR NO.	F. CONTRACTOR
Technical Data - B001 and B002	W911QY-09-C-0205	PRINTPACK, INC.

Data Item B001

Field	Value
1. DATA ITEM NO.	B001
2. TITLE OF DATA ITEM	Photodegradation Report
3. SUBTITLE	
17. PRICE GROUP	
4. AUTHORITY (*Data Acquisition Document No.*)	
5. CONTRACT REFERENCE	Sections B & F
6. REQUIRING OFFICE	
18. ESTIMATED TOTAL PRICE	
7. DD 250 REQ	NO
8. APP CODE	N/A
9. DIST STATEMENT REQUIRED	
10. FREQUENCY	ASREQ
11. AS OF DATE	
12. DATE OF FIRST SUBMISSION	
13. DATE OF SUBSEQUENT SUBMISSION	

16. REMARKS
Photodegradation Report on 10 laminations cited in Contractor's proposal will be provided as a deliverable under CLIN 0004, which will be completed by 31 January 2010.

14. DISTRIBUTION a. ADDRESSEE	b. COPIES Draft	Final Reg	Final Repro
STEPHEN MOODY	0	1	0
15. TOTAL	0	1	0

Data Item B002

Field	Value
1. DATA ITEM NO.	B002
2. TITLE OF DATA ITEM	Physical Properties Report
3. SUBTITLE	
17. PRICE GROUP	
4. AUTHORITY (*Data Acquisition Document No.*)	
5. CONTRACT REFERENCE	Sections B & F
6. REQUIRING OFFICE	
18. ESTIMATED TOTAL PRICE	
7. DD 250 REQ	NO
8. APP CODE	N/A
9. DIST STATEMENT REQUIRED	
10. FREQUENCY	ASREQ
11. AS OF DATE	
12. DATE OF FIRST SUBMISSION	
13. DATE OF SUBSEQUENT SUBMISSION	

16. REMARKS
Physical Properties Report on 10 laminations cited in Contractor's proposal will be provided as a deliverable under CLIN 0003, which will be completed by 28 February 2010.

14. DISTRIBUTION a. ADDRESSEE	b. COPIES Draft	Final Reg	Final Repro
STEPHEN MOODY	0	1	0
15. TOTAL	0	1	0

G. PREPARED BY	H. DATE	I. APPROVED BY	J. DATE
STEPHEN MOODY	17-Sep-2009	STEPHEN MOODY	17-Sep-2009

Data Item B001 Contract No. W911QY-08-C-0132

Photodegradation Report

Printpack, Inc. Atlanta, Ga

Quantification of Hexanal in Yogurt and Extra Virgin Olive Oil as an indicator of Photo Oxidation

Frank A. Kero[1], David E. Foster[1], Marty Stanley[1], Thomas Dunn[1]

Abstract

An automated headspace SPME-GC-MS (solid phase micoextraction-gas chromatography-mass spectrophotometery) method was developed to quantify the ability of polymeric packaging materials to protect food products (specifically yogurt and extra virgin olive oil) from light-catalyzed degradation of linoleic acid to hexanal. Several alternative opacifying tactics were evaluated to assess their effectiveness compared to current opaque aluminum foil laminations. All proved as effective as the foil material at the limits of detection of the method (~0.1 ppm).

Background

Military rations are currently packaged in multilayer aluminum-foil laminations which provide significant oxygen, water vapor, and light barrier. For a variety of reasons (Ratto et al., 2006) the military seeks to convert packaging for such rations to non-foil, polymeric packaging materials.

The rations contain a variety of light-sensitive lipids and micronutrients whose integrity is critical to the energy and nutritional effectiveness of the rations for the warfighter.

Mestdagh et al. (2005) found that "...an adequate light barrier, which did not transmit any wavelength of the [UV] spectrum, was apparently sufficient to avoid the light induced oxidation...is a suitable package for the storage of UHT semi-skimmed milk at room temperature during some months

Mendez and Falk (2007) found reported greater degree of oxidative rancidity in extra virgin olive oil stored in transparent or white opaque plastic bottles and glass bottles than olive oil packaged in paper/aluminum-foil laminations or metal containers.

With the diversity of photo-oxidative sensitive food systems in combat rations, previous experimental work and their commercial availability, yogurt and extra virgin olive oil were chosen to simulate the light-barrier effectiveness of ten non-foil polymeric packaging materials prepared by Printpack as candidates to replace the current aluminum foil laminations.

---

[1] Printpack, Inc. Atlanta, Georgia, USA

Materials and Methods

Laminations

The choice of polymeric materials to replace the aluminum foil laminations used by the US Army for military rations is constrained by the necessity of maintaining a three-year shelf life for the field rations. Oxygen, water vapor and light barrier, weight, stiffness, durability and ease of opening are among the other constraints in redesigning packaging materials for laminations. Table 1 summarizes the materials currently used in aluminum foil laminations to satisfy current design constraints for heat-sterilized (retort) packaging materials.

Table 1: Functional Contributions of Materials in Foil Laminations

MATERIAL	FUNCTIONS
Biaxially Oriented Polyester (OPET)	Scuff and heat resistance (while sealing)
Biaxially Oriented Nylon (BON)	Puncture resistance, durability
Aluminum Foil	Oxygen, water vapor barrier, opacity
Polyolefin	Durable, hermetic, temperature resistant seals

In designing non-foil polymeric laminations alternatives, Printpack planned to use the familiar polymeric materials use in the foil laminations, coated with robust high oxygen and water vapor coatings in order to minimize the functional impact on other design constraints. The high barrier coated films are commercially available as low-haze, highly transparent products. Printpack's options for delivering light barrier to the non-foil polymeric laminations include pigmented adhesives, and opaque polyolefin sealants.

Carbon black is the industry standard opacifying pigment. Because the sealant is in direct contact with food, the only carbon black type compliant with US FDA food contact material regulations is High-purity furnace black (CAS No. 1333-86-4) (ref: 21 CFR 178.3297(e)).

Alternatively, the "subtractive colors", cyan, magenta, and yellow (or "CMY"), can be used in combination to achieve an effectively opaque polyolefin sealant. US FDA food contact-compliant CMY pigments are much more abundant than the single carbon black alternative.

Table 2 outlines light barrier polymeric laminations produced by Printpack using various combinations of pigmented adhesive, carbon black, and CMY pigments.

Table 2: Barrier polymeric Laminations: Light barrier tactics							
Lamination	Outer Layer	Adhesive 1	Barrier Layer1	Adhesive 2	Barrier Layer2	Adhesive 3	Sealant Layer
1	OPET	Opaque	bOPET1	Clear	bBON	Clear	Carbon
2	OPET	Opaque	bOPET1	Clear	bBON	Clear	CMY
3	OPET	Opaque	bOPET1	Clear	bBON	Opaque	Clear
4	OPET	Clear	bOPET1	Clear	bBON	Clear	Carbon
5	OPET	Opaque	bOPET2	Clear	bBON	Opaque	Clear
6	OPET	Opaque	bOPET3	Clear	bBON	Opaque	Clear
7	OPET	Opaque	bOPET4	Clear	bBON	Opaque	Clear
8	OPET	Opaque	bOPET3	Clear	BON	Opaque	Clear
9	OPET	Opaque	bOPET1	Clear	BON	Opaque	Clear
10	OPET	Opaque	bOPET1	n/a	n/a	Opaque	Clear

bOPET1-4 Barrier coated OPET: grades 1-4
bBON Barrier coated BON

Light Barrier

The transmission of laminations 1-10 as listed in Table 2 was measured with a Shimadzu UV 160 scanning spectrophotometer over wavelengths 200 to 800 nm (Ultra violet B through near infrared including visible light wavelengths).

Opacity was measured using ASTM D589 (TAPPI T425). This paper-industry test is based on the fact that "reflectance" of a substrate when combined with a white backing is higher than that of the substrate when combined with a black backing because, in the former case, light transmitted through the imperfectly opaque sheet is largely reflected by the white backing, and a portion of the light is transmitted through the substrate a second time thus increasing the total reflection. A Tobias Opacimeter equipped with an accurate linear photometric system was used. The light source was compliant with CIE standard illuminant C, 2^{o} standard observer.

Standards and reagents

Hexanal, octanal, n-bromodecane, heptane, mcthylene chloride, isopropyl alcohol were obtained from Sigma Aldrich.

"Kroger" Brand extra virgin olive oil and "Dannon" all natural plain full fat yogurt were purchased from Kroger Supermarket in Douglasville, Ga.

Photo-degradation parameters:

The light box parameters were transferred from the pilot study performed at Virginia Tech. The yogurt and extra virgin olive oil samples were stored in a temperature and humidity controlled Hotpack 317322 environmental chamber (PAS #3). The energy of light exposure was measured using an Extech portable light meter. The temperature was 4°C. The relative humidity was 10%. This chamber has two setting for light exposure: 1) 2 lights on (-2000 Lux) 2) 4 lights on (- 4000 Lux). The lower setting was used to mimic the chamber at Virginia Tech. The samples were exposed for 96 hours to replicate the pilot study (this time period was verified using clear / non-UV blocking pouches as controls). Figure 2 shows the arrangement of samples. Samples were shuffled and rotated every 24 hours to minimize sample-to-sample variability. In this chamber, the light bulbs are mounted to the door, a slight difference from the overhanging light source used at Virginia Tech (Figure A).

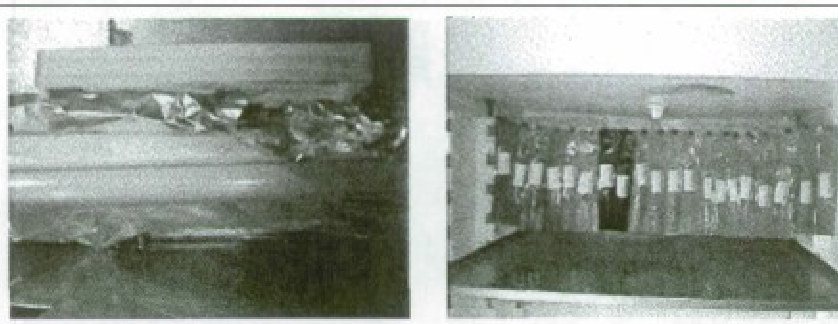


FIGURE A: Left: VA Tech's light box. Right: Printpack Analysis Services (PAS) chamber with Printpack Inc. materials 1-10 containing actual surrogate food systems.

Hardware

- Column: Agilent Carbowax 20M, 30 x 0.25 x 0.25
- Gas Chromatograph: HP-Agilent 6890N
- Detector: HP-Agilent 5973 Mass Selective Detector (MSD)
- Scan range: *m/lz* 50-550, solvent delay- off
- Autosampler: LEAP Technologies CombiPal
- 20 mL amber headspace vials with Teflon butyl caps
- SPME fiber: Supelco DYB/CAR/PDMS (50/30fun) (2 cm)
- Supelco molded thermogreen LB-2 septa with 11 mm injection hole

Software Parameters

Carrier gas: Helium 1.5 mL / min, constant flow mode
Inlet temp: 270°C
Injection mode: splitless
Oven: 40°C (I min hold), 5°C gradient / per min to 200°C (hold 2 min)
Auxiliary line to MSD: 210°C
Liner 0.75

Extraction time: 15 min with agitation 35°C (extra virgin olive oil)
Extraction temp: 15 min with agitation 60°C (yogurt)

Calibration model: yogurt

A method of internal standards was used to quantify hexanal in the headspace of yogurt. The ability of internal standard methods to improve the linear dynamic range of analytical methods has been well reported. Two candidate internal standards were evaluated. The first was n-bromodecane (nBD) due to its previously reported utility with the quantification of aldehydes in food products and has not been reported as a component of the yogUJi headspace. It was disqualified after failing to demonstrate linearity over a practical concentration range. The second candidate internal standard was octanal. Since octanal was not detected in the yogurt samples, it was evaluated and proved effective. The calibration model for this method can be described as y = mx + b, where:

1) y = (peak area hexanal / peak area octanal), m = response factor, x = (mg hexanal / mg octanal)
2) solve for the calculated weight ratio (x)
3) the calculated wt ratio x µg octanal = µg hexanal
4) µg hexanal / ~1.0-1.5 g yogurt' = µg / g

All standards and samples were prepared using amber vials. In the absence of solution stability data, all standards were prepared fresh daily. The concentration of the internal standard solution was optimized to the middle concentration of the calibration curve (maximize accuracy). The volume of the spike was 10 µL. Calculations to quantify the exact concentration were performed to correct for weight. Specifics of concentration levels are described in the following sections.

Calibration model: extra virgin olive oil

Modifications of testing procedure used for yogurt measurements:

The endogenous interferences in extra virgin olive oil were found to have a deleterious effect on the previously reported method used to measure hexanal in yogurt. For this reason, the following modifications were made.

1) Matrix-matched external calibration plot

i. Octanal, dodecane and nBD were evaluated as candidate internal standards but were disqualified after failing to produce an accurate calibration curve over the concentration region of interest.

ii. Matrix-matched standards were prepared by systematically spiking in known amounts of hexanal in to extra virgin olive that was not exposed to UV.

2) SPME optimization

i. The parameters for the extraction of hexanal in yogurt skewed the selectivity of the method to favor a competing analyte when applied to the extra virgin olive oil matrix. The parameters were re-optimized to 35 degrees C for 15 min. The %recovery for hexanal improved from 20% to 70%. The percentage recovery observed in this study was 75%-110%.

Results and Discussion

Table 3 summarizes the range of UV transmission (200-400 nm) and the visible light opacity of the 10 Printpack samples. Measured opacity was 100% for the three samples with opaque olefin sealant and ranged in the mid-to high 80's for the double opaque adhesive samples. In contrast, the maximum UV transmission in the critical range was 0.2%.

Table 3: Barrier polymeric Laminations: Light barrier Results

Lamination	% Transmission 200-400 nm	Opacity (%) ASTM D589	Opacity tactic
1	0	100	1 opaque adhesive/carbon sealant
2	0	100	1 opaque adhesive/CMY sealant
3	0-0.1	86.9	2 opaque adhesives
4	0	100	carbon sealant
5	0-0.1	85.5	2 opaque adhesives
6	0-0.1	87.8	2 opaque adhesives
7	0-0.1	88.7	2 opaque adhesives
8	0-0.2	81.4	2 opaque adhesives
9	0-0.1	85.3	2 opaque adhesives
10	0-0.1	88.9	2 opaque adhesives

Table 4 presents final conclusions regarding the precision and accuracy of the detection methods as optimized for yogurt and extra virgin olive oil respectively.

TABLE 4: Limitations of linearity		
Figure of Merit	Yogurt (internal standards)	Extra virgin olive oil (matrix-matched external standards)
Linear dynamic range (LDR)	500-5,000 ng/g	80-800 ng/g
Accuracy (% error over LDR)	<20%	2-25%
Specificity (%error due to co-eluting interferences)	<20%	<20%
Limit of detection (LOD)	80 ng/g (estimated)	40 ng/g (estimated)
Limit of quantitation (LOQ)	250 ng/g	80 ng/g (estimated)
Lower limit of quantitation (LLOQ)	500 ng/g	80 ng/g
Precision (% error at LLOQ)	< 15%	Not verified
Upper limit of quantitation (ULOQ)	10,000 ng/g	750 ng/g
%Recovery	90%	75-110%

Results of photodegradation studies:

The UV-exposed yogurt samples packaged in Printpack Inc. sample materials 1-10 did not produce a detectable level of hexanal.

Within run control to ensure data quality:

1) Internal standard peak area

A control chart was generated to monitor the peak area of the internal standard (octanal) during the run. The average peak area is pictured in green (Figure B.) The peak areas for all standards were observed within three standard deviations from the average. The error in measurements is Gaussian.

2) Bracket fortified quality control yogurt specimens

To ensure that hexanal was not generated in situ during the residence time in the autosampler, yogurt specimens that were not exposed to UV were spiked with octanal and tested at the beginning and end of the run (bracket standards). The relative error of the peak area ratio of hexanal to octanal was < 1%. The sample integrity was maintained during the test.

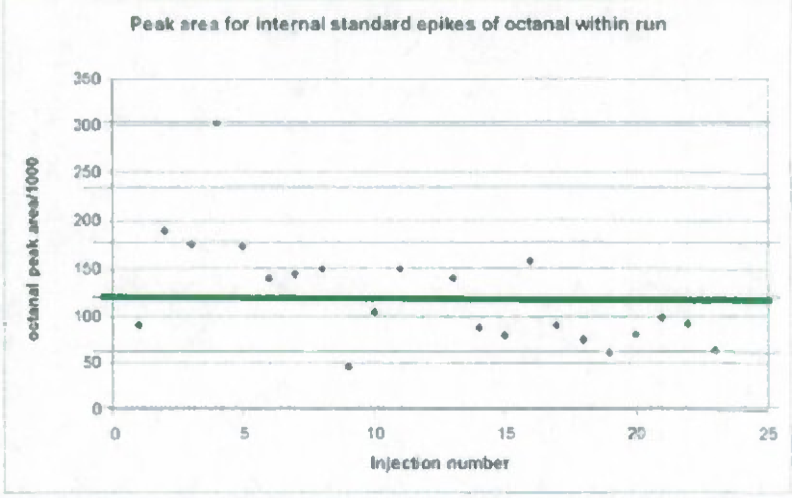


Figure B: *Control chart of the peak area for the internal standard (Yogurt) octanal as a within run quality control technique.*

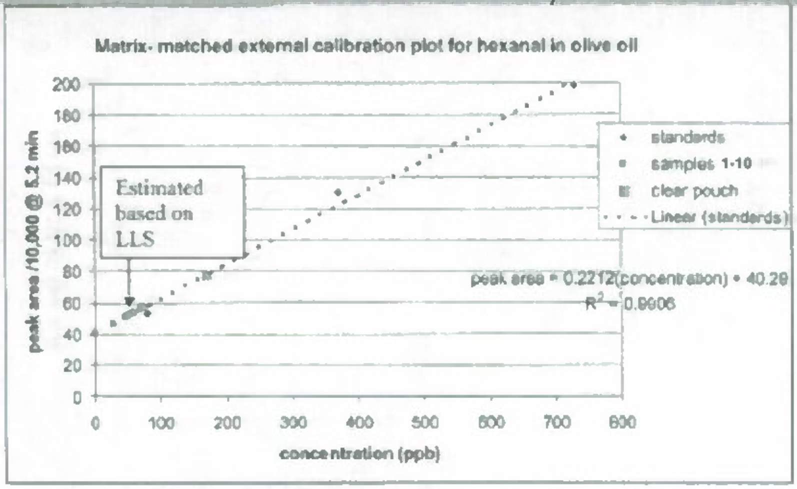
Results of study:

All light-exposed samples of yogurt had hexanal levels below the 80 ppb limits of detection of the method, as optimized, (Table 5.)

Table 5: Yogurt exposed to light for 96 hours in indicated PAS sample material	
Sample No.	Yogurt hexanal ng/g
1	< 80
2	< 80
3	< 80
4	< 80
5	< 80
6	< 80
7	< 80
8	< 80
9	< 80
10	< 80

Samples of light-exposed extra-virgin olive oil had hexanal levels below 100 ppb, the lower linearity level of the method (Figure C.)

FIGURE C: Results of measurements by HS-SPME-GC-MS:



Extra virgin olive oil exposed to light for 96 hours in sample materials 1-10 measured < 100 ppb.

Conclusions

The SPME-GC-MS protocols for yogurt and extra-virgin olive oil were able to measure hexanal in the 0.1 ppm range. All ten light-barrier polymeric samples demonstrated very good opacity to 200-400 nm ultraviolet light. Appropriate controls and calibration indicate that this UV barrier protects these food systems from lipid photooxidation.

Acknowledgements

The authors of this work gratefully acknowledge the research group of Sean O'Keefe, Ph. D. at Virginia Tech, Blacksburg, Virginia for many useful discussions during the course of this study. The authors of this work also acknowledge Walter Forrister (Printpack Inc.) for technica1 support. We acknowledge Hannah Smith (Printpack Inc.) for her support in obtaining literature references for this project. This work was funded by the United States Department of Defense (DOD).

References

Aaardt, M. v., S. Duncan. J. Marcy, T. Long, S. O'Keefe, S. Neilson Sims, 2005. *Aroma of light exposed milk stored with and without natural and synthetic antioxidants; J. Dairy Sci., 88, 881-890*

Causon, R. 1997. *Validation of chromatographic methods in biomedical analysis viewpoint and discussion J. Chromo B. 689 (I), 175-180*

Kanner, J.,I. Rosenthal;1992. *An assessment of lipid oxidation in foods; Pure & Appl. Chem. 64. 1959-1964*

Labropoulos, A., J.K. Palmer, P. Tao, 1982. *Flavor evaluation and characterization of yogurt as affected by ultra-high temperature and vat proeesses, J. Dairy Sci. 65. 191 196*

Mendez A.I., and E. Falque. 2007. *Effect of storage time and container type on the quality of extra-virgin olive oil. Food Control. 18:521-529.*

Saint-Eve, C. Levy, Y. Ducruet, I Souchon; 2008. *Quality changes in yogurt during storage in different packaging materials" Food Chem. 2008, 110 (2). 285-293*

Mestdagh F, B. De Meulenaer, J. De Clippeleer, F. Devlieghere, and A. Huyghebaert; 2005. *Protective Influence of Several Packaging Materials on Light Oxidation of Milk; J. Dairy Sci. 88:499–510*

Omar, M., N. Nor, N. ldris, 2007. *Changes of headspace volatile constituents of palm olein and selected oils after frying french fries" Pakistan J. of Bio. Sci. 10 (7), 1044-1049*

Ott, A., L. B. Fay, A. Chaintreau; 1997. *Determination and Origin of the Aroma Impact Compounds of Yogurt Flavor J. Agric. Food Chem. 45 (3), 850-858*

Pastorelli, S., L. Torri. A. Rodriguez, S. Yalzacchi. S. Limbo and C. Simoneau, 2007. *Solid-phase microextraction (SPME-GC) and sensors as rapid methods for monitoring lipid oxidation in nuts; Food Add. and Contam. 24 (II), 12191225*

Ratto, J. A., J. Lucciarini, C. Thellen, D. Froio, and N. A. D'Souza, 2006. *The reduction of Solid Waste Associated with Military Ration Packaging, , US Army Soldier System Center, Technical Report, Natick (Ma) TR-06/023. 75pp*

Saint Eve A., C. Levy, M. Moinge, V. Ducruet, I. Souchon, 2008. *Quality changes in yogurt during storage in different packaging materials; Food Chem. 110, 285-293*

Sanchez-Silva A., A. Rodriguez-Bernaldo de Quiros, J. Lopez-Hernandez, P. Pasiero-Losada. 2004. *Determination of hexanal as indicator of the lipid oxidation state in potato crisps using gas chromatography and high performance liquid chromatography J. Chrom A. 1046.75-81*

Snow, N., G. Siaek, 2002. *Head-space analysis in modern gas chromatography" TrAC Trends in Analytical Chemistry, 21,608-617*

Verhoeven, H., 1. Beurele, W. Sehwab, 1997. *Solid-phase microextraction artifact formation and its avoidance; Chromatographia, 1997,46. 63-66*

Wang Y, Ocariz J. Hammersand J, MaeDonald E, Bartczak A, Kero F, Young Y, Williams K., 2008. *Determination of Cinnamaldehyde in Cinnamon by SPME-GC-MS: An Instrumental Analysis Experiment" Journal of Chemical Education, 85,957*

Xu, H., D. Song, Y. Cui, S. Hu, Q. Yu, Y. Feng, 2009. *Analysis of hexanal in human blood by simultaneous derivatization and dispersive liquid-liquid microextraction then LC-APCI-MS-MS Chromatographia, 9, 70, 775-780.*

Data Item B002 Contract No. W911QY-08-C-0132

Physical Properties Report

Printpack, Inc. Atlanta, Ga

Thermal In-pouch Microwave Sterilization

Task 2: *Physicals Report*

Contract No. W911QY-09-C-0205   CLIN0003

Printpack Inc, Atlanta, Ga

Printpack Inc, Atlanta, Ga

Thomas Dunn, Principle Investigator

Introduction

The Combat Feeding Directorate has the following barrier targets for its MRE packaging materials (Ratto et al. 2006):

- WVTR: 0.01 gm/m^2-day
- O_2TR: 0.06 cc/m^2-day

The critical CFD design requirement for packaged MRE rations is a shelf life (as determined by organoleptic testing) of 3 years at 27°C (80 °F) or 6 months at 38°C (100 °F). Prior work (Dunn, 2009) suggested that 6 month shelf life with 38 °C storage achieved by barrier levels comparable to those achieved by the 10 trial laminations in this study (Annex I) could meet that shelf life requirement. That same work indicated the need for substantial opacity of the packaging material, especially in UV wavelengths, so as to prevent photodegradation of fats, nutrients, etc.

Other critical design parameters for MRE pouches are 1) minimal or no added weight (for ease of field use and minimal transport costs) and 2) adequate stiffness (to accommodate fill-seal line operation). In the current study, 915 MHz microwave sterilization (MWS) is intended for processing entree items (Tang, et al., 2008). Efficiency in that process requires the packaging material be 3) essentially transparent to the microwave energy. All-polymeric, non-foil, laminations were evaluated with the MWS process in mind. Again prior work (Mikhaylenko, 2009) had developed methods for characterizing microwave interactions of such flexible materials

Methods

Trial Laminations

Consideration of barriers to oxygen (O_2TR), water vapor (WVTR), and light directed selection of materials for the trial laminations. These materials and comments about the features of each are summarized in Tables 1 (the laminations) and 2 (component films).

Three approaches evaluated light barrier:

1. Carbon black-pigmented sealant
2. 3-subtractive colors-pigmented sealant
3. 1 or 2 layers of olive drab-pigmented adhesive.

Samples 1-4 (Table 1) differed in the nature of the opacifying layers but had essentially identical barrier components.

Samples 4 and 5 compared a "retort" grade Al_2O_3-coated OPET to a "sub-retort" grade reported to have better moisture barrier. The latter was expected to withstand the shorter thermal cycle of a MWS Process. Sample 7 used a polyvinylidene chloride-coated OPET film as a barrier layer. Samples 8-10 tested cost savings alternatives with an uncoated BON substituted for the hybrid coated film (samples 8 and 9) and no nylon layer at all (sample 10).

Measurements

Tensile and other properties of the laminations were measured using standard ASTM methods for flexible barrier materials. UV-visible spectrophotometry (PerkinElmer Model:

Lambda 35 UV/Vis Spectrometer) over the range 200-800 nm was used to assess the effectiveness of the light barrier features. Additionally, "opacity" (ASTM D589) measurements were obtained using a Thwing-Albert "HTM 1"opacimeter.

Standard ASTM methods for oxygen and moisture barrier determination were determined using Mocon Inc. instruments, Ox-Tran® 2/21 SL and Permatran-W® 3/33 respectively.

The Washington State University method (Mikhaylenko, 2009) was used to measure the dielectric constant (*e'*) and dielectric loss factor (*e''*) of thin film laminations. Regarding these parameters: "*e'*" reflects the ability of a material to store electromagnetic energy, and "*e''*" measures the ability of a material to dissipate electric energy as heat. For the MWS process, low *e'* indicates a minimal tendency of the packaging to absorb microwave energy and increase its temperature. For a given *e'*, a higher *e''* implies the delivery of heat energy to the packaged food more efficiently.

These Data for each lamination are presented in Annex I. Dielectric properties are summarized in Table 3 and Figure A.

Table 1: Laminated Structures

Lam Number	Outer Layer	Barrier Layer	Barrier2 Layer	Sealant Layer	Comment
1	6	1	2	Carbon black	Opacity Tests
2	6	1	2	3-Color black	
3	6	1	2	Clear	
4	6	1	2	Carbon black	
5	6	3	2	Clear	SiO_x coating Tests
6	6	4	2	Clear	
7	6	5	2	Clear	saran coating
8	6	4	7	Clear	Costs Saving Tests
9	6	1	7	Clear	
10	6	1	n/a	Clear	
	: pigmented adhesive layer				

Table 2: Component Materials for Lamination

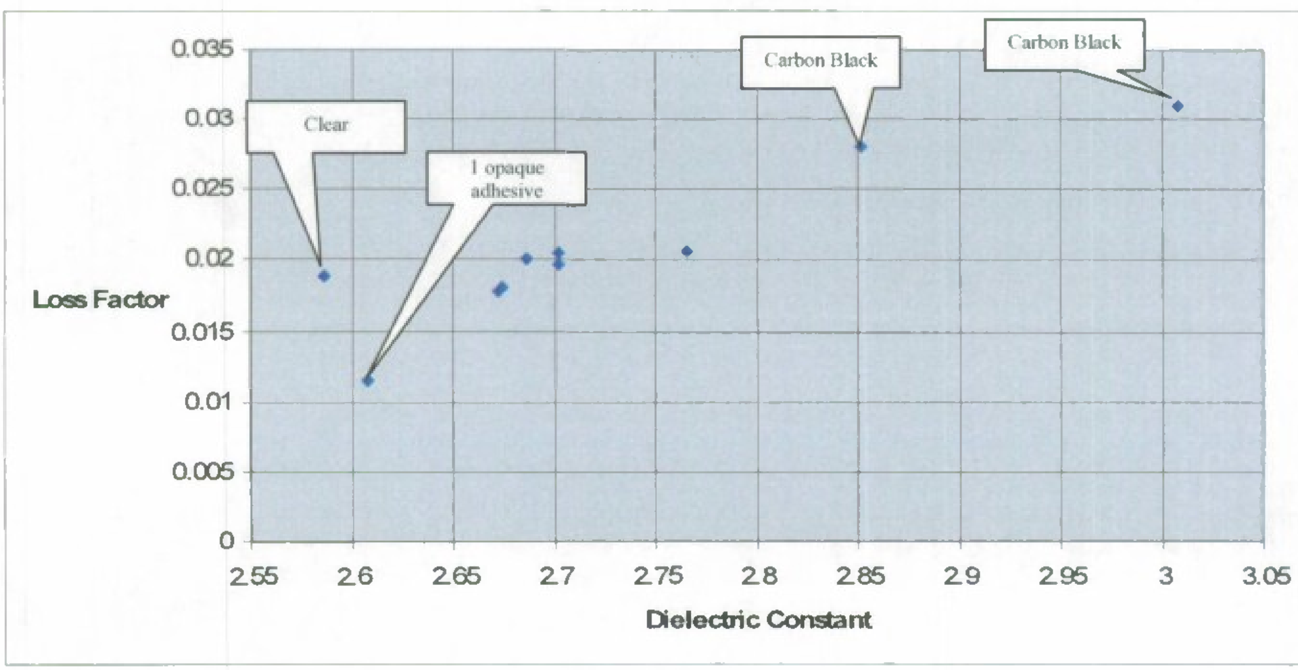
No.	Name	Description	Comment	O_2TR @ gauge cc•day/m^2	WVTR @ gauge gm•day/m^2
1	Hybrid-ctd OPET*	12µ Organic/inorganic coated OPET	PVOH and nano clay coating?	85% RH; 0.3	50
2	Hybrid-ctd BON*	15µ Organic/inorganic coated BON	PVOH and nano clay coating?	85% RH; 0.5	240
3	AlO_x-ctd OPET #1	12µ aluminum oxide coated OPET	"Standard retort" grade (primer determined)	.31	1.3
4	AlO_x-ctd OPET #2	12µ aluminum oxide coated OPET	"Sub- retort" grade (primer determined)	.31	1.1
5	PVdC-ctd OPET	12µ polyvinylidene coated OPET	"saran" coating	14	12
6	OPET	12µ biaxially oriented polyester		140	38
7	BON*	15µ biaxially oriented nylon 6		50% RH: 50 90% RH:150	50% RH: 110 90% RH: 310
8	CPP	75µ cast polypropylene	Sealant: thermally steri-lized/stabilized foods	990	4
9	mPE	75µ blend with "metal-locene" polyethylene	Sealant: hot and am-bient packed foods	2600	5

* Moisture sensitive barrier performance

Table 3: Dielectric Properties

Sample	Opacifier description	Thickness µ	e'	e"
1	Carbon black / 1 opaque adhesive	119	3.0084 ± 0.016	0.0310 ± 0.0008
2	3-Color black / 1 opaque adhesive	126	2.7661 ± 0.031	0.0206 ± 0.0007
3	Clear sealant	134	2.5863 ± 0.036	0.0189 ± 0.0009
4	Carbon black / 2 opaque adhesives	131	2.8521 ± 0.001	0.0280 ± 0.0002
5	Clear sealant / 2 opaque adhesives	124	2.7027 ± 0.046	0.0205 ± 0.0009
6	Clear sealant / 2 opaque adhesives	126	2.6869 ± 0.042	0.0200 ± 0.0009
7	Clear sealant / 2 opaque adhesives	124	2.7025 ± 0.044	0.0196 ± 0.0010
8	Clear sealant / 2 opaque adhesives	124	2.6720 ± 0.050	0.0178 ± 0.0009
9	Clear sealant / 2 opaque adhesives	125	2.6742 ± 0.009	0.0181 ± 0.0002
10	Clear sealant / 1 opaque adhesive	103	2.6076 ± 0.011	0.0115 ± 0.0002

Figure A: Dielectric properties



Results

Pouch Weight

A standard MRE entrée pouch fabricated from the specified foil lamination weighs about 5.24 grams each. Each of the 10 trial laminations makes lower weight pouches. The four ply laminations with the two hybrid-coated films weighed about the same as the foil lamination, while the three ply lamination was only 40% of the foil one.

Pouch stiffness

Stiffness (as measured by modulus) affects the efficiency and waste experienced when forming packages and filling them with product. Foil is relatively stiff and so packaging lines optimized to run foil laminations most likely require comparably stiff polymeric materials or mechanical adjustments in order to run effectively and efficiently. The polymeric laminations produced for this study all had 1% secant modulus values in the 1,200 to 1,700 N/ mm^2 range. Standard foil lamination material has a value of about 1,350. The differences indicate that no significant changes for pouch forming and filling are needed.

Dielectric properties

As expected, the opaque pouches made with carbon black pigmented sealants had the highest dielectric constants (about 3). They also had high loss factors. Pouches with color-manufactured black sealants and those with pigmented adhesives had intermediate values of both. By way of comparison, Guan et al. (2004) determined that the values of e' and e'' for mashed potatoes at 915 MHz were in the ranges of about 55-66 and 21-36 respectively. The effect of dielectric properties of the packaging material on MWS process efficiency is not quantified at this point, but appears to be small.

Barrier considerations

Table 4 summarizes the performance of each sample lamination to the respective WVTR and OTR targets. At this pass/fail level, the laminations show reasonable agreement with expected similarities and differences. The hybrid-coated OPET laminations revealed moisture sensitivity, even when over-laminated with an uncoated OPET.

Table 4: Performance to Targets for 10 Printpack Laminations: ✓ exceeds target

Treatment	Sample Number									
MVTR	1	2	3	4	5	6	7	8	9	10
Flat	×	×	×	×	×	×	×	×	×	×
5 Gelbo	×	×	×	×	×	×	×	×	×	×
10 Gelbo	×	×	×	×	×	×	×	×	×	×
O_2TR-dry	1	2	3	4	5	6	7	8	9	10
Flat	✓	✓	✓	×	✓	✓	✓	×	×	✓
5 Gelbo	×	×	×	×	×	×	×	×	×	×
10 Gelbo	×	×	×	×	×	×	×	×	×	×
O_2TR-wet	1	2	3	4	5	6	7	8	9	10
Flat	×	×	×	×	×	×	✓	×	×	×
5 Gelbo	×	×	×	×	×	×	✓	×	×	×
10 Gelbo	×	×	×	×	×	×	×	×	×	✓

To put the lamination-by-lamination data of Annex I into perspective, Figure B provides a graphical comparison of MVTR and O_2TR (wet and dry) values. These graphs use a semi-log scale to fully cover the two order of magnitude range of values for each of the datasets. CFD targets are also indicated for comparison. The target for WVTR is actually less than the lower detection limit for the Permatran-W® 3/33. The O_2TR target is represented in the Figure by the 0.010 cc/m^2 line. Some of the measured values were reported as less than the 0.009 lower detection limit of the Ox-Tran® 2/21. These are reflected in the figure as extending below the 0.010 cc/m^2 line.

Conclusions

As in previous work (Dunn, 2009) on non-foil barrier laminations, these laminations are able to meet the DOD target for oxygen barrier, but fall short of the water vapor target. Structure 6 (with the sub-retort grade Al_2O_3-coated OPET) in flat, protected form, did demonstrate improved moisture barrier compared to Structure 5 (with the retort grade Al_2O_3-coated OPET), but the advantage was not maintained after the gelbo flexing abuse. Future work will attempt to relate the laboratory flexing abuse to that experienced by the packaging material during actual food processing.

Physical properties for stiffness and unit weight confirmed previous research findings that polymeric pouches are comparable to or better than foil laminations in these matters.

Dielectric properties of the polymeric laminations followed expected patterns. Light barrier levels needed for protecting package contents from photodegradation effects can be provided without impairing the efficiency of the MWS process.

References

Dunn, T., 2009 *Task 5 Report*, US Army Soldier System Center, Technical Report, Natick (Ma), Contract W911QY-08-C-0132. 4pp.

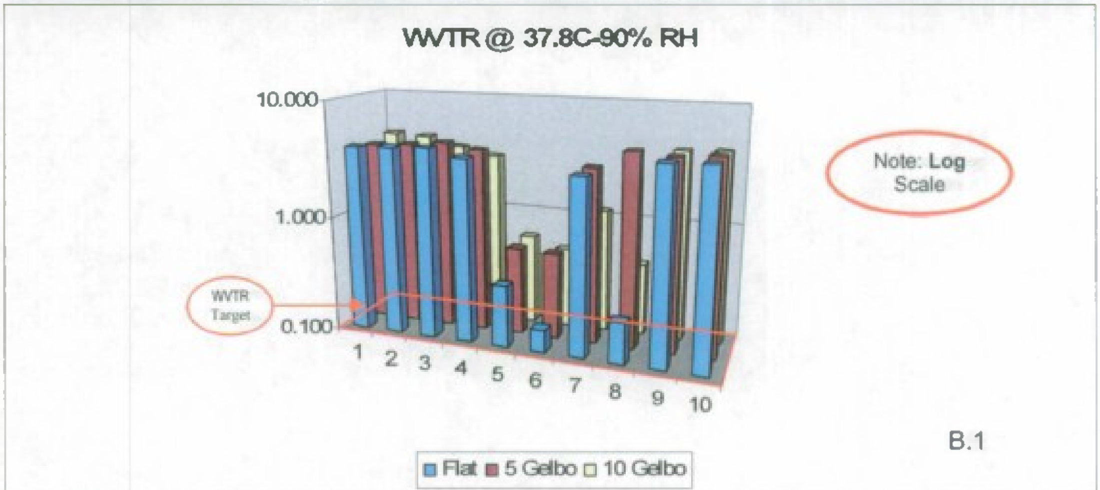
Guan, D., M. Cheng, Y. Wang, and J. Tang, 2004, *Dielectric Properties of Mashed Potatoes Relevant to Microwave and Radio-frequency Pasteurization and Sterilization Processes , J. Food Sci,.69, (1)*,FEP30-FEP37.

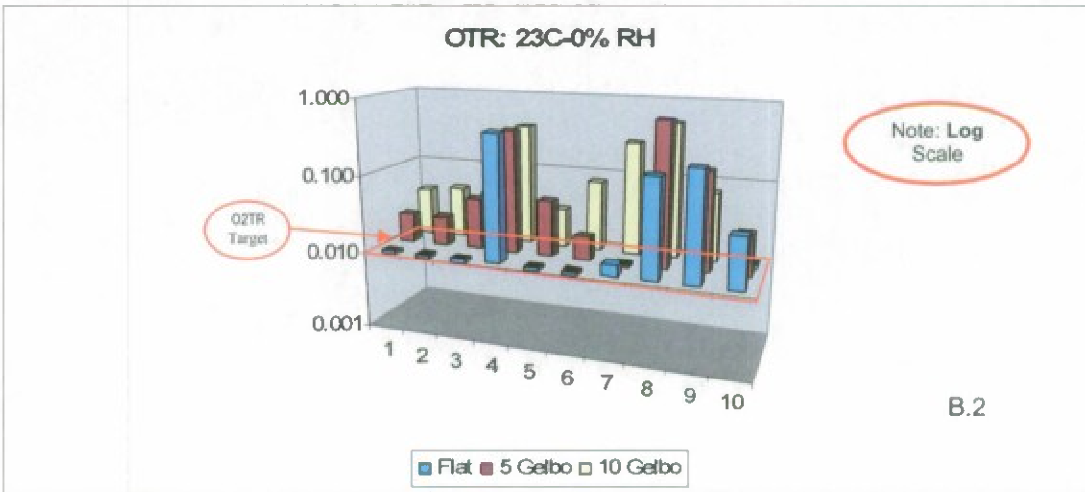
Mikhaylenko, G., 2009. *Task Report Dielectric Properties of Selected High Barrier Laminated Films Relevant to a Microwave Sterilization Process*. US Army Soldier System Center, Technical Report, Natick (Ma), Contract W911QY-08-C-0132. 6pp.

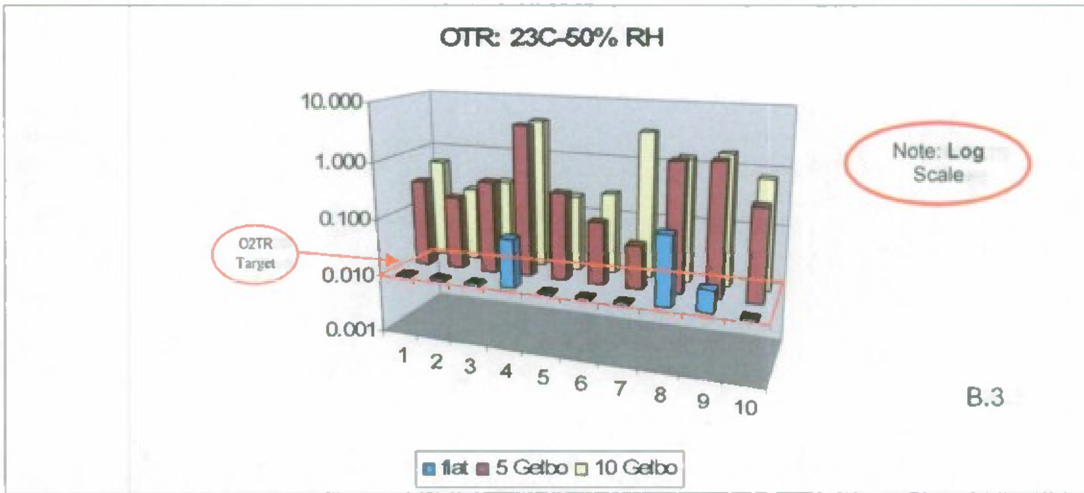
Ratto, Jo Ann, J. Lucciarini, C. Thellen, D. Froio, and N. A. D'Souza, 2006, *The reduction of Solid Waste Associated with Military Ration Packaging* , US Army Soldier System Center, Technical Report, Natick (Ma) TR-06/023. 75pp.

Tang, Z., Galina Mikhaylenko, Fang Liua, Jae-Hyung Mah, Ram Pandit, Frank Younce and Juming Tang, 2008,, *Microwave sterilization of sliced beef in gravy in 7-oz trays, J. Food Sci. 89, (4), 375-383.*

Figure B: Comparative barrier performance

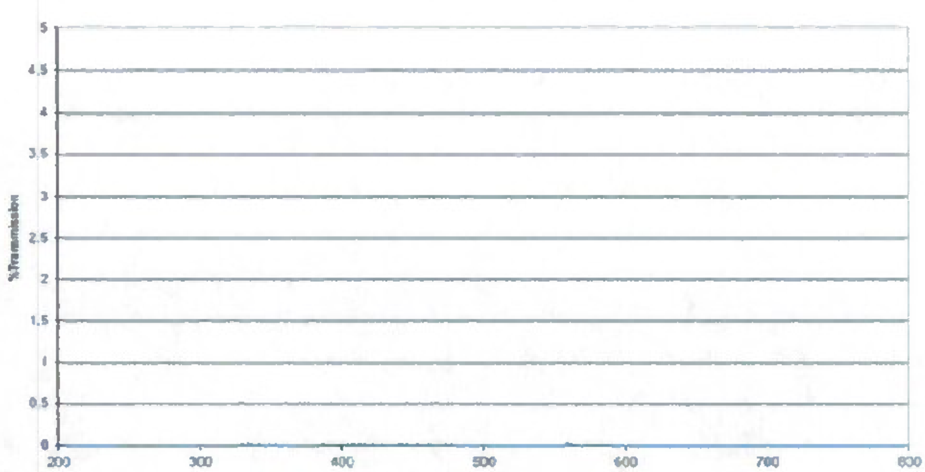






STRUCTURE:	OPET/Kur-C/Kur-N/Cblack B343-997			
		Structure No. 1 (#21)		
PROPERTY		UNITS	METHOD	VALUE
Gauge		micron	ASTM F2251	119.888
Yield		cm² / Kg	ASTM D4321	7.564297
Basis Weight		gm / m²	ASTM D646	0.1322
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	100
Tensile Strength	MD	kg / 25 mm	ASTM D882	23.1234
	CMD			25.19746
Elongation @ Break	MD	%	ASTM D882	137
	CMD			120
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	4879.091
	CMD			4236.262
Elmendorf Tear (notched)	MD	gm	ASTM D689	172
	CMD			172
Coefficient of Friction (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.214
	in/in			0.117
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	4.88
Heat Seal Strength	250 F	gm / 25 mm	ASTM F88	11,291
WVTR-37.8°C-90% RH	flat	gm·day/m^2	ASTM F1249	4.061
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8°C-90% RH	10 gelbo		ASTM F392	4.233
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	0.042354
OTR-23°C-90% RH	5 gelbo		ASTM D3985	
OTR-23°C-90% RH	10 gelbo		ASTM F392	
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	<0.009
OTR-23°C-0% RH	5 gelbo		ASTM D3985	
OTR-23°C-0% RH	10 gelbo		ASTM F392	0.567

Structure No. 1

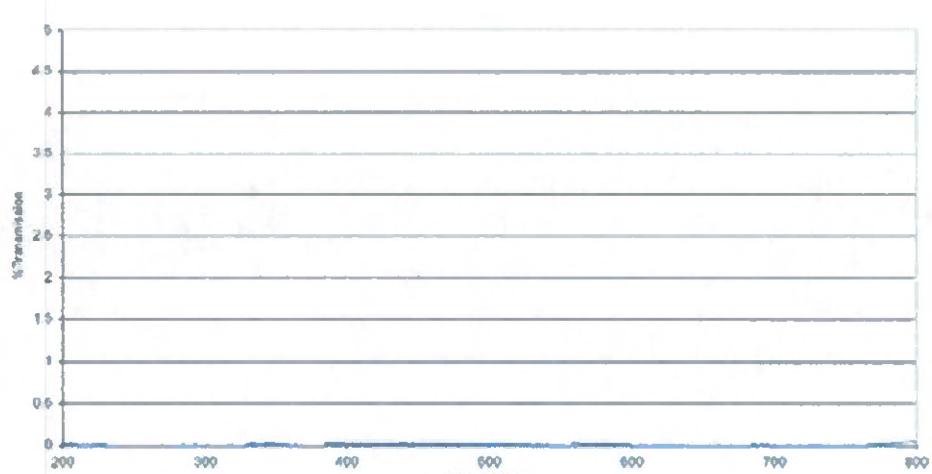


STRUCTURE:	OPET/Kur-C/Kur-N/CMYW B343T-997			

Structure No. 2 (#22)

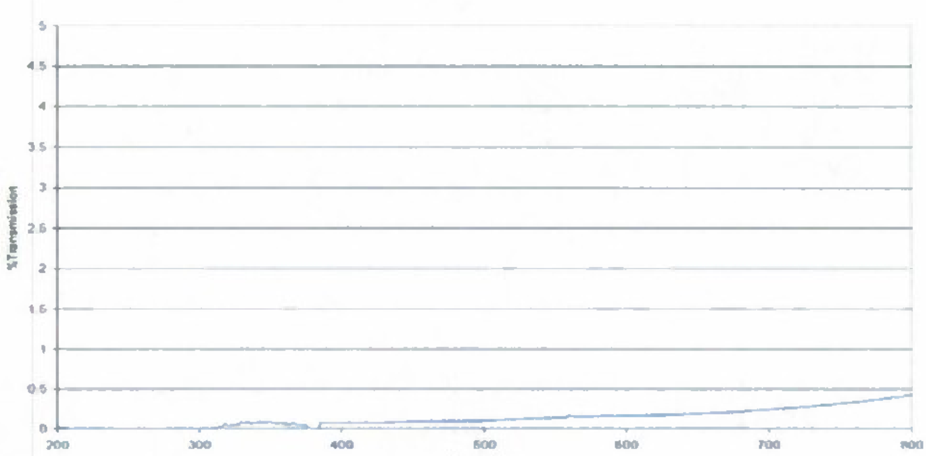
PROPERTY		UNITS	METHOD	VALUE
Gauge		micron	ASTM F2251	119.38
Yield		cm² / Kg	ASTM D4321	7.168459
Basis Weight		gm / m²	ASTM D646	0.1395
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	100
Tensile Strength	MD	kg / 25 mm	ASTM D882	24.49081
	CMD			24.86387
Elongation @ Break	MD	%	ASTM D882	139
	CMD			104
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	5201.033
	CMD			5026.864
Elmendorf Tear (notched)	MD	gm	ASTM D689	198
	CMD			252
Coefficient of Friction (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.24
	in/in			0.348
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	5.96
Heat Seal Strength	260 F	gm / 25 mm	ASTM F88	2,371
WVTR-37.8°C-90% RH	flat	gm·day/m²	ASTM F1249	4.244
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8°C-90% RH	10 gelbo		ASTM F392	4.165
OTR-23°C-90% RH	flat	cc·day/m²	ASTM D3985	-0.01861
OTR-23°C-90% RH	5 gelbo		ASTM D3985	
OTR-23°C-90% RH	10 gelbo		ASTM F392	
OTR-23°C-0% RH	flat	cc·day/m²	ASTM D3985	<0.009
OTR-23°C-0% RH	5 gelbo		ASTM D3985	
OTR-23°C-0% RH	10 gelbo		ASTM F392	0.192

Structure No. 2



STRUCTURE:	OPET/Kur-C/Kur-N/Clear B343-997			
		Structure No. 3 (#23)		
PROPERTY		UNITS	METHOD	VALUE
Gauge		micron	ASTM F2251	128.5
Yield		cm² / Kg	ASTM D4321	7.3
Basis Weight		gm / m²	ASTM D646	0.1
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	86.9
Tensile Strength	MD	kg / 25 mm	ASTM D882	25.2
	CMD			25.2
Elongation @ Break	MD	%	ASTM D882	114.0
	CMD			25560.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	5007.3
	CMD			382.7
Elmendorf Tear (notched)	MD	gm	ASTM D689	246
	CMD			236
Coefficient of Friction (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.47
	in/in			0.45
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	25
Heat Seal Strength	330 F	gm / 25 mm	ASTM F88	6542
WVTR-37.8°C-90% RH	flat	gm·day/m²	ASTM F1249	4.405
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8°C-90% RH	10 gelbo		ASTM F392	3.514
OTR-23°C-90% RH	flat	cc·day/m²	ASTM D3985	-0.202
OTR-23°C-90% RH	5 gelbo		ASTM D3985	
OTR-23°C-90% RH	10 gelbo		ASTM F392	
OTR-23°C-0% RH	flat	cc·day/m²	ASTM D3985	<0.009
OTR-23°C-0% RH	5 gelbo		ASTM D3985	
OTR-23°C-0% RH	10 gelbo		ASTM F392	0.294

Structure No. 3

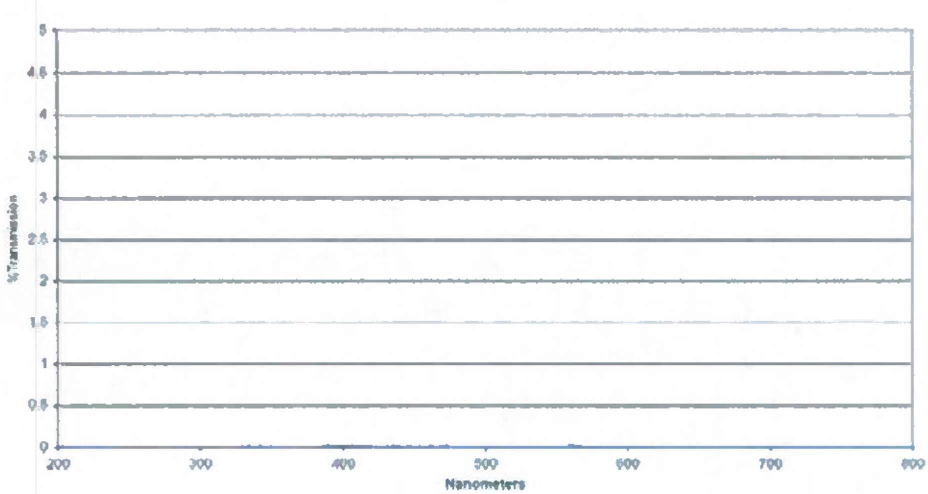


STRUCTURE:	OPET/Kur-C/Kur-N/C Black B343T-997

Structure No. 4 (#24)

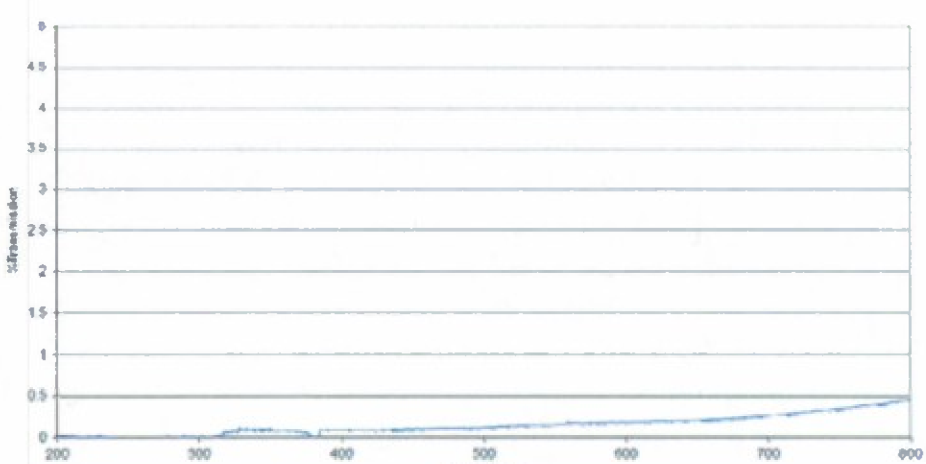
PROPERTY		UNITS	METHOD	VALUE
Gauge		micron	ASTM F2251	125.5
Yield		cm² / Kg	ASTM D4321	7.3
Basis Weight		gm / m²	ASTM D646	0.1
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	100.0
Tensile Strength	MD	kg / 25 mm	ASTM D882	24.5
	CMD			25.0
Elongation @ Break	MD	%	ASTM D882	136.0
	CMD			145.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	4548.8
	CMD			4411.7
Elmendorf Tear (notched)	MD	gm	ASTM D689	201
	CMD			243
Coefficient of Friction (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.30
	in/in			0.14
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	5
Heat Seal Strength	280 F	gm / 25 mm	ASTM F88	4888
WVTR-37.8°C-90% RH	flat	gm·day/m²	ASTM F1249	3.766
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8°C-90% RH	10 gelbo		ASTM F392	3.007
OTR-23°C-90% RH	flat	cc·day/m²	ASTM D3985	-0.202
OTR-23°C-90% RH	5 gelbo		ASTM D3985	
OTR-23°C-90% RH	10 gelbo		ASTM F392	
OTR-23°C-0% RH	flat	cc·day/m²	ASTM D3985	0.431
OTR-23°C-0% RH	5 gelbo		ASTM D3985	
OTR-23°C-0% RH	10 gelbo		ASTM F392	4.002

Structure No. 4



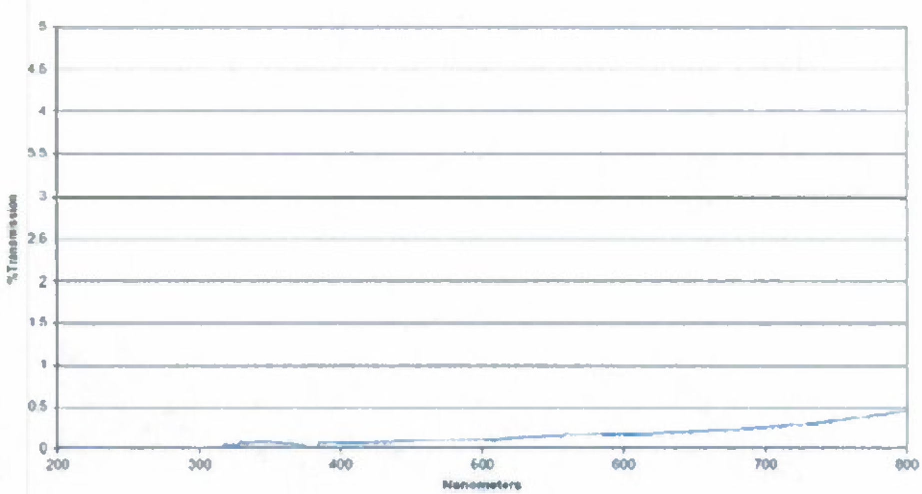
STRUCTURE:	OPET/GL-PET-ARH/Kur-N/Clear B343-997			
Structure No. 5 (#25)				
PROPERTY		UNITS	METHOD	VALUE
Gauge		micron	ASTM F2251	130.8
Yield		cm² / Kg	ASTM D4321	7.3
Basis Weight		gm / m²	ASTM D646	0.1
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	85.5
Tensile Strength	MD	kg / 25 mm	ASTM D882	20.8
	CMD			25.4
Elongation @ Break	MD	%	ASTM D882	133.0
	CMD			115.0
Young's Modulus	MD	N / 25 mm	ASTM D882	5495.3
(1% Secant Modulus)	CMD			4788.0
Elmendorf Tear	MD	gm	ASTM D689	262
(notched)	CMD			256
Coefficient of Friction	out/out	gm vertical/gm lateral	ASTM D1894	0.47
(kinetic)	in/in			0.46
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	29
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	3765
WVTR-37.8°C-90% RH	flat	gm·day/m²	ASTM F1249	0.3
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8°C-90% RH	10 gelbo		ASTM F392	0.6
OTR-23°C-90% RH	flat	cc·day/m²	ASTM D3985	0.730
OTR-23°C-90% RH	5 gelbo		ASTM D3985	
OTR-23°C-90% RH	10 gelbo		ASTM F392	
OTR-23°C-0% RH	flat	cc·day/m²	ASTM D3985	<0.009
OTR-23°C-0% RH	5 gelbo		ASTM D3985	
OTR-23°C-0% RH	10 gelbo		ASTM F392	0.198

Structure No. 5



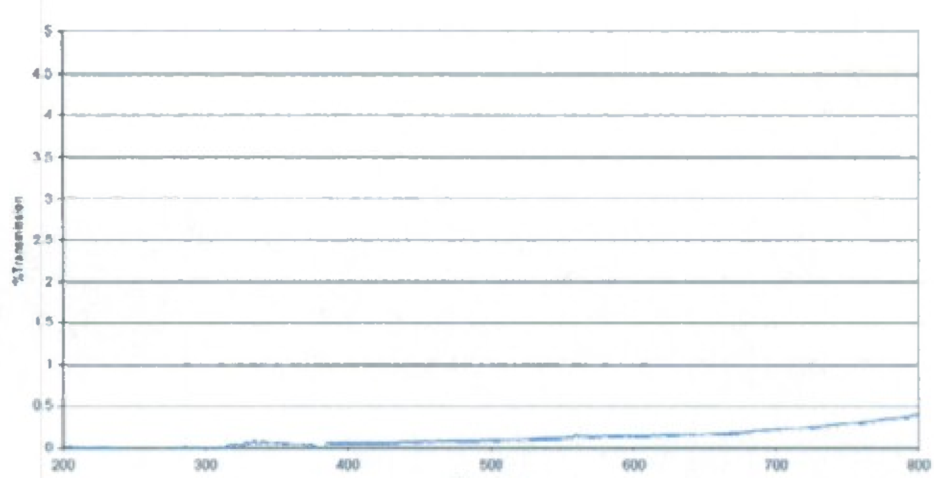
STRUCTURE:	OPET/GL-PET-ARHF/Kur-N/Clear B343-997			
Structure No. 6 (#26)				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	128.0
Yield		cm² / Kg	ASTM D4321	7.3
Basis Weight		gm / m²	ASTM D646	0.1
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	87.8
Tensile Strength	MD	kg / 25 mm	ASTM D882	24.9
	CMD			24.6
Elongation @ Break	MD	%	ASTM D882	157.0
	CMD			103.0
Young's Modulus	MD	N / 25 mm	ASTM D882	5006.8
(1% Secant Modulus)	CMD			5064.2
Elmendorf Tear	MD	gm	ASTM D689	214
(notched)	CMD			230
Coefficient of Friction	out/out	gm vertical/gm lateral	ASTM D1894	0.45
(kinetic)	in/in			0.47
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	29
Heat Seal Strength	330 F	gm / 25 mm	ASTM F88	3338
WVTR-37.8ºC-90% RH	flat	gm·day/m²	ASTM F1249	0.2
WVTR-37.8ºC-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8ºC-90% RH	10 gelbo		ASTM F392	0.5
OTR-23ºC-90% RH	flat	cc·day/m²	ASTM D3985	2.101
OTR-23ºC-90% RH	5 gelbo		ASTM D3985	
OTR-23ºC-90% RH	10 gelbo		ASTM F392	
OTR-23ºC-0% RH	flat	cc·day/m²	ASTM D3985	<0.009
OTR-23ºC-0% RH	5 gelbo		ASTM D3985	
OTR-23ºC-0% RH	10 gelbo		ASTM F392	0.253

Structure No. 6

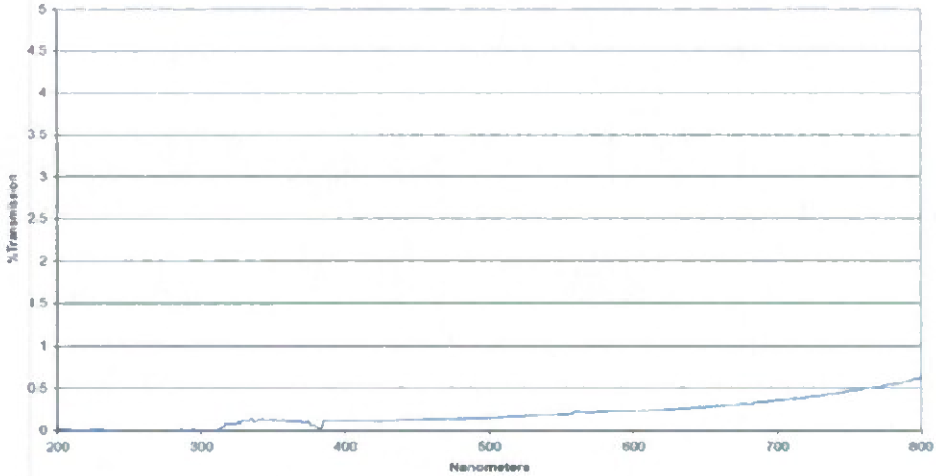


STRUCTURE:	OPET/WSX 03 Y07/Kur-N/Clear B343-997			
	Structure No. 7 (#27)			
PROPERTY		UNITS	METHOD	VALUE
Gauge		micron	ASTM F2251	129.0
Yield		cm² / Kg	ASTM D4321	7.3
Basis Weight		gm / m²	ASTM D646	0.1
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	88.7
Tensile Strength	MD	kg / 25 mm	ASTM D882	23.8
	CMD			28.1
Elongation @ Break	MD	%	ASTM D882	115.0
	CMD			108.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	5376.0
	CMD			4980.2
Elmendorf Tear (notched)	MD	gm	ASTM D689	230
	CMD			275
Coefficient of Friction (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.40
	in/in			0.44
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	23
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	4123
WVTR-37.8°C-90% RH	flat	gm·day/m^2	ASTM F1249	3.2
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8°C-90% RH	10 gelbo		ASTM F392	1.2
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	-0.631
OTR-23°C-90% RH	5 gelbo		ASTM D3985	
OTR-23°C-90% RH	10 gelbo		ASTM F392	
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.014
OTR-23°C-0% RH	5 gelbo		ASTM D3985	
OTR-23°C-0% RH	10 gelbo		ASTM F392	3.212

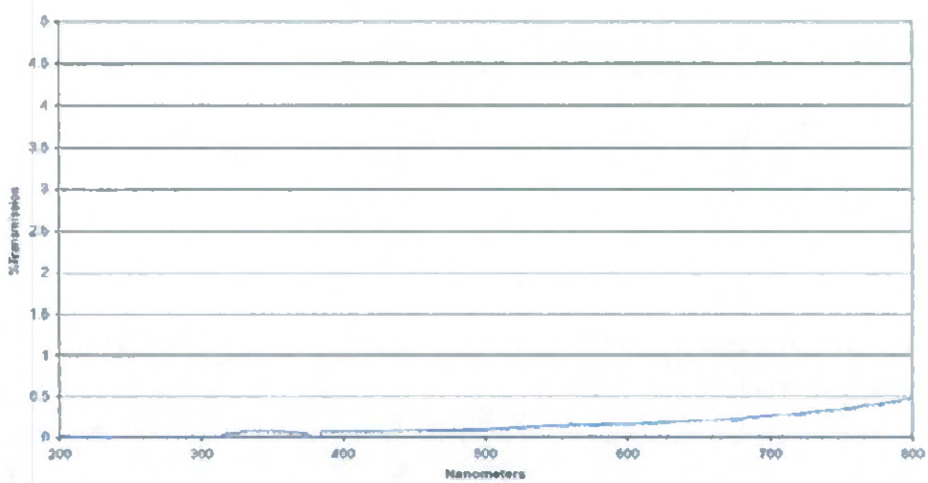
Structure No. 7



STRUCTURE:	OPET/GL-PET-ARHF/BON/Clear B343-997			
Structure No. 8 (#28)				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	129.0
Yield		cm^2 / Kg	ASTM D4321	7.5
Basis Weight		g / m^2	ASTM D646	0.1
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	81.4
Tensile Strength	MD	kg / 25 mm	ASTM D882	26.1
	CMD			24.6
Elongation @ Break	MD	%	ASTM D882	133.0
	CMD			123.0
Young's Modulus	MD	N / 25 mm	ASTM D882	5144.0
(1% Secant Modulus)	CMD			4936.0
Elmendorf Tear	MD	gm	ASTM D689	230
(notched)	CMD			217
Coefficient of Friction	out/out	gm vertical/gm lateral	ASTM D1894	0.44
(kinetic)	in/in			0.47
Hot Tack Strength	300 F	g / 25 mm	ASTM F1921	24
Heat Seal Strength	320 F	g / 25 mm	ASTM F88	4764
WVTR-37.8°C-90% RH	flat	gm·day/m^2	ASTM F1249	0.229
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8°C-90% RH	10 gelbo		ASTM F392	0.420
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	0.834
OTR-23°C-90% RH	5 gelbo		ASTM D3985	
OTR-23°C-90% RH	10 gelbo		ASTM F392	
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.180
OTR-23°C-0% RH	5 gelbo		ASTM D3985	
OTR-23°C-0% RH	10 gelbo		ASTM F392	1.293



STRUCTURE:	OPET/Kur-C/BON/Clear B343-997			
Structure No. 9 (#29)				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	128.3
Yield		cm² / Kg	ASTM D4321	7.4
Basis Weight		gm / m²	ASTM D646	0.1
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	85.3
Tensile Strength	MD	kg / 25 mm	ASTM D882	28.1
	CMD			24.3
Elongation @ Break	MD	%	ASTM D882	140.0
	CMD			146.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	4906.7
	CMD			4593.4
Elmendorf Tear (notched)	MD	gm	ASTM D689	198
	CMD			198
Coefficient of Friction (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.43
	in/in			0.46
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	19
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	11010
WVTR-37.8°C-90% RH	flat	gm·day/m^2	ASTM F1249	4.464
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8°C-90% RH	10 gelbo		ASTM F392	4.214
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	-0.056
OTR-23°C-90% RH	5 gelbo		ASTM D3985	
OTR-23°C-90% RH	10 gelbo		ASTM F392	
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.237
OTR-23°C-0% RH	5 gelbo		ASTM D3985	
OTR-23°C-0% RH	10 gelbo		ASTM F392	1.677



STRUCTURE:	OPET/Kur-C/Clear B343-997			
Structure No. 10 (#30)				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	111.0
Yield		cm² / Kg	ASTM D4321	8.9
Basis Weight		gm / m²	ASTM D646	0.1
Gloss @ 45°		%	ASTM D2457	0
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	88.9
Tensile Strength	MD	kg / 25 mm	ASTM D882	4.8
	CMD			5.2
Elongation @ Break	MD	%	ASTM D882	606.0
	CMD			702.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	4126.8
	CMD			3919.2
Elmendorf Tear (notched)	MD	gm	ASTM D689	234
	CMD			246
Coefficient of Friction (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.42
	in/in			0.46
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	49
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	3545
WVTR-37.8°C-90% RH	flat	gm·day/m^2	ASTM F1249	4.596
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249	
WVTR-37.8°C-90% RH	10 gelbo		ASTM F392	4.368
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	-0.050
OTR-23°C-90% RH	5 gelbo		ASTM D3985	
OTR-23°C-90% RH	10 gelbo		ASTM F392	
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.045
OTR-23°C-0% RH	5 gelbo		ASTM D3985	
OTR-23°C-0% RH	10 gelbo		ASTM F392	0.732

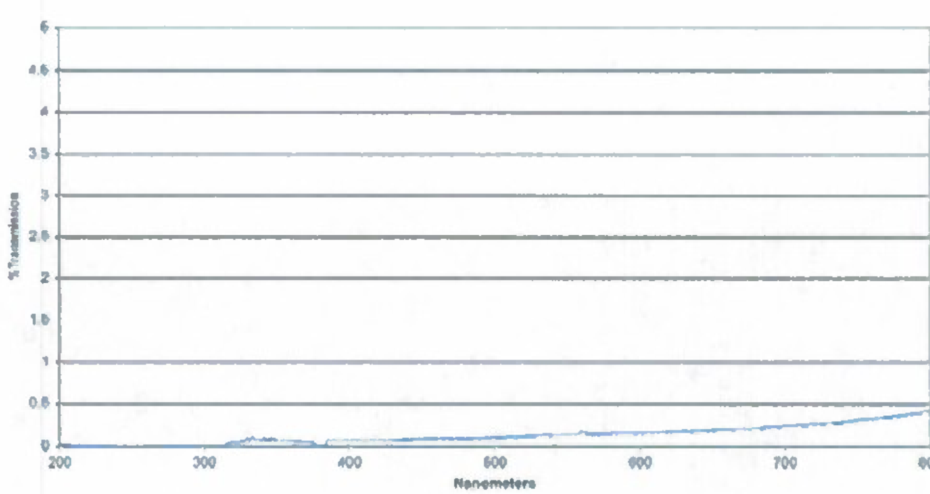


Exhibit C for CLIN 0016

CONTRACT DATA REQUIREMENTS LIST
(2 Data Items)

Form Approved OMB No. 0704-0188

A. CONTRACT LINE ITEM NO.	B. EXHIBIT	C. CATEGORY
0016	C	● TDP ○ TM ○ Other

D. SYSTEM / ITEM	E. CONTRACT / PR NO.	F. CONTRACTOR
Technical Data - C001 and C002	W911QY-09-C-0205	PRINTPACK, INC.

Data Item C001

Field	Value
1. DATA ITEM NO.	C001
2. TITLE OF DATA ITEM	Validation Report
3. SUBTITLE	
4. AUTHORITY (Data Acquisition Document No.)	
5. CONTRACT REFERENCE	Sections B & F
6. REQUIRING OFFICE	
7. DD 250 REQ	NO
8. APP CODE	N/A
9. DIST STATEMENT REQUIRED	
10. FREQUENCY	ASREQ
11. AS OF DATE	
12. DATE OF FIRST SUBMISSION	
13. DATE OF SUBSEQUENT SUBMISSION	
17. PRICE GROUP	
18. ESTIMATED TOTAL PRICE	

16. REMARKS
Validation report cited in the Contractor's proposal will be provided as a deliverable under CLIN 0008, which will be completed by 30 June 2010.

14. DISTRIBUTION a. ADDRESSEE	b. COPIES Draft	Final Reg	Final Repro
STEPHEN MOODY	0	1	0
15. TOTAL	0	1	0

Data Item C002

Field	Value
1. DATA ITEM NO.	C002
2. TITLE OF DATA ITEM	Label TTI Evaluations
3. SUBTITLE	
4. AUTHORITY (Data Acquisition Document No.)	
5. CONTRACT REFERENCE	
6. REQUIRING OFFICE	
7. DD 250 REQ	NO
8. APP CODE	N/A
9. DIST STATEMENT REQUIRED	
10. FREQUENCY	ASREQ
11. AS OF DATE	
12. DATE OF FIRST SUBMISSION	
13. DATE OF SUBSEQUENT SUBMISSION	
17. PRICE GROUP	
18. ESTIMATED TOTAL PRICE	

16. REMARKS
Label TTI Evaluations cited in the Contractor's proposal will be provided as a deliverable under CLIN 0011, which will be completed by 30 April 2010.

14. DISTRIBUTION a. ADDRESSEE	b. COPIES Draft	Final Reg	Final Repro
STEPHEN MOODY	0	1	0
15. TOTAL	0	1	0

G. PREPARED BY	H. DATE	I. APPROVED BY	J. DATE
STEPHEN MOODY	17-Sep-2009	STEPHEN MOODY	17-Sep-2009

Data Item C001 Contract No. W911QY-09-C-0205

Microwave Sterilization Validation Report

Printpack, Inc. Atlanta, Ga

WASHINGTON STATE UNIVERSITY
World Class. Face to Face.

REPORT ON PROGRESS OF CHICKEN-DUMPLING-POUCH PROJECT

Submitted to PrintPack

By

WSU MW Group

Department of Biological Systems Engineering
Washington State University

June, 2011

This report summarizes major progress of the project "Microwave Sterilization of Chicken and Dumplings packaged in 8-oz Pouches" for the period between January and June, 2011.

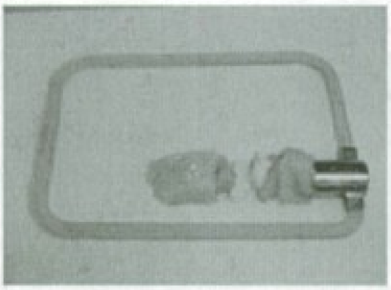
I. Identification of the Food Component Getting the Lowest Thermal Lethality

The chicken – dumpling pouch we developed is filled with four components: cut chicken breast pieces, dumplings, sauce, and vegetables. The components have different dielectric properties, thermal properties and heat resistances to microorganisms. In heat penetration tests, the temperature sensor needs to be placed in the component located at the cold spot which obtains the lowest thermal lethality, to monitor the food temperature. Therefore, it is necessary to identify the food component receiving the lowest thermal lethality.

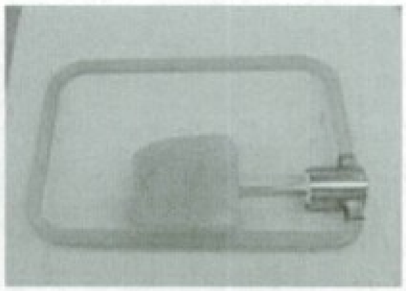
MW processing tests for measuring temperatures inside the three different components (chicken breast pieces, dumplings, and sauce) placed at the cold spot (identified by the chemical-marker-based computer-vision method) inside pouches were conducted. The pouches were filled with designated rations of the following food components: 95 g chicken breast, 80 g sauce, 16 g dumplings, and 7 g vegetables. Ellab sensors were used to measure the temperatures profiles (Figs. 1.1 & 1.2). Two sizes of cut chicken pieces were used for the temperature measurement: a normal size of 16×16×16 mm and a larger size of 40×40×16 mm.

Tests were conducted under the following conditions:

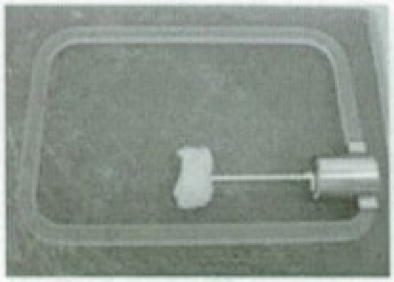
- 8-oz PrintPack pouches
- MW power setting: 7.0 / 6.2 / 2.6 / 2.5 kW for 4 MW heating cavities
- Moving speed: 40 inch/min
- Water temperature: 72 / 124 / 123°C for preheating, MW heating and holding sections
- System pressure: 34 psig
- Water flow rate: 69 / 51 / 72 / 61 liter/min for pre-heating, MW heating, holding, and cooling sections
- Pre-heating time: 30 min
- Cooling time: 4 min.



a)



b)



c)

d)

Fig. 1.1 Placement of Ellab sensor. a) sensor tip inside chicken piece of normal size (16×16×16 mm) at cold spot; b) sensor tip inside chicken piece of larger size (40×40×16 mm) at cold spot; c) sensor tip inside dumpling at cold spot; d) sample pouch with Ellab sensor after processing.

Fig. 1.2 Dumpling and vegetables

The thermal process level is usually described by thermal lethality at 121.1°C, F_0, (in min). The value of F_0 at a point in a thermal-processed product is calculated based on the temperature history at the point as follows:

$$F_0 = \int_0^t 10^{(T-T_r)/z} \, dt \tag{1}$$

where T is the measured temperature (°C); Tr is the reference temperature (121.1°C); z is usually a value of 10°C; and t is the heating time (min).

The values of F_0 achieved in different components at the cold spot location were determined based on the temperature profiles measured in the process including preheating, heating, holding and cooling (Tables 1.1 and 1.2). Results show that chicken pieces receive less thermal treatment at the cold spot than dumplings or sauce. In addition, chicken has higher heat resistance to microorganisms than dumplings or sauce as mentioned in Section 4.1. Both lower thermal treatment and higher heat resistance to microorganisms cause chicken pieces to receive lower thermal lethality. Therefore, chicken pieces were chosen as the target component for temperature measurement in MW processing development.

Table 1.1 F_0 values in different components at cold spot in pouches with a normal-size chicken piece for temperature measurement

date	F0, min chicken	F0, min dumpling	F0, min sauce
Test-1, Jan-12-2011	11.4	20.2	19.8
	15.9		
Test-2, Jan-12-2011	20.8	15	23.9
	22.2		
Test-3, Jan-12-2011	13.6	19.6	21.3
	13.6		
average F0, min	16.3	**18.3**	**21.7**
Stdev	**4.3**	**2.8**	**2.1**

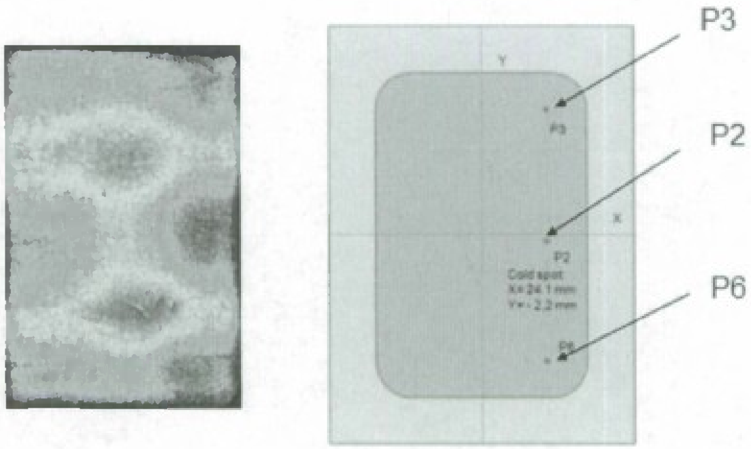
Table 1.2 F_0 values in different components at cold spot in pouches with a larger-size chicken piece for temperature measurement

testing date	F0, min chicken	F0, min dumpling	F0, min sauce
Test-2, Jan-11	6.2	25	20.8
	9.5		
Test-3, Jan. 11	8.1	26.2	23.7
		24.1	
Test-1, Jan. 14	6.5		
	7.7	15.5	33.9
average F0, min	7.6	**22.7**	**26.1**
Stdev, min	1.3	4.9	6.9

2. Validation of Cold Spot by Temperature Measurement inside Chicken Dumpling Pouches

2.1. Temperature measurement at cold regions in chicken dumpling pouches

Tests were conducted to measure temperature profiles and F_0 values inside chicken pieces (40×40×16 mm) in chicken dumpling pouches using Ellab sensors. The chicken pieces with Ellab sensors were placed in three cold regions identified by the chemical-marker-based computer-vision method. The tips of the Ellab sensors were placed at central points (P2, P3, and P6) of the cold regions (Figs. 2.1 & 2.2).



Heating pattern measured by WPG model food

Temperature measurement points

Fig. 2.1 Measuring points in cold regions

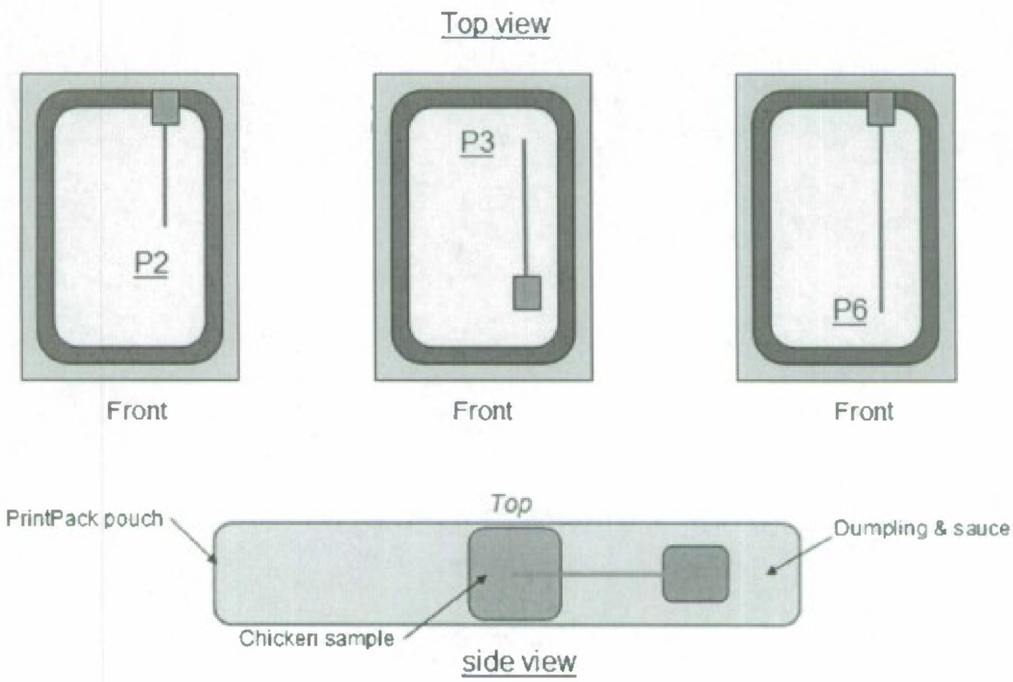


Fig. 2.2 Measuring points with Ellab sensors

Tests were conducted under the same conditions described in Section 1. Table 2.1 shows the measured F_0 values. The F_0 at point 2 (identified cold spot by chemical-marker-based computer-vision method for WPG samples) in the chicken-dumpling pouch had the lowest value.

Table 2.1 F_0 values measured at 3 points in 3 cold regions in chicken-dumpling pouches

Testing date	F0, min at P2	F0, min at P3	F0, min at P6
Test-3, Jan. 12, 2011	9.1		13.6
	6.2	21.3	
Test-1, Jan. 13, 2011	6.9	17.9	18.3
		11.8	
Test-2, Jan. 13, 2011	7.3	19.2	12.7
			12.6
average F0, min	7.4	**17.6**	**14.3**
Stdev, min	**1.2**	4.1	2.7

2.2. Temperature measurement at points surrounding the identified cold spot in chicken-dumpling pouches

To further confirm the cold spot identified by the chemical-marker-based computer-vision method for WPG samples to be the actual cold spot inside chicken-dumpling pouches, temperature profiles and F_0 values at the identified cold spot (Point 2) and its surrounding points (up, down, front, back, left, and right, 4 or 5 mm away from the cold spot) were measured using Ellab sensors. Figure 2.3 shows the locations of the measuring points inside the chicken piece (40×40×16 mm) in chicken-dumpling pouches.

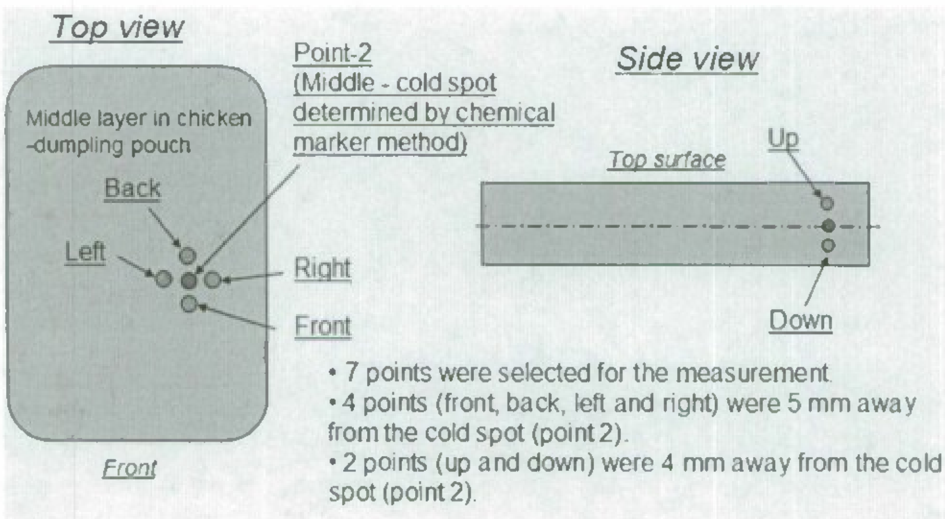


Fig. 2.3 Location of measuring points

Testing conditions were same as those stated in Section 1. Testing results (Table 2.2) indicate that MW processing provided higher thermal treatment at the surrounding points than at Point 2. The cold spot identified by the chemical-marker-based computer-vision method is indeed the actual cold spot inside the chicken-dumpling pouches.

Table 2.2 F_0 values at identified cold spot and its surrounding points

Location	P2	Up	Down	Front	Back	Left	Right
F0, min	9.11	8.81	9.37	14.19	15.04	7.67	7.1
	6.22	9.22	7.72	9.42	14.46	8.6	9.8
	6.2	6.94	8.64	10.98	14.05	16.61	18.96
	7.34	13.12	7.09	20.38	23.9	24.8	14.79
	6.51		10.03				
	7.71						
	6.81						
	8.21						
	10.15						
Average	7.58	9.52	8.57	13.74	16.86	14.42	12.66
Stdev	1.29	2.25	1.07	4.20	4.08	6.93	4.56

3. Heat Penetration Tests

Heat penetration (HP) tests were conducted to achieve a target F_0 of 6.0 minutes inside the chicken piece (40×40×16 mm) placed at the cold spot in chicken-dumpling pouches at the end of complete thermal process. The 8-oz PrintPack pouch was filled with food components of the pre-selected ration (95 g chicken breast pieces, 80 g sauce, 16 g dumplings, and 7 g vegetables) and sealed with an UltraVac 250 vacuum pouch sealer (KOCH Packaging Supplies Inc., Kansas City, MO) under pre-selected conditions (vacuum setting: 2.5; sealing time setting: 4). The size of cut chicken pieces was 16×16×16 mm except for the piece for temperature measurement at the cold spot. Temperature profiles in the chicken piece at cold spot were measured by Ellab sensors during the tests. The test parameters and conditions were same as those stated in Section 1.

A total of 37 data points were collected from 19 HP tests runs conducted over 17 days. Figure 3.1 shows sample temperature profiles measured by Ellab sensors during one test. Table 3.1 summarizes F_0 values obtained from all the tests. The F_0 varied from 6.2 to 15.1 min during the tests performed with the selected processing schedule. The thermal contribution during the cooling period was considered in the F_0 calculation for the HP tests. Table 3.2 summarizes the important processing parameters for the 37 data sets including MW power, processing time, and water temperature in heating and holding sections.

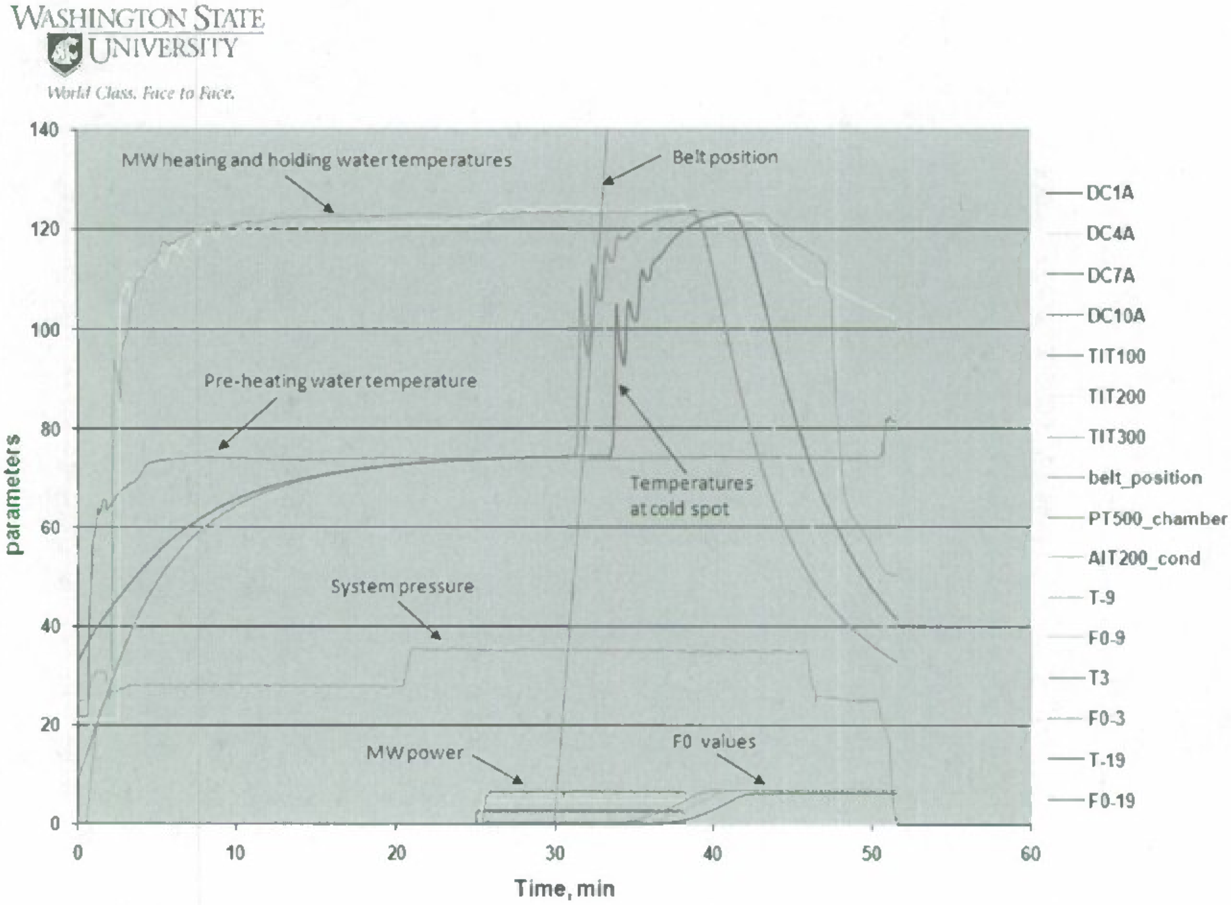


Fig. 3.1 Sample temperature profiles measured by four Ellab sensors during one test.

Washington State University
World Class. Face to Face.

Table 3.1 Location of pouches on the mesh belt and F_0 at the cold spot of the pouches at the end of processing

Testing date	Jan 12-11 test3	Jan 13-11 test1	Jan 13-11 test2	Jan 14-11 test1	Jan 14-11 test2	Jan 18-11 test2	Jan 18-11 test3	Jan 19-11 test1	Jan 21-11 test1	Jan 24-11 test1	Jan 24-11 test2	Jan 25-11 test1	Jan 25-11 test2	Jan 28-11 test1	Jan 28-11 test2	Jan 27-11 test1	Jan 27-11 test2	Jan 28-11 test1	Jan 28-11 test2
Pouch location on the mesh belt	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min	F0, min
1																			
2																			
3																6.88			
4																			
5																			12.65
6	9.11			6.51	6.81														
7															8.16				
8														7.65					
9																6.89			
10			7.34																
11														8.21					
12	6.22	6.9		7.71															
13															8.95				
14																	16.14		
15											12.23								
16														7.92					
17															12.19				
18						8.21												14.38	
19																6.26			
20																			7.15
21																			
22							10.15		7.58										
23																	11.23		
24								13.56											
25										8.81									
26																		14.06	
27									6.45										
28																			
29													9.01						
30																			
31																			
32											14.71								
33																		13.36	
34													9.14						
35																	14.00		
36																			
37										9.86									
38																			
39																			13.65
40												14.44							
41																			
42																			

WASHINGTON STATE UNIVERSITY

World Class. Face to Face.

Table 3.2 MW HP Test Matrix and Data Summary

Microwave Assisted Sterilizer - Heat Penetration Test Data Summary

MW Section Lengths: Preheat: 20.0 ft; MW Heating: 10.625 ft; Holding: 10.917 ft

Belt Speed: 3.33 ft/min

	Run / TC	I.T. (°F)	Preheat Time (min)	Max.* Preheat Temp. (°F)	Time in Heating Section (min)	Max.* Temp. in Heating Section (°F)	Time in Holding Section (min)	Max.* Temp. in Holding Section (°F)	Max.* MW Power Cavity 1 (kW)	Max.* MW Power Cavity 2 (kW)	Max.* MW Power Cavity 3 (kW)	Max.* MW Power Cavity 4 (kW)	General Method Lethality (F_0) *	Belt Speed (ft/min)	System Pressure (psig)	Fill Wt of Chicken (oz)	Fill Wt of Dumpling (oz)	Fill Wt of Vegetable (oz)	Fill Wt of Sauce (oz)
1	Jan/12/11-T3/6	43.97	30.00	164.81	3.19	256.17	3.28	254.93	7.18	6.32	2.59	2.55	9.11	3.33	34.65	3.35	1.27	0.56	2.82
2	Jan/12/11-T3/12	44.31	30.00	164.81	3.19	255.79	3.28	255.00	7.18	6.32	2.59	2.55	6.22	3.33	34.65	3.35	1.27	0.56	2.82
3	Jan/13/11-T1/12	43.18	30.00	165.00	3.19	256.08	3.28	255.09	7.26	6.44	2.59	2.53	8.90	3.33	34.92	3.35	1.27	0.56	2.82
4	Jan/13/11-T2/10	42.75	30.00	164.82	3.19	256.41	3.28	255.06	7.22	6.42	2.60	2.54	7.34	3.33	34.96	3.35	1.27	0.56	2.82
5	Jan/14/11-T1/06	41.78	30.00	165.02	3.19	256.59	3.28	254.70	7.28	6.44	2.59	2.58	8.51	3.33	34.96	3.35	1.27	0.56	2.82
6	Jan/14/11-T1/12	41.29	30.00	165.02	3.19	256.44	3.28	254.70	7.28	6.44	2.59	2.59	7.71	3.33	34.96	3.35	1.27	0.56	2.82
7	Jan/14/11-T2/06	43.25	30.00	165.02	3.19	256.26	3.28	254.70	7.17	6.38	2.59	2.59	8.81	3.33	34.86	3.35	1.27	0.56	2.82
8	Jan/18/11-T2/18	44.69	30.00	165.06	3.19	256.64	3.28	254.80	7.26	6.42	2.59	2.54	6.21	3.33	34.75	3.35	1.27	0.56	2.82
9	Jan/18/11-T3/22	43.56	30.00	165.00	3.19	255.87	3.28	254.46	7.18	6.39	2.59	2.58	10.15	3.33	34.72	3.35	1.27	0.56	2.82
10	Jan/19/11-T1/24	40.51	30.00	165.27	3.19	255.72	3.28	254.80	7.20	6.35	2.59	2.55	13.56	3.33	35.25	3.35	1.27	0.56	2.82
11	Jan/21/11-T1/22	39.58	30.00	165.15	3.19	256.19	3.28	254.46	7.24	6.40	2.59	2.62	7.56	3.33	34.84	3.35	1.27	0.56	2.82
12	Jan/21/11-T1/27	39.69	30.00	165.15	3.19	256.01	3.28	254.57	7.24	6.40	2.59	2.62	6.45	3.33	34.84	3.35	1.27	0.56	2.82
13	Jan/24/11-T1/25	38.93	30.00	165.18	3.19	256.69	3.28	254.82	7.21	6.40	2.59	2.58	6.81	3.33	34.87	3.35	1.27	0.56	2.82
14	Jan/24/11-T1/37	39.47	30.00	165.18	3.19	256.46	3.28	255.09	7.21	6.40	2.59	2.56	9.80	3.33	34.87	3.35	1.27	0.56	2.82
15	Jan/24/11-T2/15	40.06	30.00	165.02	3.19	255.80	3.28	254.71	7.25	6.39	2.58	2.57	12.23	3.33	34.77	3.35	1.27	0.56	2.82
16	Jan/24/11-T2/32	40.08	30.00	165.02	3.19	256.62	3.28	254.93	7.25	6.39	2.59	2.57	14.71	3.33	34.77	3.35	1.27	0.56	2.82
17	Jan/25/11-T1/40	40.12	30.00	166.05	3.19	256.77	3.28	255.11	7.27	6.39	2.59	2.57	14.44	3.33	34.82	3.35	1.27	0.56	2.82
18	Jan/25/11-T2/29	41.07	30.00	165.54	3.19	256.80	3.28	254.86	7.17	6.36	2.59	2.63	9.01	3.33	34.79	3.35	1.27	0.56	2.82
19	Jan/25/11-T2/34	41.38	30.00	165.54	3.19	257.09	3.28	254.98	7.17	6.36	2.59	2.63	9.14	3.33	34.79	3.35	1.27	0.56	2.82
20	Jan/26/11-T1/08	40.64	30.00	165.74	3.19	256.19	3.28	254.61	7.29	6.42	2.58	2.58	7.65	3.33	34.93	3.35	1.27	0.56	2.82
21	Jan/26/11-T1/11	40.84	30.00	165.74	3.19	255.72	3.28	254.61	7.29	6.42	2.59	2.56	8.21	3.33	34.93	3.35	1.27	0.56	2.82
22	Jan/26/11-T1/16	40.78	30.00	165.74	3.19	256.19	3.28	254.61	7.29	6.42	2.59	2.56	7.92	3.33	34.93	3.35	1.27	0.56	2.82
23	Jan/26/11-T2/07	41.22	30.00	165.69	3.19	256.42	3.28	254.75	7.22	6.42	2.59	2.56	6.16	3.33	34.79	3.35	1.27	0.56	2.82
24	Jan/26/11-T2/13	42.46	30.00	165.69	3.19	256.01	3.28	254.97	7.22	6.42	2.59	2.56	6.85	3.33	34.79	3.35	1.27	0.56	2.82
25	Jan/26/11-T2/17	41.47	30.00	165.69	3.19	256.86	3.28	254.97	7.22	6.42	2.59	2.56	12.19	3.33	34.79	3.35	1.27	0.56	2.82
26	Jan/27/11-T1/03	41.16	30.00	165.70	3.19	256.41	3.28	254.37	7.18	6.35	2.59	2.57	6.88	3.33	35.00	3.35	1.27	0.56	2.82
27	Jan/27/11-T1/09	41.13	30.00	165.70	3.19	255.61	3.28	254.75	7.18	6.35	2.59	2.57	6.89	3.33	35.00	3.35	1.27	0.56	2.82
28	Jan/27/11-T1/19	42.03	30.00	165.70	3.19	256.33	3.28	254.84	7.18	6.35	2.59	2.57	6.26	3.33	35.00	3.35	1.27	0.56	2.82
29	Jan/27/11-T2/14	40.59	30.00	165.45	3.19	255.88	3.28	254.61	7.20	6.37	2.59	2.58	15.14	3.33	34.85	3.35	1.27	0.56	2.82
30	Jan/27/11-T2/23	39.97	30.00	165.45	3.19	256.06	3.28	254.61	7.20	6.37	2.59	2.58	11.23	3.33	34.85	3.35	1.27	0.56	2.82
31	Jan/27/11-T2/35	40.64	30.00	165.45	3.19	256.59	3.28	255.16	7.20	6.37	2.59	2.56	14.00	3.33	34.85	3.35	1.27	0.56	2.82
32	Jan/28/11-T1/18	38.57	30.00	165.89	3.19	255.51	3.28	254.53	7.18	6.36	2.59	2.56	14.38	3.33	34.87	3.35	1.27	0.56	2.82
33	Jan/28/11-T1/26	38.68	30.00	165.69	3.19	255.70	3.28	254.88	7.18	6.36	2.59	2.56	14.06	3.33	34.87	3.35	1.27	0.56	2.82
34	Jan/28/11-T1/33	38.41	30.00	165.89	3.19	256.06	3.28	255.18	7.18	6.38	2.59	2.56	13.38	3.33	34.87	3.35	1.27	0.56	2.82
35	Jan/28/11-T2/05	41.07	30.00	165.70	3.19	256.64	3.28	254.53	7.24	6.38	2.59	2.59	12.65	3.33	34.69	3.35	1.27	0.56	2.82
36	Jan/28/11-T2/20	41.52	30.00	165.70	3.19	256.01	3.28	254.53	7.24	6.38	2.59	2.59	7.15	3.33	34.69	3.35	1.27	0.56	2.82
37	Jan/28/11-T2/39	41.07	30.00	165.70	3.19	256.73	3.28	255.00	7.24	6.38	2.59	2.59	13.65	3.33	34.69	3.35	1.27	0.56	2.82
	HP Values	44.69	30.00	166.05	3.19	257.09	3.28	255.18	7.29	6.44	2.60	2.63	6.16	3.33	35.25	8oz			

4. Microbiological Validation of MW Process

4.1. Update of microbial work – determination of D- and z-values of PA 3679 *Clostridium sporogenes* spores in chicken breast

Raw skinless chicken breast was ground in a small electric food blender for 2 min. Ten g of blended chicken was placed in a 50 ml disposable conical centrifuge tube. Five hundred µl of PA 3679 # 308 *Clostridium sporogenes* spore crop (Mah July 2007 bottle no. 1) was placed in a depression formed in the chicken. A sterile metal spatula was used to thoroughly mix the spores and chicken for 10 min. A hypodermic syringe with a snipped yellow 0-200 µl pipette tip was used to inject chicken to a length of 50 mm inside a 1.8 mm glass capillary tube, then a 1.5 mm glass capillary tube was used to transfer the sample to the center of the 1.8 mm capillary tube. A lightly alcohol-wetted piece of Kimwipe wrapped around a 24 ga steel wire was used to clean traces of chicken from the end of the tube, to facilitate better flame-sealing with a Bunsen burner. Heat treatment was performed at pre-selected temperatures (113.0, 115.0, 118.0, and 121.1°C) in an oil bath for a variety of time intervals appropriate for each selected temperature. A 12 sec come-up time was included for all temperatures studied. Samples were cooled immediately for 2 min in an ice-water bath. Capillary tubes were opened aseptically with a file and contents were transferred to pre-weighed 15 cm conical centrifuge tubes containing 3 ml of sterile 0.1% peptone water. Tubes containing chicken were re-weighed and net weight of chicken was calculated. Chicken was homogenized by hand using the base of a sterile metal transfer loop handle or flame-polished glass rod using a grinding motion against the centrifuge tube bottom. Tenfold serial dilutions were performed using tubes containing 4.5 ml of 0.1% sterile peptone water. One ml of appropriate dilutions was duplicate spread-plated with TPGY agar and incubated 3 days at 32°C under anaerobic conditions. Plate counts were taken and CFU/ml and CFU/g chicken were calculated. Experiments were replicated 2-3 times.

Average D-values for the different temperatures were calculated and the z-value determined (Table 4.1 & Fig. 4.1). The D-value of PA 3679 spores in chicken breast at 121.1°C was 0.97 min; the z-value of PA 3679 spores in chicken breast was determined to be 9.26°C.

D-values of PA 3679 spores in dumplings and sauce at 121.1°C were determined previously: 0.47 min and 0.68 min, respectively.

Table 4.1 Summary of D-value results

Temp, °C	D-value, min					Log_{10} D-value				
	Rep 1	Rep 2	Rep 3	Average	Std Dev	Rep 1	Rep 2	Rep 3	Average	Std Dev
121.1	0.95	0.99		0.97	0.03	-0.02	0.00		-0.01	0.01
118	2.99	2.30	2.03	2.44	0.50	0.48	0.36	0.31	0.38	0.09
115	5.01	5.03		5.02	0.01	0.70	0.70		0.70	0.00
113	5.89	7.95	7.66	7.17	1.12	0.77	0.90	0.88	0.85	0.07

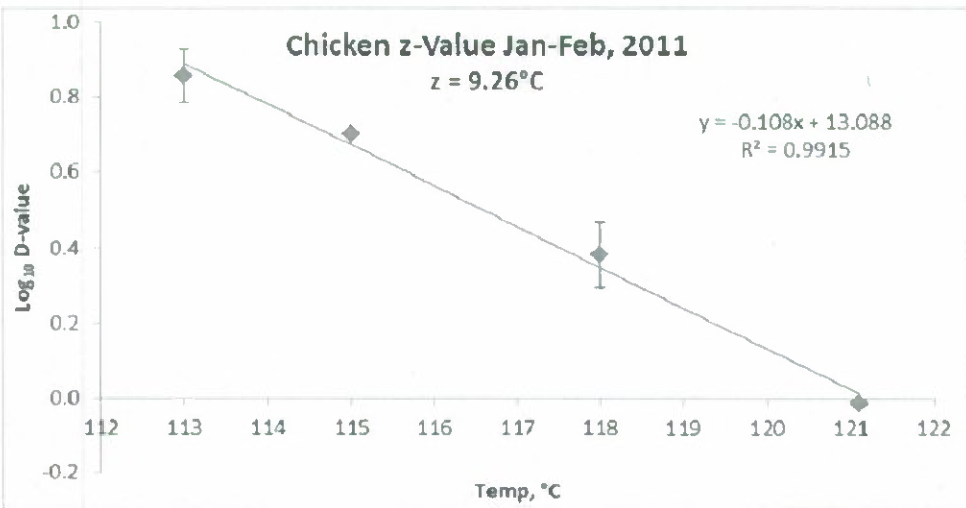


Fig. 4.1 Test results for determination of z-value of PA 3679 spores in chicken breast

4.2. Development of processing schedules for inoculated pack studies

Systematic tests were conducted with different belt speeds to achieve different F_0 values at the cold spot inside chicken-dumpling pouches. After each test run, F_0 values for the selected pouches were determined by the general method based on the temperature profiles measured by the Ellab sensors. The thermal contribution during the cooling period was included in the calculation of the F_0 values. The moving speeds of the food pouches were selected for achieving the F_0 of 2.4, 4.2, 6.2, and 8.6 min. Table 4.2 summarizes the developed processing schedules.

Table 4.2 Processing schedules for inoculated studies

Process level	F_0, min	Moving speed, inch/min	MW power setting, kW			
			Cavity 1	Cavity 2	Cavity 3	Cavity 4
Level-1	2.4	46	7.0	6.2	2.6	2.5
Level-2	4.2	43	7.0	6.2	2.6	2.5
Level-3	6.2	40	7.0	6.2	2.6	2.5
Level-4	8.6	39	7.0	6.2	2.6	2.5

4.3. Selection of inoculation level for inoculated pack studies

Inoculation level is a critical parameter for inoculated pack studies. The inoculation level should be selected based on the following rule: there are surviving spores in all or most of the inoculated packages after processing under the lowest process level (Level 1); there are surviving spores in some of the inoculated packages after processing under a lower process level (Level 2); there are no surviving spores in any of the inoculated packages after processing under a higher process level (Level 3) and the highest process level (Level 4). An inoculation level of 5×10^3 CFU/pouch was selected for the inoculated pack studies in this project. Theoretically, after processing under process level 1, 2, 3, or 4, the number of spores surviving in each inoculated pouch are 17, 0.234, 0.002, and 0.0000068. Consequently, the chance of a single spore surviving in each inoculated pouch is 100%, 23.4%, 0.2% and 0.00068%, respectively (Table 4.3).

Table 4.3 Chance of spore survival under different process levels (with inoculation of 5×10^3 CFU/pouch)

Processing level	Moving speed, inch/min	F_0	Log_{10} reduction	Inoculation level option : 5×10^3 CFU/pouch	
				Expected number of surviving spores per pouch	Expected chance of survival of a single spore in a pouch
Level-1	46	2.4	2.474	16.7781163	100%
Level-2	43	4.2	4.330	0.2339231	23.4%
Level-3	40	6.2	6.392	0.0020287	0.20%
Level-4	39	8.6	8.866	0.0000068	0.00068%

4.4. Preparation of samples and inoculation of the pouches

Each 8-oz Printpack pouch was filled with 95 g cut chicken breast pieces, 80 g sauce, 16 g dumplings, and 7 g vegetables. Among the fillings, a piece of cut chicken breast (40×40×16 mm) was inoculated by pipetting 10 µl of spore crop containing 5×10^3 CFU spores and was placed at the cold spot inside the pouch (Fig. 4.2). The pouches were sealed with an UltraVac 250 vacuum pouch sealer (KOCH Packaging Supplies Inc., Kansas City, MO) using a custom program (vacuum setting: 2.5; sealing time setting: 4) permitting a small amount of residual air (less than 3.5 cc) in the package. For each test run, two pouches with an Ellab sensor placed at the cold spot were prepared. The sealed pouches were kept in a cold room (4°C) prior to MW sterilization.

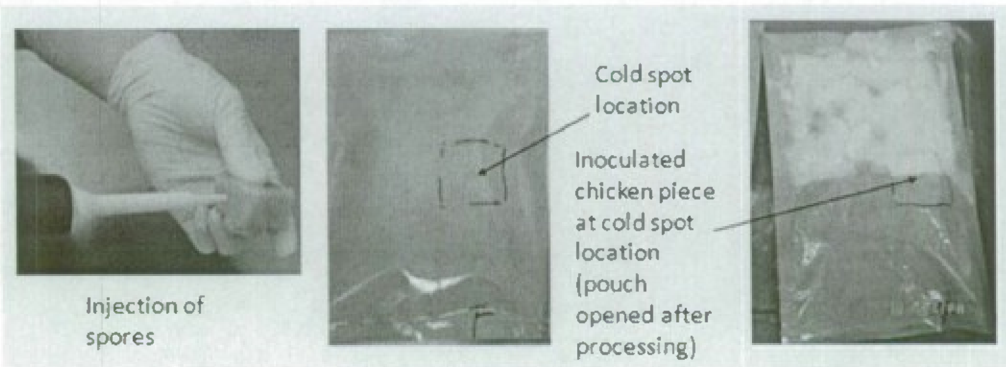


Fig. 4.2 Inoculation of sample and location of inoculated sample

4.5. Preliminary inoculated pack studies

Preliminary inoculated pack studies were conducted at three process levels (Level 1, 2, and 3) (Table 4.4). One test run was performed for each processing schedule. Five or ten inoculated pouches and two pouches with Ellab sensors were processed in each test. Five control pouches were inoculated with spores which were heat-shock activated by pre-treatment (heated for 20 min at 80°C then immediately cooled in ice-water). All the processed and un-processed control pouches were placed in a walk-in incubator at 36.5 ± 0.5°C for incubation (Fig. 4.3). Table 4.5 summarizes the observation results after 60 days of incubation (updated on April 30, 2011). All 5 control pouches swelled within 1 day due to gas production resulting from the growth of *C. sporogenes* PA 3679. Three out of 5 pouches processed at Level 1 (F_0 = 2.4 min) and 4 out of 10 pouches processed at Level 2 (F_0 = 4.2 min) swelled in 3 days. The other pouches have shown no evidence of gas production.

Table 4.4 Experimental design for preliminary inoculated pack studies

Processing level	Moving speed, inch/min	F_0	Inoculated pouches	Inoculum, CFU/pouch
Level-1	46	2.4	5	5×10^3
Level-2	43	4.2	10	5×10^3
Level-3	40	6.2	5	5×10^3
Control	un-processed		5	5×10^3

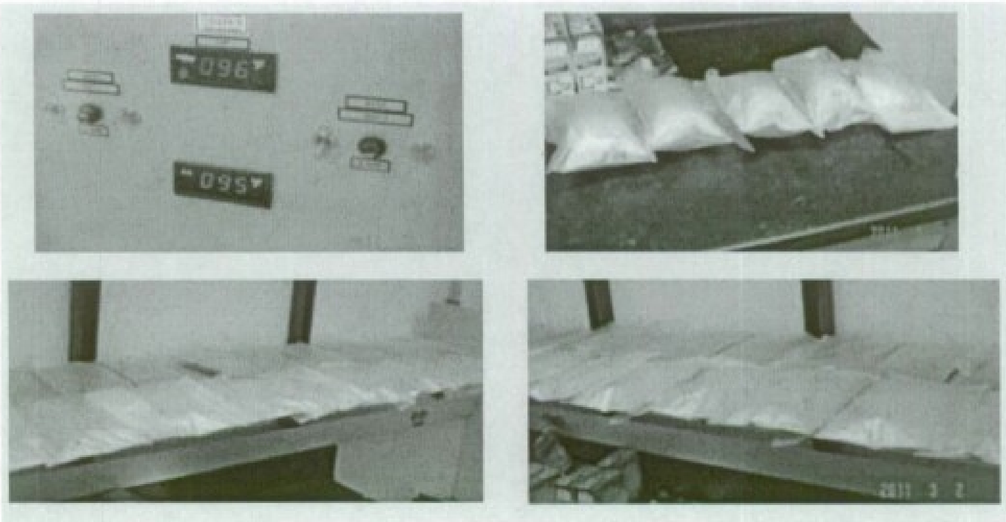


Fig. 4.3 MW processed and control pouches being incubated in walk-in incubator

Table 4.5 Incubation results for preliminary inoculated pack studies (updated on April 30, 2011; after 60 days' incubation)

Observation Sheet (preliminary chicken dumpling inoculated pack studies)													
Days of incubation		0	1	2	3	4	5	10	20	30	40	50	60
Observation date		1-Mar	2-Mar	3-Mar	4-Mar	5-Mar	6-Mar	11-Mar	21-Mar	31-Mar	10-Apr	20-Apr	30-Apr
Control with spores	Pouch #1	Neg	B	B	B	B	B	B	B	B	B	B	B
	Pouch #2	Neg	B	B	B	B	B	B	B	B	B	B	B
	Pouch #3	Neg	B	B	B	B	B	B	B	B	B	B	B
	Pouch #4	Neg	B	B	B	B	B	B	B	B	B	B	B
	Pouch #5	Neg	B	B	B	B	B	B	B	B	B	B	B
Fo= 2.4 (L1)	Pouch #7	Neg	Neg	B	B	B	B	B	B	B	B	B	B
	Pouch #8	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #9	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #11	Neg	Neg	B	B	B	B	B	B	B	B	B	B
	Pouch #12	Neg	Neg	B	B	B	B	B	B	B	B	B	B
Fo= 4.2 (L2)	Pouch #7	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #8	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #9	Neg	Neg	B	B	B	B	B	B	B	B	B	B
	Pouch #10	Neg	Neg	Neg	B	B	B	B	B	B	B	B	B
	Pouch #11	Neg	Neg	Neg	B	B	B	B	B	B	B	B	B
	Pouch #13	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #14	Neg	Neg	B	B	B	B	B	B	B	B	B	B
	Pouch #15	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #16	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #17	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
Fo= 6.2 (L3)	Pouch #7	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #8	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #9	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #11	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
	Pouch #12	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
Observer(s):		FL, ZT, HL	FL, ZT, HL	FL, ZT, HL	FL, ZT, HL	HL	HL	HL	HL	HL	HL	HL	HL
Note: B-bulging; Neg-negative													
FL-Frank Liu; ZT-Zhongwei Tang; HL-Huimin Lin													

4.7. Final full-scale inoculated pack studies

Tests were conducted in two replicates under each of the four process levels (Table 4.6). In each test, 25 inoculated pouches, 5 un-inoculated pouches, 2 pouches with Ellab sensors, and 10 dummy pouches (5 placed at each end of the conveyor belt) were processed. A total of 8 runs of tests were performed for the inoculated pack studies. All the MW-processed and control pouches were moved into the walk-in incubator on March 25, 2011 for incubation (Fig. 4.4).

Table 4.6 Experimental design for full scale inoculated pack studies

Processing level	Moving speed, inch/min	F_0, min	Inoculated Pouches (per replicate)	Inoculum/ Pouch	Un-inoculated/ Treated Pouches (per replicate)	Replicate Runs	Total Pouches
Level-1	46	2.4	25	5×10^3	5	2	60
Level-2	43	4.2	25	5×10^3	5	2	60
Level-3	40	6.2	25	5×10^3	5	2	60
Level-4	39	8.6	25	5×10^3	5	2	60
Control	un-processed		30	5×10^3	N/A	N/A	30
Total							270

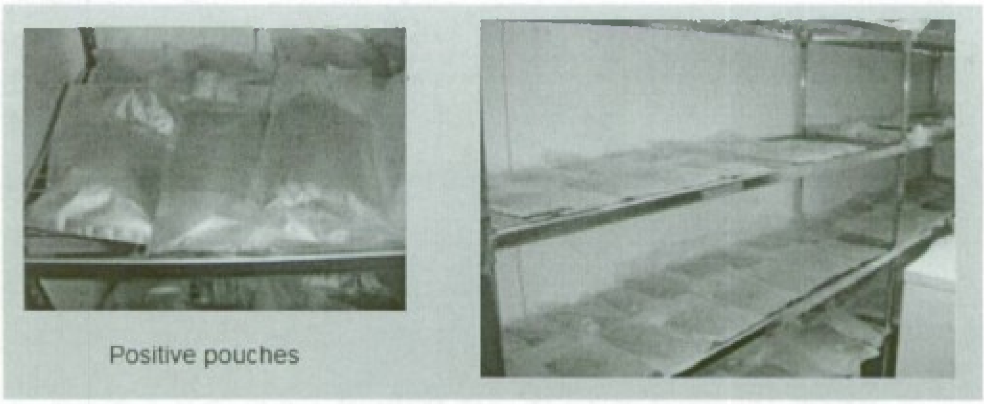


Fig. 4.4 MW processed and control pouches placed in walk-in incubator for incubation.

The walk-in incubator was controlled at 36.5 ± 0.5°C (Fig. 4.5), which was monitored every 5 days with 3 thermometers placed at different locations and recorded on a 24-h circular chart recorder. The pouches were / are / will be observed every day for the first 5 days and every 5 days thereafter for 3 months.

Table 4.7 summarizes the observation results after 80 days of incubation (updated on June 13, 2011). All 30 untreated inoculated control pouches swelled within 1 day due to gas production resulting from the growth of *C. sporogenes* PA 3679. All the 10 un-inoculated pouches processed at each level were negative. Bulging was detected in 27 of 50 inoculated pouches (54%) processed under Level 1 (F_0 = 2.4 min), and in 2 of 50 pouches (4 %) processed under Level 2 (F_0 = 4.2 min), respectively. The inoculated pouches processed under Level 3 & 4 (F_0 = 6.2 & 8.6 min) have shown no evidence of gas production. The incubation results suggest that the MW sterilization processing delivered expected lethalities to *C. sporogenes* PA 3679 spores.

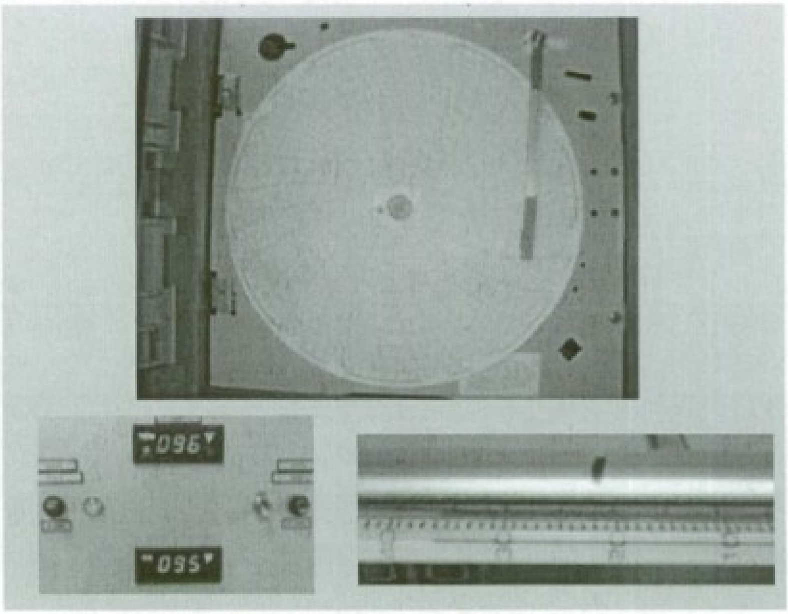


Fig. 4.5 Temperature controlled for incubation

Table 4.7 Incubation results for final full-scale inoculated pack studies (updated on June 13, 2011; after 80 days' incubation)

Process Level	F_0, min	Inoculum / Pouch	Replicate Runs	Number of		Observed Date (days)
				Sample Pouches	Positive Pouches [a]	
Control	N/A	5×10^3	N/A	30	30	1
Level-1	2.4	5×10^3	1	25	13	2 - 3
			2	25	14	2 - 3
		Un-inoculated	1	5	0	
			2	5	0	
Level-2	4.2	5×10^3	1	25	1	25
			2	25	1	2
		Un-inoculated	1	5	0	
			2	5	0	
Level-3	6.2	5×10^3	1	25	0	
			2	25	0	
		Un-inoculated	1	5	0	
			2	5	0	
Level-4	8.6	5×10^3	1	25	0	
			2	25	0	
		Un-inoculated	1	5	0	
			2	5	0	

a: When a complete bulging is detected, the pouch was considered positive.

5. Others

- Forty chicken dumpling pouches were processed with the MW processing schedule for F_0=6.2 min. After 10 days' incubation at 36.5°C, the pouches were shipped to Natick for evaluation.
- Forty chicken dumpling pouches were processed in hot water for F_0= 6 min and were shipped to Natick for evaluation after 10 days' incubation at 36.5°C.

General Summary

- The temperature profiles and F_0 values inside different food components at the cold spot identified by the chemical-marker-based computer-vision method inside chicken-dumpling pouches were measured with Ellab sensors. The chicken piece received the lowest thermal treatment and was chosen as the target component for temperature measurement in MW processing development.

- The temperature profiles and F_0 values at selected points inside chicken-dumpling pouches were measured with Ellab sensors. The cold spot identified by the chemical-marker-based computer-vision method was confirmed as the actual cold spot inside the real food pouch.

- Heat penetration (HP) test results show that, under the HP test conditions, the MW sterilization system delivered a thermal process to achieve F_0 higher than 6.0 min at the cold spot in chicken-dumpling pouches (each 8-oz PrintPack pouch filled with 95 g chicken breast pieces, 80 g sauce, 16 g dumplings, and 7 g vegetables) at the end of processing.

- Four processing schedules for inoculated pack studies were developed to achieve different target F_0 values varying from 2.4 to 8.6 min. An inoculation level of 5×10^3 CFU/pouch was selected for the inoculated pack studies.

- Preliminary inoculated pack studies were conducted in a small scale under three lower process levels (Level 1, 2, and 3).

- Full scale inoculated pack studies were finally conducted. Results showed that the developed MW sterilization processing delivered expected lethality to *C. sporogenes* PA 3679 spores.

- Forty chicken-dumpling pouches processed in MW for F_0=6.2 min and 40 pouches processed in hot water for F_0=6 min were shipped to Natick.

Future Work

- Prepare documentation for supporting USDA acceptance of the MW process for chicken-dumpling pouches.

Data Item B002 Contract No. W911QY-09-C-0205

TTI Label Report

Printpack, Inc. Atlanta, Ga

Development of Time/temperature Indicator Labels for Microwave Sterilization Process

Hans Ribi[1], Galina Mikhaylenko[2], Thomas Dunn[3]

Abstract

Co-topo-polymeric indicator compositions have been adapted as an ink medium suitable for confirming the exposure of a printed label on a flexible pouch to a target temperature for an indicated interval. The ink was printed onto heat resistant pressure sensitive-coated film and adhered to the outer surface (oriented polyester) of polymeric laminated pouches and processed in a microwave sterilization process. The observed color change confirmed the time/temperature exposure of the pouches in the process as confirmed by packaged electronic sensors.

Background

Military rations are currently packaged in multilayer aluminum-foil laminations which provide significant oxygen, water vapor, and light barrier. For a variety of reasons (Ratto et al., 2006) the military seeks to convert packaging for such rations to non-foil, polymeric packaging materials.

Microwave Sterilization (MWS) represents one major objective for replacing foil laminations (Tang et al. 2008). The process is a thermal one with the advantage of being able to raise pre-packaged contents of containers to sterilizing temperatures (121-125°C) rapidly (3-5 minutes) and maintaining target temperatures for the time required to kill pathogenic spores. This heating is quicker and degradation from heating is much less than in conventional retort processing (e.g. 20-30 minutes).

Operating and verifying the operation of a commercial MWS process requires reliable conformance to validated process conditions. Such conformance calls for sophisticated real time instrumentation of all parameters identified in the validation process. Reliable and accurate devices are of course crucial to this end. However, should such controls and backups fail, the shorter target time at sterilizing temperature for MWS implies that relatively small shortfalls will be more unsafe than in conventional thermal processes. An integral time/temperature indicator on the container will provide independent food safety and quality assurance for such contingencies.

As a step towards a heat resistant ink that can be printed on the packaging material, this research effort was devoted to evaluating the precision and accuracy of a model ink printed on pressure-sensitive labels and adhered to the outside of filled pouches.

The model ink is based on "Co-topo-polymers" disclosed in Ribi (2010). Compositions of these polymers are produced via polymerization of one or more monomeric components. The precursor compositions may have various ratios of distinct monomers, such as monomeric analogs, and may include one or more functional additives, e.g., that find use during co-crystallization. By way of example, consider the diacetylenic fatty acid, 2,4-

[1] Segan Industries, Burlingame, CA

[2] Washington State University, Dept. Biol. Sys. Eng., Pullman, WA

[3] Printpack Inc. Atlanta, GA

Heneicosadiynoic acid (Cas No. 69288-33-1) [CH_3-$(CH_2)_{15}$C≡C–C≡C–COOH]. The many areas of bond conjugation present in mixture of polymers including this and analogous diacetylenic monomers interact with light to produce color effects. Additionally, the inter-molecular rigidity resulting from multiple diacetylenic bonds in the polymer causes temperature dependence of the tertiary molecular and cystalline structure. This in turn changes interaction with light in reversible or irrreversible ways.
Design latitude in time/temperature dependency of the pigment polymers results from selection of monomer hydrocarbon chain length (e.g., 10 to 30 carbon atoms long), head-group structure (e.g., ester, amide, etc.), bond positioning, appendages, chirality, related features, and/or combinations thereof. Table 1 summarizes the design specifications used for the composition developed here:

Table 1: Design Specifications for TTI label ink

Print/Process Conditions	Duration	Exposure	State Change	Pressure
Flexographic drying	< 1 sec.	80 – 100°C	reversible	Ambient
Heat laminating Nip	< 1 sec.	80 – 90°C	reversible	20-60 psi
Storage stability	3-6 Months	20 – 25°C	reversible	Ambient
Hot filling	10 – 30 min.	70 – 90 °C	reversible	Ambient
Pre warming	10 – 30 min.	70 – 100°C	reversible	Ambient
Microwave sterilization	3-5 Min	120 – 125°C	irreversible	30 psig
Post processing storage	3 years	0 – 60°C	no reversion	Ambient

The plan to develop a time/temperature indicator ink for MWS processing includes a sequence of:

1. Laboratory calibration to an irreversible color change of select co-topo-polymers after simulated (heated oil-bath) MWS-exposure for indicated duration at target processing temperatures.
2. Pilot-plant verification of the co-topo-polymer effect using pressure sensitive labels on packaged food pouches as they are microwave sterilized.
3. Commercial validation of the co-topo-polymer incorporated into a flexographic ink and reverse printed onto oriented polyester film to be laminated to the outside of functional barrier polymeric pouches by processing them in the MWS pilot-plant.

The initial two steps of the plan are addressed in this report.

Materials and Methods

Laboratory calibration

Proprietary formulations of the co-topo-polymeric pigments were prepared and milled into a high solids content "screen" ink vehicle. This ink was then applied with a hand proofer to a heat-resistant oriented polyester film coated with a pressure sensitive adhesive (PSA). The printed film was cut into approximately 4 cm long pieces and adhered to one end of thin aluminum strips, about 2 x 10 cm.

The printed film ends of the aluminum strips were dipped into a temperature-controlled (±1 °C) silicon oil bath for increasing intervals (10 seconds to 5 minutes, as measured by a stopwatch). These intervals were repeated at increasingly higher temperatures.

The strips were allowed to cool to ambient temperature and color-compared to each other and untreated strips. Two formulations were chosen for future evaluation (Table 2):

Table 2: TTI ink candidates

Property	Ink type A	Ink type B
Color Density	Very Dense	Less Dense
Initial Color	Dark Blue	Light Blue
Color change: 124°C; >4 min	magenta	pinkish magenta

Pilot-plant verification

Strips (approximately 3 x 7 cm) of the same PSA coated polyester film printed with the 2

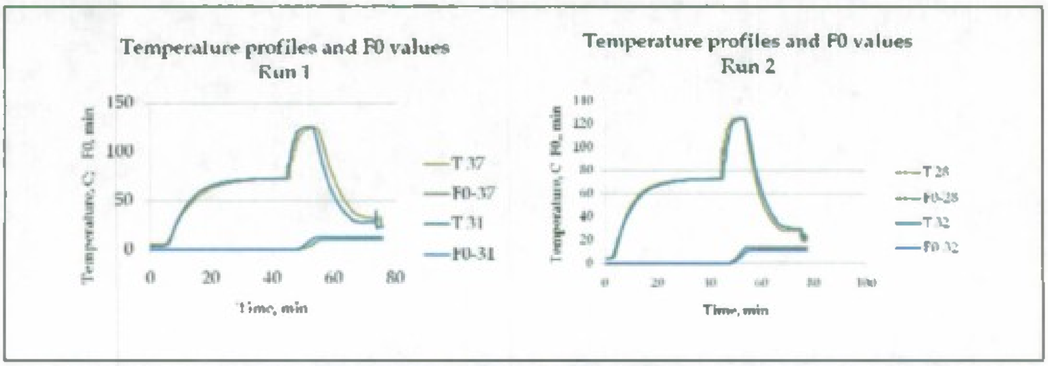


Figure A: MWS Process Conditions

best inks found in the calibration process were adhered to the outside of barrier all-polymeric pouches filled with salmon patties with Alfredo sauce. The pouches also contained the Ellab sensors used by WSU.

The MWS pilot plant is described in Tang et al. (2008). Specifically for this test, the MWS process was conducted using microwave power at 7.5, 7.5, 4.7 and 4.7 kW in the 4 cavities. Temperatures were set to: 72/124/123 °C for preheating, heating, and holding sections respectively with belt moving at 35 inch/min. Figure A summarizes the Time/temperature profile for the two runs with labeled pouches.

Results and Discussion

Laboratory calibration:

Color comparisons of the two preferred ink pigments are presented in Figure B. Each of the strips (comprised of an oriented polyester film-based pressure sensitive label adhered to a thin aluminum shim stock.) was submerged in the hot silicon oil bath for the time and temperature indicated. Each has two strips of printed film, one with ink A (left) and ink B (right). The image provided here (Figure B) presents the color of each strip after returning to room temperature. Here Ink A indicates little color change until about 50 seconds at 130°C. This change to magenta is clearly established by 120 seconds at 130°C, and too bright magenta by 180 seconds at 130°C. Ink B exhibited less reliable color dependability over the entire range of time and temperature, but demonstrated a clear change to pinkish magenta by 50 seconds exposure at 130°C. By 120 seconds at 130°C, the change was clear and noticeably differed from the untreated color.

These results were used to enhance the two formulations for the PSA labels sent to WSU for pilot plant runs there. (Actual formulation adjustments are proprietary, but are as indicated in the disclosures of Ribi (2010)).

Pilot-plant verification

Pre-run dielectric testing verified that no microwave field / ink interaction occurs.

Color comparisons of pouches labeled with the two ink pigments are presented in Figure C. Electronic thermocouples in the pouches were used to correlate the internal temperatures reached by the salmon with the external temperature of the pouches. Both inks can be optimized for distinct and irreversible color change following the selected time at the desired temperature

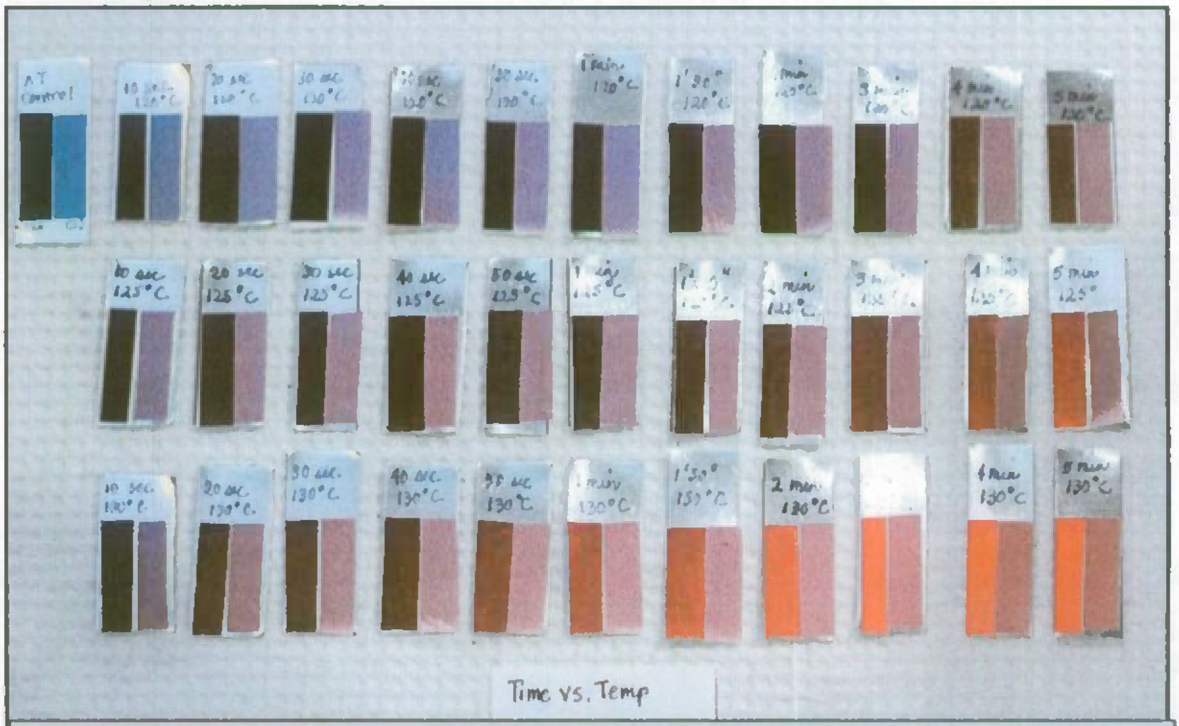


Figure B: Color comparison of time temperature exposures of indicator inks

Figure C: Color comparison of TTI labels untreated and exposed to MWS conditions

Conclusions

Co-topo-polymeric compositions can be developed and adapted for the time and temperature process conditions present during microwave sterilization. A bench top procedure for screening and evaluation of compositions satisfactorily predicts behavior of the label in the MWS structure.

Advancing these findings to commercial printing processes requires:

- Incorporation of the co-topo-polymeric compositions into a heat resistant ink vehicle.
- Adjustment of the ink's viscosity to ink-metering requirements of the printing process.
- Compatibility of the reverse-printed dried ink film with the adhesive to be applied over it in a subsequent laminating step.

Research is currently underway to address these intermediate assessments and to begin production of printed, laminated high barrier all polymeric pouches.

References

Ratto, Jo Ann, J. Lucciarini, C. Thellen, D. Froio, and N. A. D'Souza, 2006, *The reduction of Solid Waste Associated with Military Ration Packaging*, , US Army Soldier System Center, Technical Report, Natick (Ma) TR-06/023. 75pp.

Ribi, H.O., 2010. Co-topo-polymeric compositions, Devices and Systems for Controlling Threshold and Delay Activation Sensitivities. US Patent App. # 2010/12018.

Tang Z., Mikhaylenko G., Liu F., Mah J.H., Tang J. , Pandit R., Younce F., 2008. *Microwave Sterilization of Sliced Beef in Gravy in 7-Oz Trays. Journal of Food Engineering, 89.* (4), 375-383.

Exhibit D for CLIN 0017

CONTRACT DATA REQUIREMENTS LIST
(2 Data Items)

Form Approved
OMB No. 0704-0188

A. CONTRACT LINE ITEM NO.	B. EXHIBIT	C. CATEGORY
0017	D	● TDP ○ TM ○ Other

D. SYSTEM / ITEM	E. CONTRACT / PR NO.	F. CONTRACTOR
Technical Data - D001 and D002	W911QY-09-C-0205	PRINTPACK, INC.

Data Item D001

1. DATA ITEM NO.	2. TITLE OF DATA ITEM	3. SUBTITLE	17. PRICE GROUP
D001	Standard Scenarios		

4. AUTHORITY (Data Acquisition Document No.)	5. CONTRACT REFERENCE	6. REQUIRING OFFICE	18. ESTIMATED TOTAL PRICE
	Sections B & F		

7. DD 250 REQ	9. DIST STATEMENT REQUIRED	10. FREQUENCY	12. DATE OF FIRST SUBMISSION
NO		ASREQ	
8. APP CODE		**11. AS OF DATE**	**13. DATE OF SUBSEQUENT SUBMISSION**
N/A			

16. REMARKS

Standard scenarios predictions for shelf life models report cited in the Contractor's proposal will be provided as a deliverable under CLIN 0009, which will be completed by 30 April 2010.

14. DISTRIBUTION

a. ADDRESSEE	b. COPIES: Draft	Final: Reg	Final: Repro
15. TOTAL	0	0	0

Data Item D002

1. DATA ITEM NO.	2. TITLE OF DATA ITEM	3. SUBTITLE	17. PRICE GROUP
D002	Extreme Scenarios		

4. AUTHORITY (Data Acquisition Document No.)	5. CONTRACT REFERENCE	6. REQUIRING OFFICE	18. ESTIMATED TOTAL PRICE
	Sections B & F		

7. DD 250 REQ	9. DIST STATEMENT REQUIRED	10. FREQUENCY	12. DATE OF FIRST SUBMISSION
NO		ASREQ	
8. APP CODE		**11. AS OF DATE**	**13. DATE OF SUBSEQUENT SUBMISSION**
N/A			

16. REMARKS

Extreme scenarios predictions for shelf life models report cited in the Contractor's proposal will be provided as a deliverable under CLIN 0010, which will be completed by 31 May 2010.

14. DISTRIBUTION

a. ADDRESSEE	b. COPIES: Draft	Final: Reg	Final: Repro
STEPHEN MOODY	0	1	0
15. TOTAL	0	1	0

G. PREPARED BY	H. DATE	I. APPROVED BY	J. DATE
STEPHEN MOODY	17-Sep-2009	STEPHEN MOODY	17-Sep-2009

CLIN 0017 Data Item

"Thermal In-Pouch Microwave Sterilization" Contract No. W911QY-90-C-0205

Data Item D001 & D002 Contract No. W911QY-90-C-0205

Shelf Life Modeling Report – Standard and Extreme Scenarios

Printpack, Inc. Atlanta, GA

Shelf Life Model Calibration

Introduction

The M-RULE® Container Performance Model for Foods operates by integrating the fundamentals of permeant diffusion and solubility through polymeric (organic) materials, permeant vapor-liquid equilibriums, and time-dependent stress-relaxation behaviors with critically evaluated physical data for the component packaging materials.

Typical technical data available for flexible packaging films provides an oxygen transmission rate (O_2TR) for the material (typically "ASTM D3985 - 05 Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor") The rate is expressed in terms of the volume of oxygen (cubic centimeters at standard conditions) passing through a unit area (1 meter squared) of film with unit thickness[1] (25 microns) over a 24 hour period at specific temperature (°C), humidity (%RH) and partial pressure differential (atmosphere). This is a measure of the steady-state rate of transmission of oxygen gas through the polymeric material plastics. It provides for the determination of (*1*) oxygen gas transmission rate (O_2TR), (*2*) the permeance of the film to oxygen gas (PO_2), and (*3*) oxygen permeability coefficient ($P'O_2$) in the case of homogeneous materials. As such it is a contrived laboratory benchmark useful for inter-material comparisons, but not an effective, predictive tool for shelf life prediction (unless temperature, humidity and the oxygen partial pressure differential for the packaged product are sustained as specified for the steady state testing).

The model accommodates *inorganic coatings* on standard polymeric materials with a user-supplied "Barrier Improvement Factor (BIF)". Instead of the diffusion and solubility appropriate for polymeric materials, the model calculates mass movement of permeant through such coatings by its inferring its flux through voids in the coating. The M-RULE® handling of inorganic barrier coatings simply assumes the mass transport through whatever voids exist in that coating as a function of the delivery of the permeant to the film/coating interface and the ability of whatever lies on the opposite face of the coating to remove the permeant (e.g. absorption by another polymer, dilution in a free atmosphere, etc).

The model's handling of *polymeric barrier coatings* assumes sequential solubility in and diffusion across the boundary of two polymers. The partial pressure differential on either side of the coated film determines the sequence of transport, through coating into film or vice versa.

The objectives of this analysis are to validate various model inputs about the packaging materials with known O_2TR values for base and coated films and then using these inputs to dynamically model the shelf life of combat rations with M-RULE®.

[1] In the case of coated film or multilayered materials, this assumption of uniform transport over a unit thickness is not appropriate and the O_2TR is reported per actual thickness.

Method

Inorganic Coatings

Technical data on the O_2TR of base films and coated films are typically available. If attention is given to ensure consistency of temperature, humidity, and partial pressure conditions, these data can be used to directly compute BIF values for the coated film:

$$BIF = \frac{O_2TR_{base}}{O_2TR_{ctd}}$$

In effect, a BIF value is an indirect measurement of the integrity of the inorganic coating.

Polymeric Coatings

To model layered composite polymeric structures, the model must be supplied critical characteristics of each component. It then calculates mass transport of oxygen through the coated film using these characteristics both to compute the absorption into and diffusion through the respective layers and to define the immediate desorption/adsorption environment at the interface of the layers. With technical data for base and coated films, assumptions about the (usually proprietary) critical components of coatings can be inferred in order to fit the model to the technical data.

Hybrid Coatings

M-RULE® allows a user to define the nature and distribution of clay nanoparticles (inorganic materials) dispersed within a polymeric matrix. This definition controls changes in diffusion of oxygen trough the neat polymer. In this way, a hybrid coated-film can be modeled with various assumptions until the results fit published technical data.

Storage Conditions

The following assumed values for temperature and humidity were modeled using the system. The assumed scenarios represented this logistics sequences:

Scenario	Stage 1	Stage 2	Stage 3
Standard	Domestic warehouse	marine shipment	jungle warehouse
Extreme	Domestic warehouse	marine shipment	desert warehouse

Specifically, these are:

Standard:	27°C – 50% RH – 365 days
	27°C – 90% RH – 90 days
	38°C – 90% RH – 640 days
Extreme:	27°C – 50% RH – 90 days
	38°C – 90% RH – 90 days
	49°C – 20% RH – 915 days

Results

Individual film components

Conditions and barrier values were provided by the suppliers of the materials used in the MRE non-foil pouch structure. The same conditions were entered into M-RULE® and used to optimize the material characteristics until they matched the known data, as presented below in Table 1.

Table 1: Data Sheet and Modeled barrier values for films					
	Data Sheet Values		Model Values		
	O_2TR cc•day/m^2	WVTR gm•day/m^2	O_2TR cc•day/m^2	WVTR gm•day/m^2	BIF
@12µ OPET-hybrid	85% RH; 0.4-0.8	50	20°C, 85% RH: 0.717	24.6	66
@15µ OBON-hybrid	85% RH; 0.5	240	0.713	26.1	66
*12µ OPET-Al_2O_3 #1	.62	2.02	0.695	1.01	42.5
*12µ OPET-Al_2O_3 #2	.62	1.09	0.695	1.01	42.5
#12µ OPET-PVdC	12	14	12.2	16.3	2.4
12µ OPET	29.4	38	29.56	35.3	n/a
15µ OBON	0% RH: 47-62	100% RH: 310 - 357	0% RH: 47.08	100% RH: 347.5	n/a
75µ CPP	207.9	4	200.97	1.66	n/a
75µ mPE	546	5	571.83	4.15	n/a
* Inorganic Coating # Polymeric Coating @ Hybrid Coating					

The only significant difference between reported values from suppliers and model results is with regards to the hybrid-coated BON, highlighted in yellow. The model inputs could estimate the oxygen barrier of the material very closely, but those same inputs lead to a 10-fold difference in moisture barrier. However, when used in the non-foil composite structure, this 10-fold difference did not appear to have any impact on the results for the composite MRE non-foil pouch, as is shown below.

Composite structure

The current structure for the MRE non-foil pouch is constructed as follows:

12µ OPET//12µ OPET-Al_2O_3 #2//15µ OBON-hybrid//75µ CPP

The MRE non-foil pouch (structure #6) was evaluated using the model under the same conditions entered for the OTR and WVTR analyses completed as part of Task 2: Physical, Barrier & Optical Data.

Test Type	Conditions	Tested Values	Model Values
OTR	23°C; 0% RH	<0.009 – 0.253 cc·day/m2	0.017 cc·day/m2
OTR	23°C; 90% RH	<0.009 – 0.079 cc·day/m2	0.017 cc·day/m2
WVTR	37.8°C; 90% RH	0.158 – 0.555 gm·day/m2	0.259 gm·day/m2

The conditions and characteristics as input into the model provided a close approximation of the conditions and results achieved through lengthy, expensive barrier property testing. With proper optimization of material characteristics and conditions, the M-Rule system can provide consistent OTR and MVTR data for complex packaging structures.

The following charts are based on values computed for a 7.25" high x 5.25" wide (76.125 sq in packaging surface) pouch filled nominally with 227g of chicken and dumplings, a 5.25" high x 3.75" wide (39.375 sq in packaging surface) pouch filled nominally with 40g of peanut butter dessert bar and a 7.375" high x 4.75" wide (73.625 sq in packaging surface) filled nominally with 128g of mango peach applesauce, respectively. Maximum fill model scenarios were also run, with very little variation in results from those seen at nominal fill.

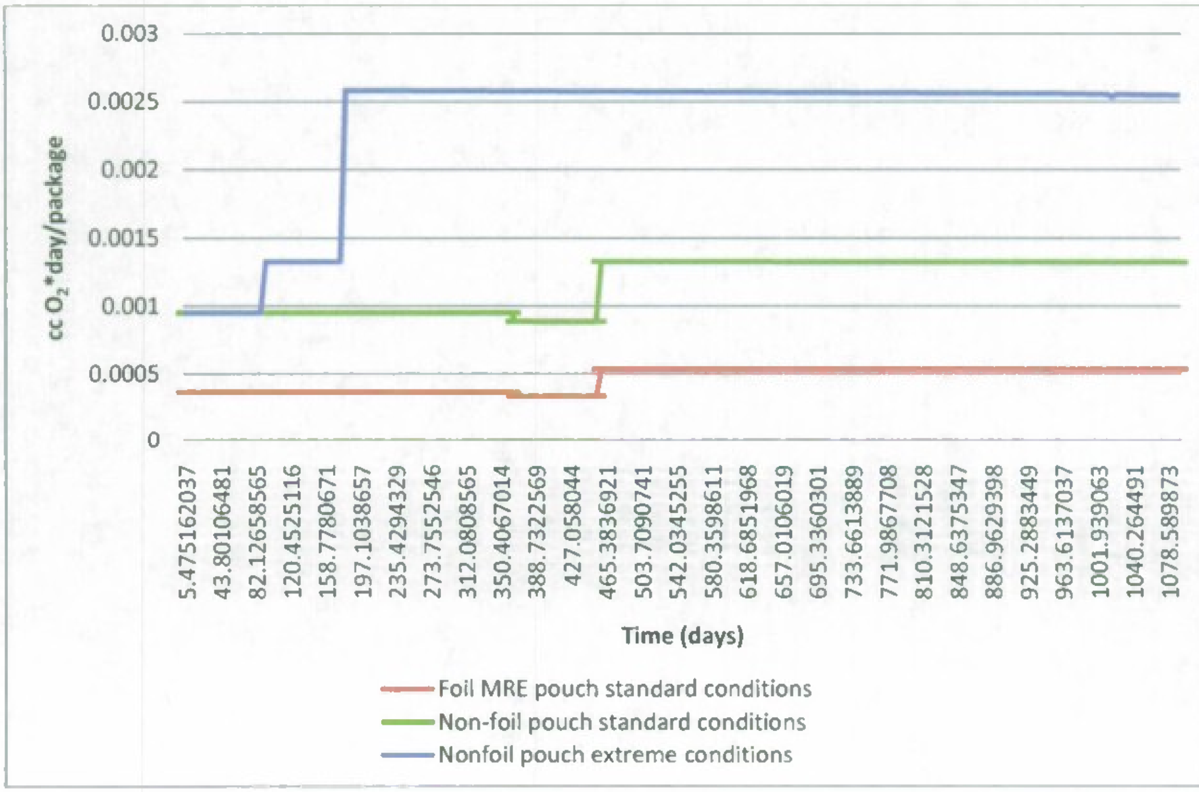


Figure 1. Chicken & Dumplings Package Incremental O_2 content (cc*day/package) is clearly increased during the extreme storage conditions but remains below 0.003 cc*day/package for the non-foil pouch structure. In comparison, foil MRE pouches remain below 0.001 cc*day/package throughout the entire 3 year shelf life of the product under standard storage conditions.

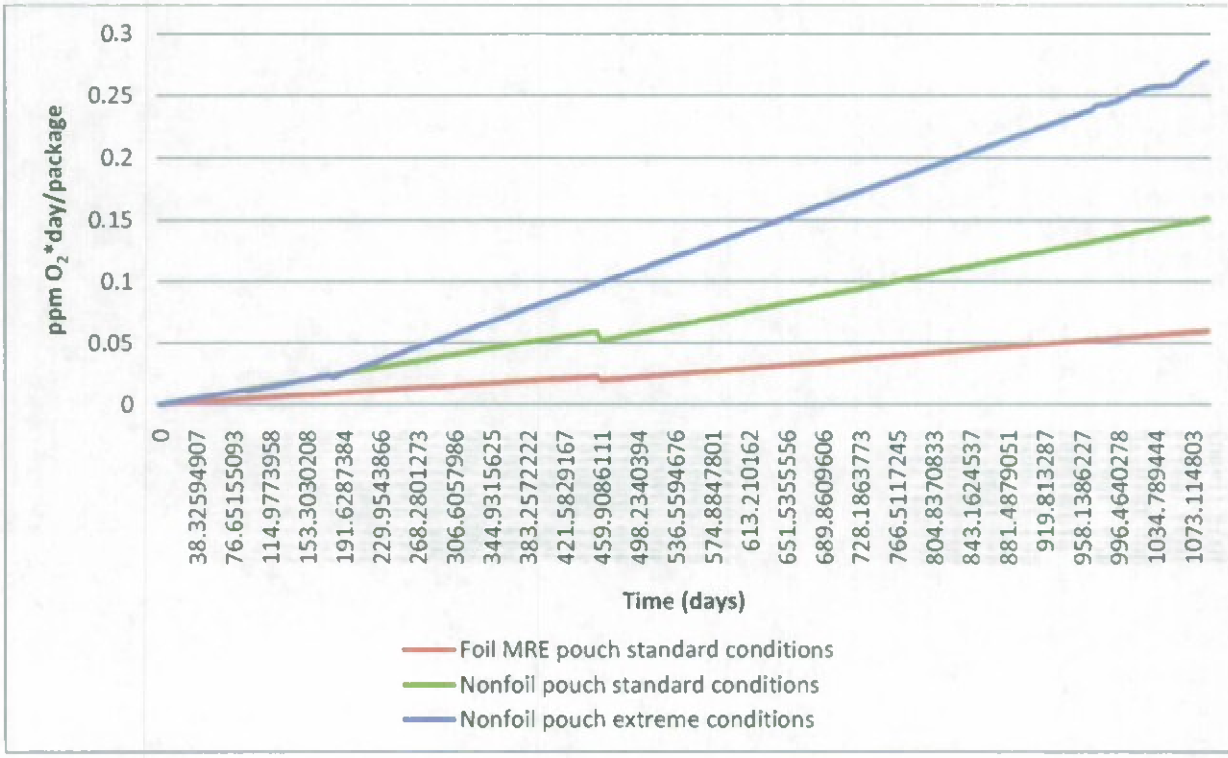


Figure 2. Chicken & Dumplings Product O_2 content (ppm*day/package) rose throughout the shelf-life but stayed relatively low under standard conditions for the non-foil pouch. Under extreme conditions, the product O_2 content nearly doubled from 0.15 ppm *day/package to 0.28 ppm*day/package. If particular vitamins or compounds that are oxygen-sensitive could be affected even by such low-level increases, the model inputs can be altered to track vitamin content and activity.

Chicken & Dumplings Product Moisture content (%RH/day) was maintained at approximately 76% for all package types under both sets of conditions, which used 50% RH as the environmental condition and 0% RH in the headspace gas composition (degassed fill) at filling time. The chicken and dumplings were given a lower moisture specification of 50% RH and an upper moisture specification of 100% RH. If more refined moisture specifications are vital for product quality and regulatory requirements, the current non-foil structure as well as future material changes can be modeled to determine the effect on moisture content as necessary.

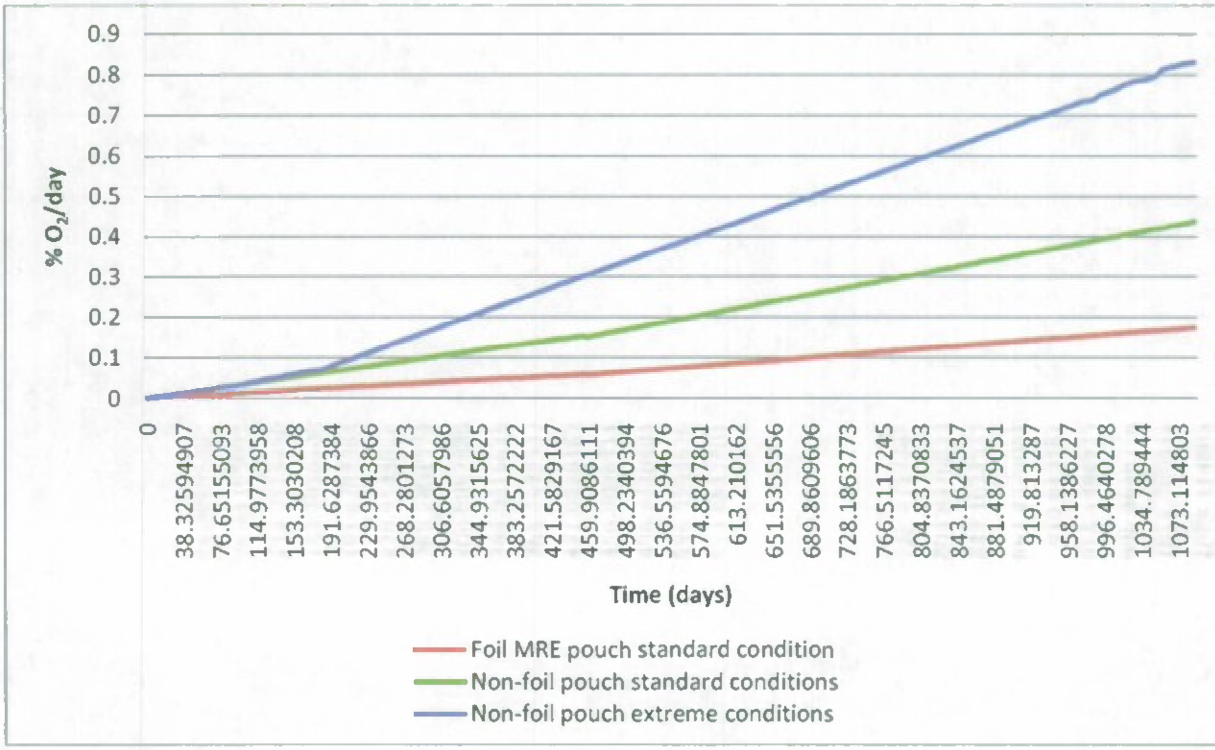


Figure 3. Chicken & Dumplings Headspace O_2 content (%/day) increased with time, and increased more rapidly under the extreme conditions. The foil structure maintained headspace O_2 at below 0.2% over the standard 3 year shelf-life, while the non-foil stayed below 0.45% during the standard shelf-life and below 0.85% during the extreme storage conditions. As with the product O_2 content, this can be monitored more closely over the period of concem and with respect to oxygen-sensitivity.

Chicken & Dumplings Headspace Relative Humidity (%/day) was maintained at 100% for both the foil and non-foil structures under both sets of conditions due to the high moisture content of the food.

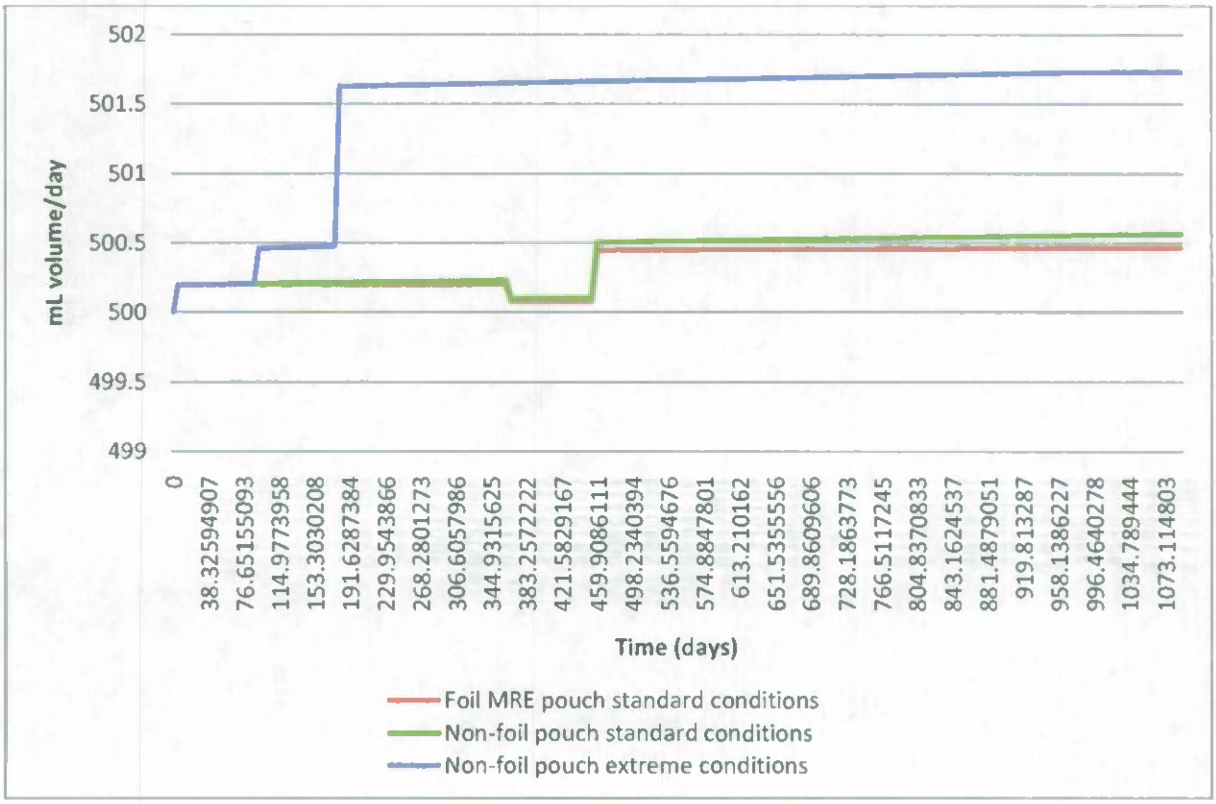


Figure 4. Chicken & Dumplings Package Volume (mL/day) started at 500 mL and maintained fairly steadily with a high of 500.6 during standard conditions. During extreme conditions, the package volume swelled more but stayed under 501.8 mL at the highest. This represents a percent volume increase of 0.12% for the foil and non-foil pouch under standard conditions and a percent volume increase of 0.36% for the non-foil pouch under extreme conditions.

Figure 5. Peanut Butter Bar Package Incremental O_2 content (cc*day/package) was maintained below 0.001 cc*day/package in both structures under standard as well as extreme conditions. The oxygen content was kept lowest in the foil pouch at 0.000128 cc*day/package under standard conditions, whereas the non-foil structure resulted in 0.00034 cc*day/package under standard conditions and 0.00062 cc*day/package under extreme conditions.

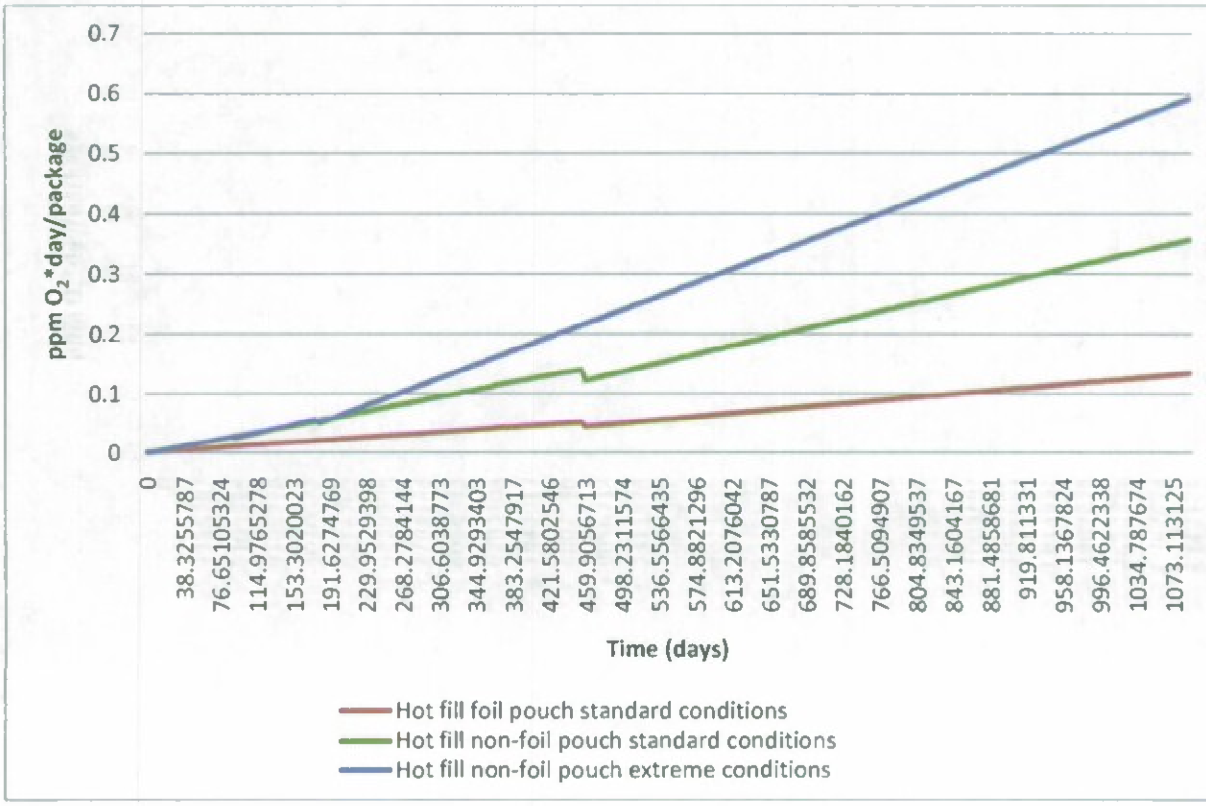


Figure 6. Peanut Butter Bar Product O_2 content (ppm*day/package) increased over the shelf life of the bar to 0.134 ppm*day/package for the foil pouch at standard conditions, 0.356 ppm*day/package for the non-foil pouch at standard conditions and 0.590 ppm*day/package for the non-foil pouch at extreme conditions.

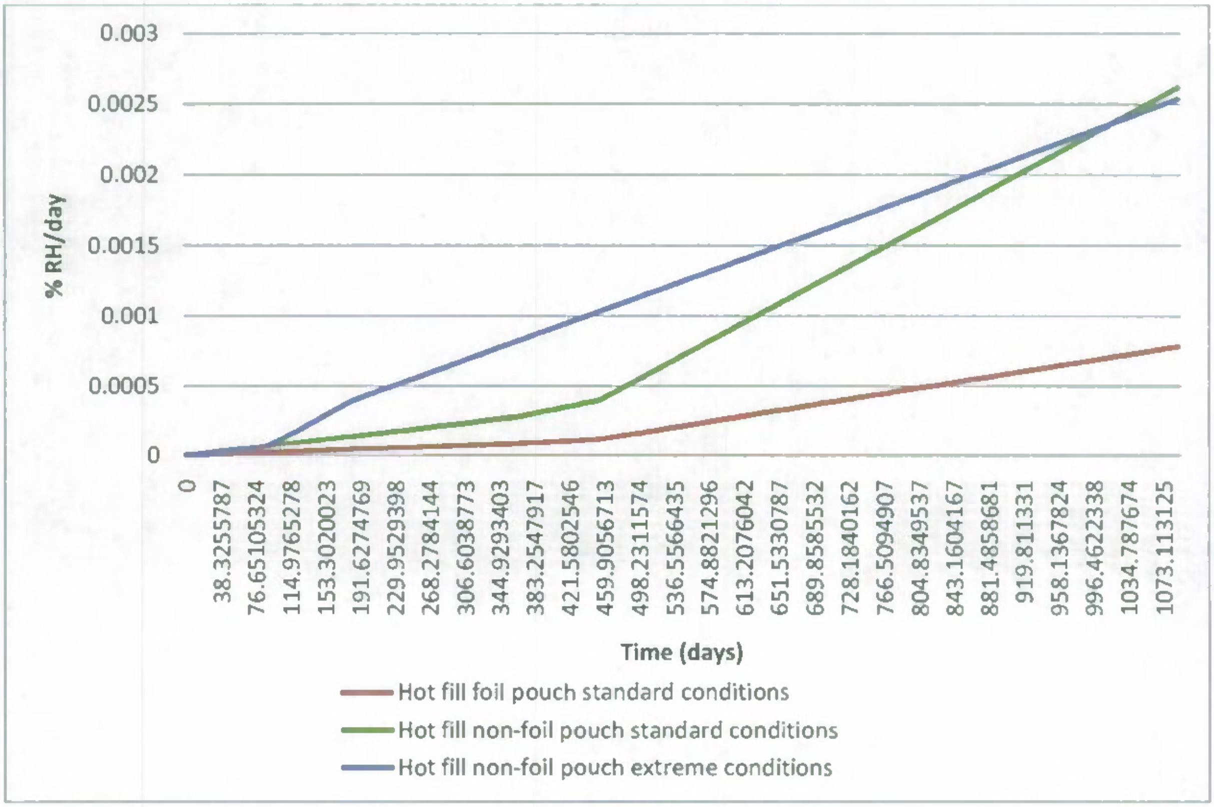


Figure 7. Peanut Butter Bar Product Moisture content (%RH/day) reached 0.0008 %RH/day in the foil pouch over the course of the 3 year shelf life under standard conditions, while storage in the non-foil pouch under standard conditions and extreme conditions yielded a moisture content of 0.0026. This is a significant increase on product moisture content, and while it may still be within the permissible limits, it is obviously an area for improvement in the package capabilities.

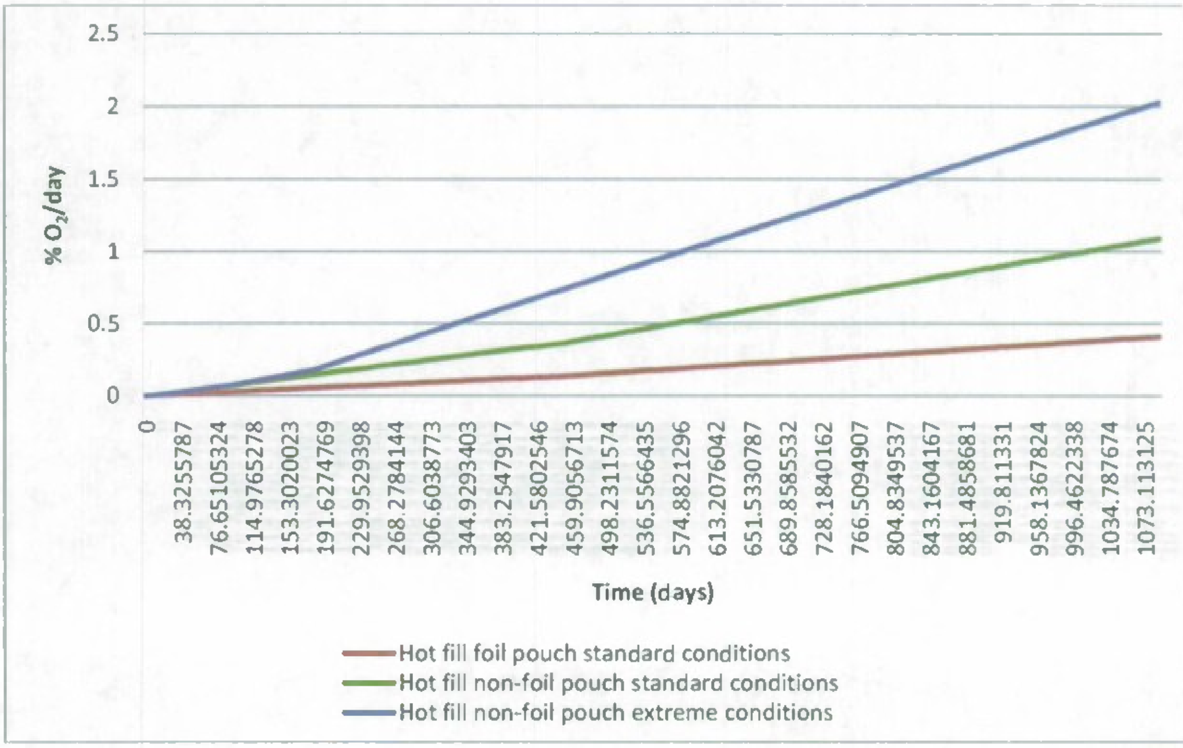


Figure 8. Peanut Butter Bar Headspace O_2 content (%/day) increased more rapidly under the extreme conditions. The foil structure maintained headspace O_2 at below 0.5% over the standard 3 year shelf-life, while the non-foil stayed below 1.1% during the standard shelf-life and at 2% during the extreme storage conditions.

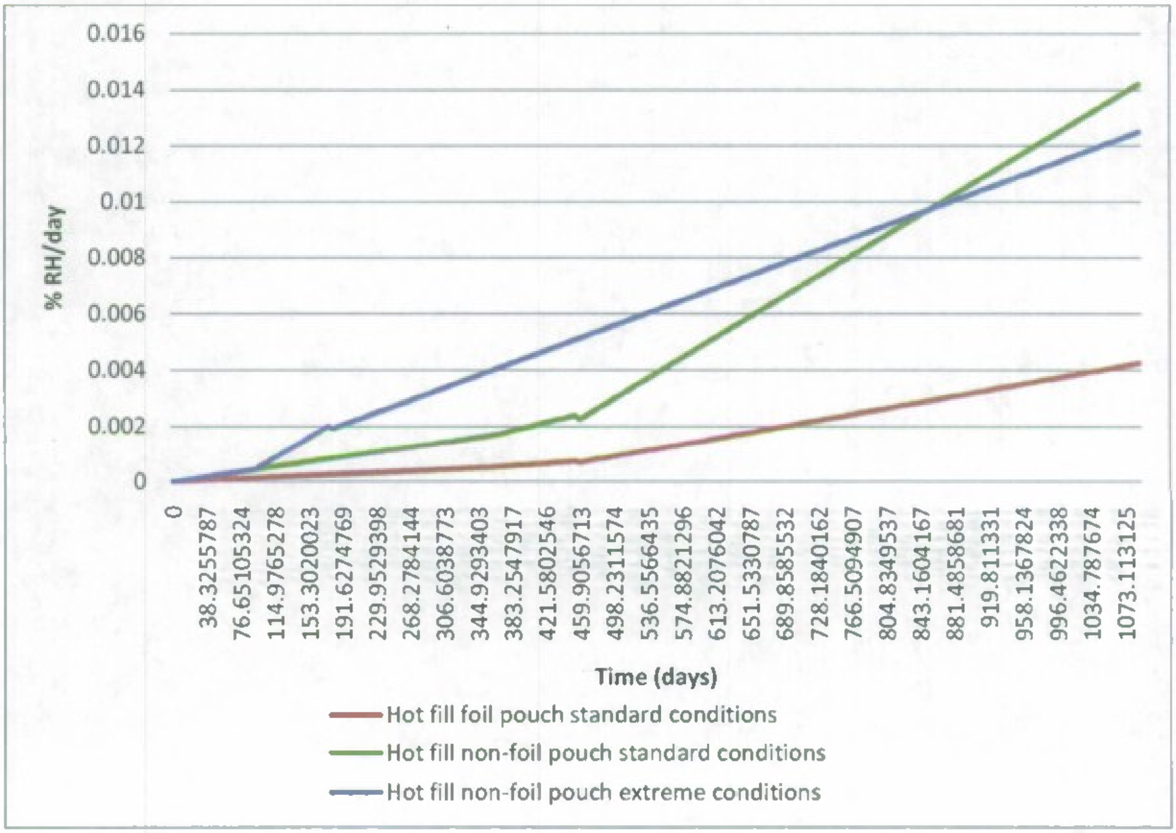


Figure 9. Peanut Butter Bar Headspace Relative Humidity (%/day) reached a high of 0.0042%/day in the foil pouch at standard conditions. The non-foil pouches showed a large increase in headspace RH over the 3 year shelf-life, reaching 0.014 under standard storage conditions and 0.0125 under extreme storage conditions.

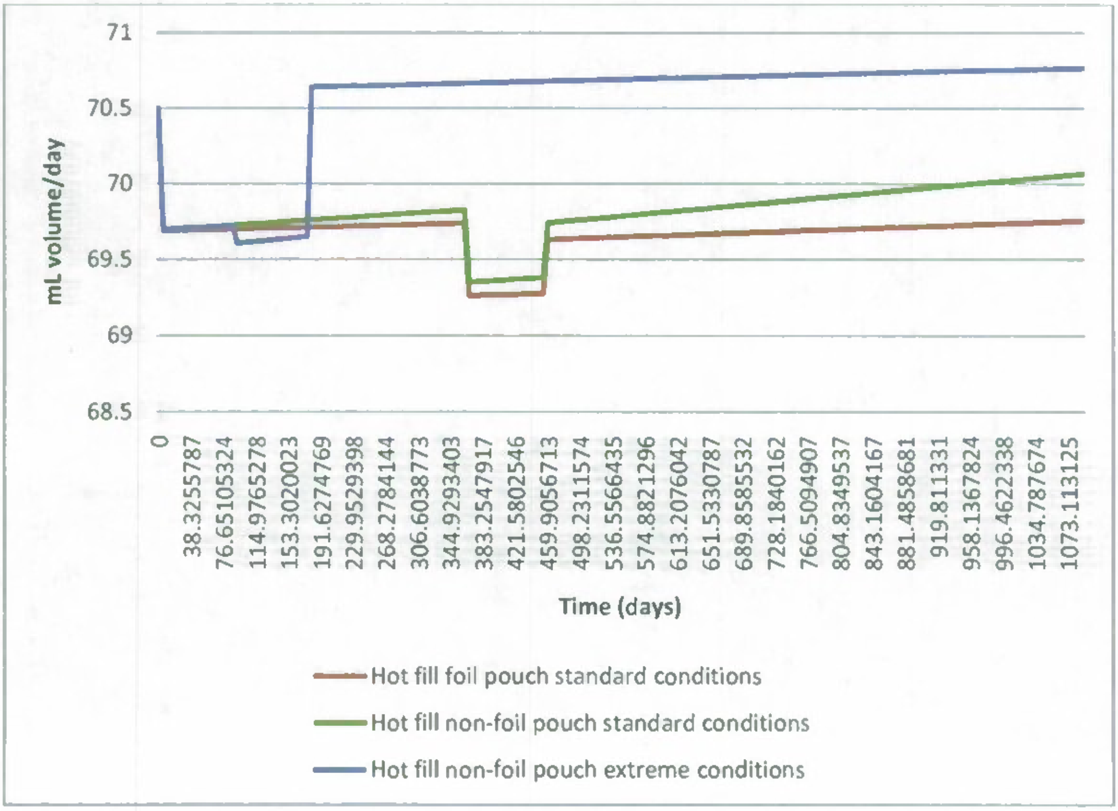


Figure 10. Peanut Butter Bar Package Volume (mL/day) decreased from 70.5 mL to 69.75 in the foil pouch and to 70.07 in the non-foil pouch under standard storage conditions. Volume increased to 70.77 mL in the non-foil pouch under extreme storage conditions. This represents a percent volume decrease of 1.0 % in the foil pouch and 0.6% in the non-foil pouch at standard storage conditions. The non-foil pouch volume increased by 0.38% under extreme storage conditions.

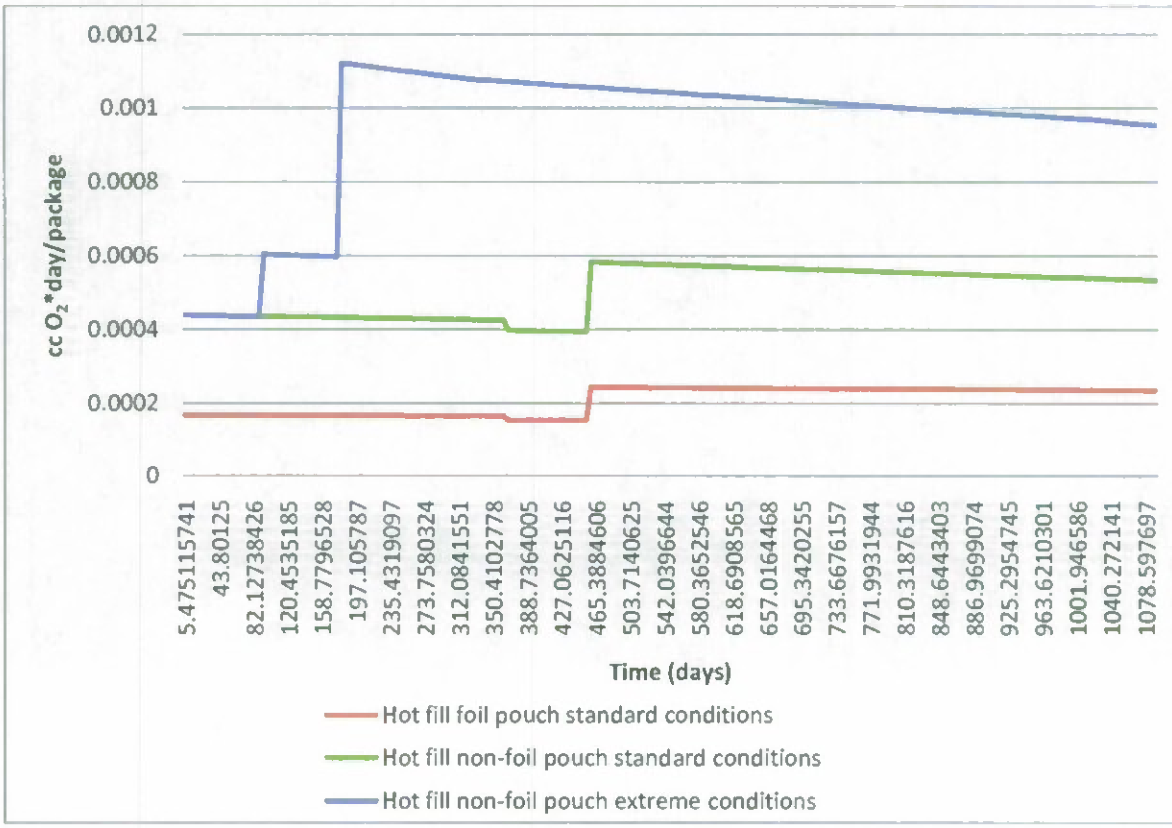


Figure 11. Mango Peach Applesauce Package Incremental O_2 content (cc*day/package) fluctuated over the 3 year shelf life for all samples, settling at approximately 0.0002 cc*day/package for the foil pouch at standard conditions, 0.0005 cc*day/package for the non-foil pouch at standard conditions and 0.00095 cc*day/package for the non-foil pouch at extreme conditions.

Figure 12. Mango Peach Applesauce Product O_2 content (ppm*day/package) reached 1.04 ppm*day/package in the foil pouches under standard storage conditions, 2.53 ppm*day/package in the non-foil pouches under standard storage conditions and 4.12 in the non-foil pouches under extreme storage conditions.

Mango Peach Applesauce Product Moisture content (%RH/day) was maintained at approximately 77.5% for all package types under both sets of conditions, which used 50% RH as the environmental condition and 0% RH in the headspace gas composition (degassed fill) at filling time. The mango peach applesauce was given a lower moisture specification of 77% RH and an upper moisture specification of 100% RH.

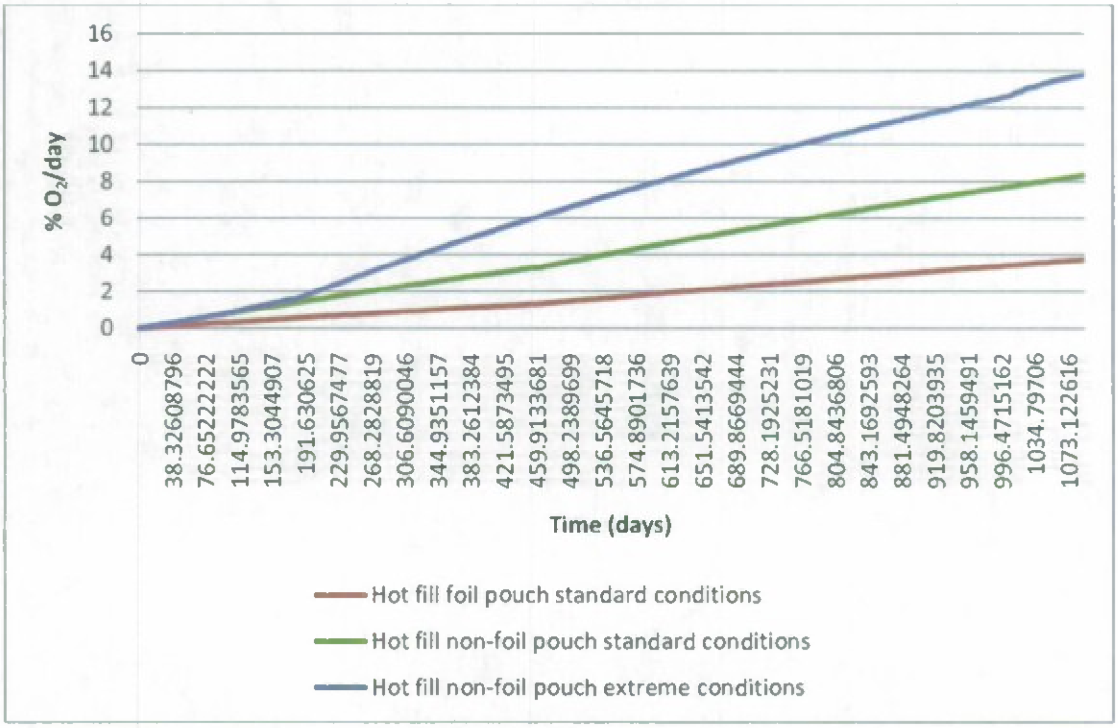


Figure 13. Mango Peach Applesauce Headspace O_2 content (%/day) increased with time, and increased more rapidly under the extreme conditions. The foil structure maintained headspace O_2 at below 4% over the standard 3 year shelf-life, while the non-foil stayed below 8.5% during the standard shelf-life and below 14% during the extreme storage conditions. This is a relatively rapid increase in headspace O_2, even in the foil pouch, and therefore requires additional research.

Mango Peach Applesauce Headspace Relative Humidity (%/day) was maintained at 100% for both the foil and non-foil structures under both sets of conditions due to the high moisture content of the food.

Mango Peach Applesauce Package Volume (mL/day) was maintained at 128 mL in the foil pouch and in the non-foil pouch under standard storage conditions. Volume increased to 128.55 mL in the non-foil pouch under extreme storage conditions. This represents a percent volume increase of 0.43%.

Discussion

Moisture barrier and oxygen barrier are of critical importance when packaging a product that undergoes long-term storage under fluctuating storage conditions, like combat rations. Water activity (also known as the relative vapor pressure of water) is temperature dependant, with the degree of dependence being a function of the moisture content (Fennema, Owen R. (1996). *Food Chemistry, Third Edition*, Marcel Dekker Inc., New York, NY). Water activity can affect multiple areas of food stability, including microbial growth, lipid oxidation and Maillard browning reactions. Oxygen is necessary for many key reactions in food products, including deleterious reactions like lipid oxidation, discoloration (whether by oxidative browning or pigment oxidation) and the growth of aerobic spoilage microorganisms (Eskin, N.A. Michael & Robinson, David S. (2001). *Food Shelf Life Stability: Chemical, Biochemical and Microbiological Changes*, CRC Press LLC, Boca Raton, FL.)

Moisture content and headspace relative humidity for the chicken & dumplings as well as the mango peach applesauce do not appear to undergo extreme variability over the shelf life. The peanut butter bar (moisture content per specification: 0.64 g in a 40 g bar, or 0.016 g H_20/g dry matter) experiences more changes in the moisture content and relative humidity. The current foil MRE pouch structure provides a better barrier than the non-foil pouch structure; however, even in the non-foil pouch during extreme conditions, the moisture content and relative humidity do not appear to increase to unacceptable levels. At low water activity levels, the limiting factor of food acceptability will not be microbial spoilage but lipid oxidation. As the peanut butter bar has 17.16 g of fat in a 40 g bar, as well as fat-soluble vitamins A and E, lipid oxidation is a matter of real concern over the shelf-life of the product.

Oxidative reactions contribute to lipid breakdown, vitamin degradation, phenolic browning and breakdown of color compounds in packaged food products. It is fairly clear from the results for all three foods that the ingress of oxygen is highly dependent on the temperature fluctuations seen over the three year shelf-life. The rate of oxygen ingress through the non-foil package into the headspace and product dramatically increases during the extreme storage scenario, in some cases at the 90 day mark where the conditions change from 27°C/50% RH to 38°C/90% RH, and in others at the 180 day mark of the shelf-life where the conditions change again to 49°C/20% RH for the duration of the shelf-life. However, the oxygen sensitivity can vary based on the proportions and importance of different macronutrients and micronutrients. High-moisture foods like applesauce or chicken & dumplings will not be overly susceptible to lipid or Vitamin A degradation, while the low-moisture, high-fat dessert bar could be greatly impacted by oxidation of various nutrients. However, the high level of Vitamin C in the mango peach applesauce will be susceptible to oxygen degradation as well.

Conclusion

The M-RULE® Container Performanee Model for Foods has elearly been shown to validate various model inputs for base and coated films with known O_2TR and MVTR values as well as composite foil and non-foil structures. These inputs have subsequently been used in modeling the anticipated shelf-life of representative combat ration items (an entrée, a fruit sauce and a dessert) over varying storage conditions in the foil and non-foil packages. The results have clarified the progress made in the oxygen and moisture barriers of the non-foil film while pinpointing areas for improvement in future research.

Development of On-Pack Time-Temperature Indicator Ink for Microwave Sterilization

Linda Minkow[1], Hans Ribi[2], Zhongwei Tang[3], Tom Dunn[1]

Abstract

Co-topo-polymeric indicator compositions have been adapted as an ink medium suitable for confirming the exposure of a printed label on a flexible pouch to a target temperature for an indicated interval. The ink was reverse-printed onto the outer surface (oriented polyester) of polymeric laminated pouches and backed with a retort-grade white ink for visualization. Some samples were laminated without white ink to determine effects of adhesive chemistry and pigmentation on the color development of the TTI ink. The observed color change confirmed the time/temperature exposure of the pouches in the process as corroborated by packaged electronic sensors.

Background

Military rations are currently packaged in multilayer aluminum-foil laminations which provide significant oxygen, water vapor, and light barrier. For a variety of reasons (Ratto et al., 2006) the military seeks to convert packaging for such rations to polymeric packaging materials.

Microwave Sterilization (MWS) represents one major objective for replacing foil laminations (Tang et al. 2008). The process is thermal but with the advantage of being able to raise pre-packaged contents of containers to sterilizing temperatures (121-125°C) rapidly (3-5 minutes) and maintaining target temperatures for the time required to kill pathogenic spores. This heating is quicker and degradation from heating is much less than in conventional retort processing.

Operating and verifying the operation of a commercial MWS process requires reliable conformance to validated process conditions. Such conformance calls for sophisticated real time instrumentation of all parameters identified in the validation process. Reliable and accurate devices are of course crucial to this end. However, should such controls and backups fail, the shorter target time at sterilizing temperature for MWS implies that relatively small shortfalls will be more unsafe than in conventional thermal processes. An integral time/temperature indicator on the container will provide independent food safety and quality assurance for such contingencies.

Previously reported data (CLIN 0011) outlined the development of the TTI ink, as based on "Co-topo-polymers" disclosed in Ribi (2010), as well as the testing performed in the MWS unit at WSU using on-pack labels to demonstrate proof-of-concept.

---

[1]Printpack, Inc., Atlanta, GA
[2]Segan Industries, Burlingame, CA
[3]Washington State University, Dept. Biol. Sys. Eng., Pullman, WA

Table 1 summarizes the design specifications used for the composition developed here:

Table 1: Design Specifications for TTI label ink				
Print/Process Conditions	**Duration**	**Exposure**	**State Change**	**Pressure**
Flexographic drying	< 1 sec.	80 – 100°C	reversible	Ambient
Heat laminating Nip	< 1 sec.	80 – 90°C	reversible	20-60 psi
Storage stability	3-6 Months	20 – 25°C	reversible	Ambient
Hot filling	10 – 30 min.	70 – 90 °C	reversible	Ambient
Pre warming	10 – 30 min.	70 – 100°C	reversible	Ambient
Microwave sterilization	3-5 min	120 – 125°C	irreversible	30 psig
Post processing storage	3 years	0 – 60°C	no reversion	Ambient

The plan to develop a time/temperature indicator ink for MWS processing includes a sequence of:

1. Laboratory calibration to an irreversible color change of select co-topo-polymers after simulated (heated oil-bath) MWS-exposure for indicated duration at target processing temperatures.
2. Pilot-plant verification of the co-topo-polymer effect using pressure sensitive labels on packaged food pouches as they are microwave sterilized.
3. Commercial validation of the co-topo-polymer incorporated into a flexographic ink and reverse printed onto oriented polyester film to be laminated to the outside of functional barrier polymeric pouches by processing them in the MWS pilot-plant.

The third and final steps of the plan are addressed in this report.

Materials and Methods

Calibrations, printing and MATS processing

Laboratory calibration was carried out as outlined previously regarding CLIN 0011. Substrates for printing were weighed and subsequently flood coat printed. Printing sequences in the laboratory have been optimized and carried out as illustrated in Figure 1. This printing protocol was created with commercial printing processes in mind and therefore will be easily translatable for large-scale production. Table 2 provides the specification ranges for the TTI ink.

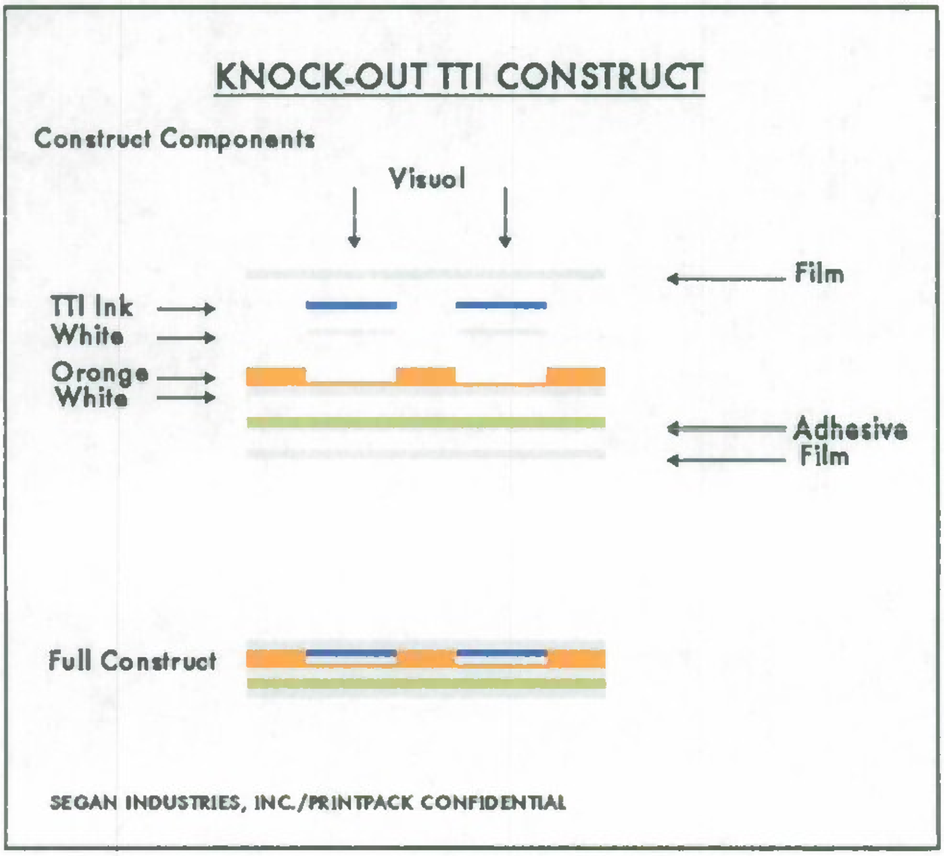


Figure 1. Printing sequence for TTI ink with knock-out, white and reference backgrounds.

Table 2: Specification Ranges for TTI Ink	
TTI chemistry concentration range	8-15% by weight
MO Augmenting concentration range	5-15% by weight
Lay down comparison	156 – 110 screen mesh
Thinner/drying additive	0 – 10% by weight
Reference clear/adjustment additive	0-20% by weight
Reference color range	Pantone 178C-180C
TTI color range	Pantone 273C-275C

The TTI ink was hand-printed in circles on the PET, then backed with white retort-grade ink for visualization purposes. Some samples were not backed with the white ink, with the intention of visualizing the TTI ink directly against the green-tinted adhesive for comparison purposes.

The PET was then laminated to the rest of the structure with the ink buried, pouched in the pilot plant and shipped to WSU. The pouches were filled with chicken and dumplings, sealed and processed with MATS using microwave power at 7.0, 6.2, 2.6 and 2.5 kW in the 4 cavities. Temperatures were set to: 72/124/123 ºC for preheating, heating, and holding sections respectively with belt moving at 40 inch/min. Preheating time was 30 min and cooling time was 4 min.

Results and Discussion

Sensor printing, stability and cost analysis

Sensors printed in the laboratory were visualized against a reference color (orange) background. Figure 2 provides the color development during processing. Stability was tested by using ink that had been stored for 2 months and the color comparison scale proved identical to ink stored for one or two days. Figure 3 provides color comparisons for printed sensors after 2 days, 30 days and 60 days of storage to show stability of post-processed sensor color over time. This storage study will be continued for 4-6 months.

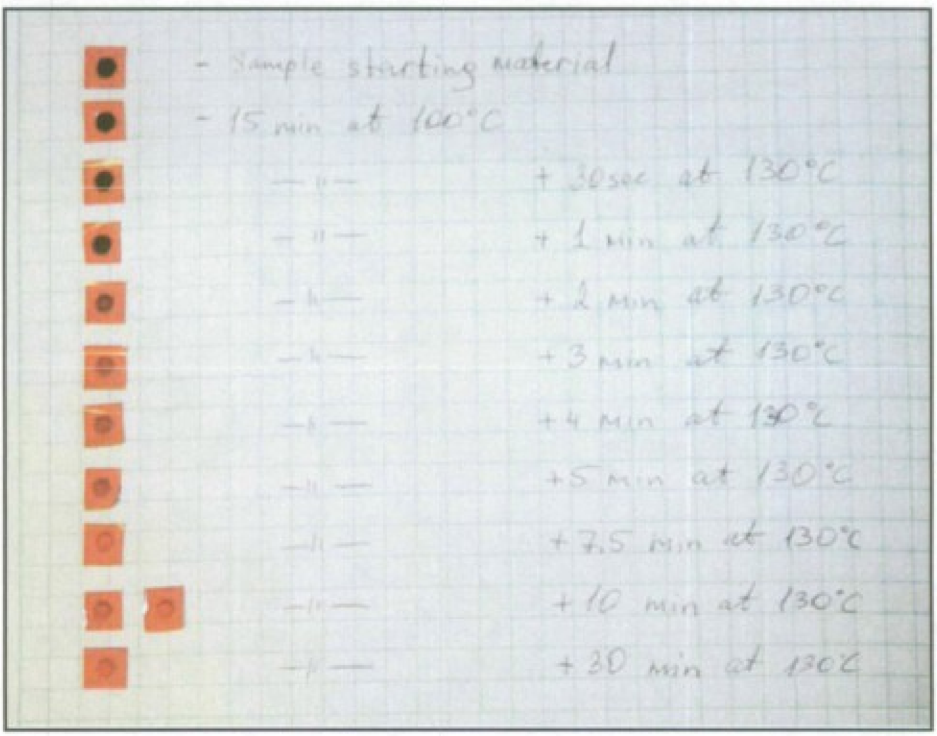


Figure 2. Pre-printing Ink Stability: 2 x 156 mesh TTI Printed retains printed subsequent to two months of storage of finished TTI ink.

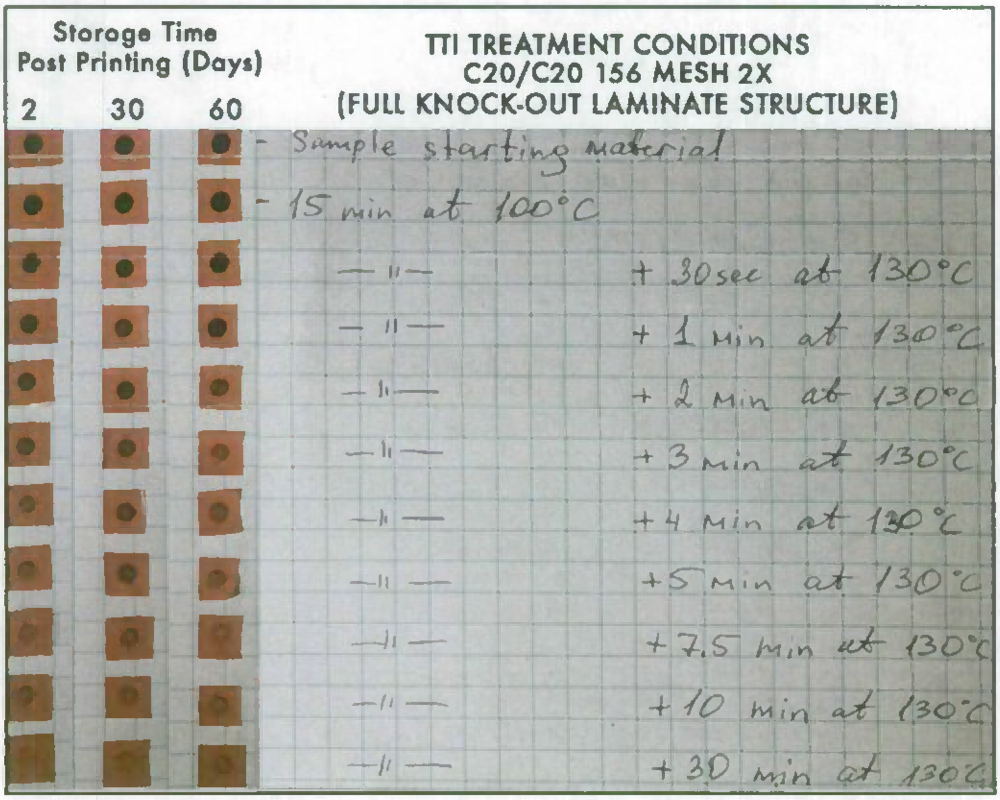


Figure 3. Post-printing Sensor Stability: Color comparison of printed retains after 2, 30 and 60 days of storage post-activation of TTI ink sensor.

Figure 4 demonstrates 2 examples of laboratory printing and lamination without backing ink, simulating the condition achieved in the pilot plant when TTI ink was printed without a backing of white retort-grade ink and subsequently laminated, pouched and processed. The left image is the color development simulating TTI ink that was printed on the PET and green adhesive was applied to the barrier PET layer, while the right image is color development simulating green adhesive applied to the PET layer with TTI ink printed on the interior film. Both processes retain the distinct color change in the ink during the processing conditions corresponding to the ideal printing sequence, but it is clear that the visualization suffers when the TTI ink is not backed by white.

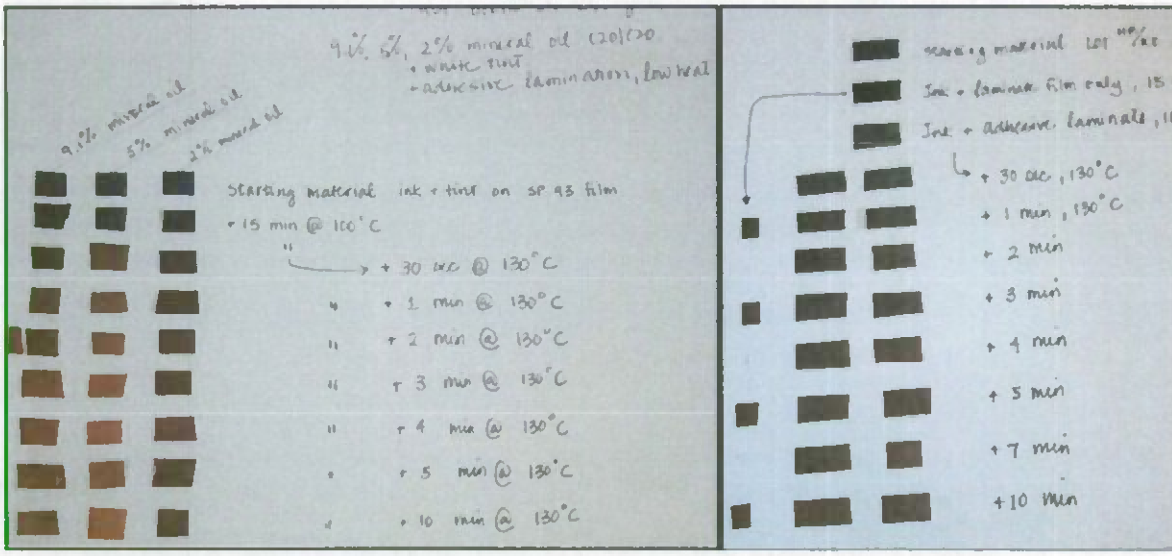


Figure 4. (Left side) TTI Ink printed with green adhesive behind and no white backing and (right side) printed with green adhesive in front. Observe visible, but muted colors as compared to previous images.

Total ink weight/area was established based on surface area measurement. Weight/6mm diameter circular print zones were calculated. These costs are estimated based on actual area of the sensor without accounting for ink waste required by rotogravure or flexographic printing techniques, so actual cost estimates for printing TTI-labeled non-foil MRE pouch material will require additional calculation and consideration.

Wet ink weight/6mm TTI sensor zone based on 6mm dia. spot = 214.5 micrograms
Estimated TTI sensors per kilo ink = 4 – 5 million
Preliminary estimated ink charge/TTI sensor zone: approximately 0.4¢ – 0.6¢

WSU processing results

The MATS processing conditions were selected to achieve an F_0 = 6.2 min. Actual processing achieved results of F_0 = 9.1 -15.7 as measured by Ellab sensors used during the 3 processing runs. Figures 4 and 5 clearly illustrate the success of the TTI ink sensors' color development through the MATS process when printing directly on the packaging material, both with and without white ink backing the sensor. Some residual darkness may be apparent on the sensor due to uneven distribution of the ink during the hand-printing procedure. This will clearly be eliminated during commercial printing.

Figure 5. Pouch Type 1: PET reverse-printed with TTI ink backed by retort-grade white ink, unprocessed pouch on the left (dark blue ink) and processed pouch on the right (orange ink).

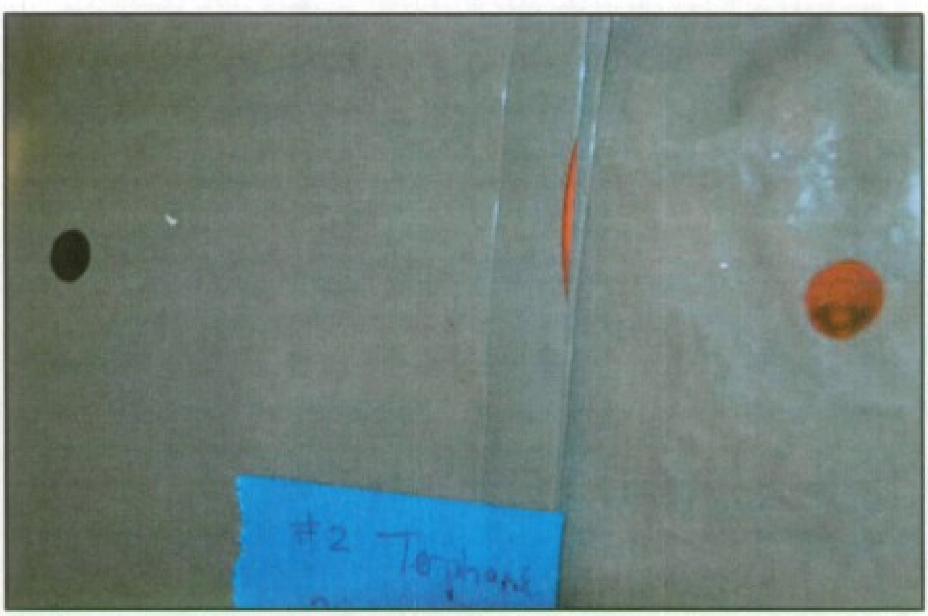


Figure 6. Pouch Type 2: PET reverse-printed with TTI ink directly in contact with green adhesive, unprocessed pouch on the left (dark blue ink) and processed pouch on the right (orange ink). TTI final color is noticeably darker than when backed with the white ink, but color development is still apparent.

Conclusions

The Time-Temperature Indicator ink technology is effective when printed on an orange background, as performed under laboratory conditions, but final color referencing is difficult to achieve compared with printing the TTI in the previously illustrated method with a white backing and knockout reference color. Visualization of TTI ink through green laminating adhesive is possible, but muted compared to direct visualization through a clear overlay with adhesive behind printed layers. Ideally for production articles, the TTI ink should not be in direct contact with the laminating adhesive. Interferences between laminating adhesive components and the TTI ink may occur under processing conditions.

Smaller particle sizes in the range of 10-50 microns react quickly and shorten TTI ink triggering time. Larger particle sizes in the range of 50-100 microns react more slowly and prolong the TTI triggering profile. A distribution of particle sizes can be utilized to provide a gradual color change leading to the determination of "non-treatment" where the TTI sensor remains dark, "partially treated" where the TTI sensor is partially dark; and "fully treated" where the TTI sensor is bright orange. Sharper distributions of color change can be explored by further milling using a rotostator, sonicator, or 3 roll mill. If necessary as an alternative to physical milling, chemical milling (including controlled crystallization of monomer compositions) can be addressed.

The current TTI testing results provided above should be interpreted when printed on orange and with visualization through the adhesive due to limitations of printing technique at Segan's facility, but final product formats including white background printing, knockout reference color formats, and adhesive lamination behind printed layers and not in contact with the TTI are considered optimal for large-scale printing and production of TTI-labeled pouch material.

References

Ratto, Jo Ann, J. Lucciarini, C. Thellen, D. Froio, and N. A. D'Souza, 2006, *The reduction of Solid Waste Associated with Military Ration Packaging*, , US Army Soldier System Center, Technical Report, Natick (Ma) TR-06/023. 75pp.

Ribi, H.O., 2010. Co-topo-polymeric compositions, Devices and Systems for Controlling Threshold and Delay Activation Sensitivities. US Patent App. # 2010/12018.

Tang Z., Mikhaylenko G., Liu F., Mah J.H., Tang J. , Pandit R., Younce F., 2008. *Microwave Sterilization of Sliced Beef in Gravy in 7-Oz Trays. Journal of Food Engineering, 89.* (4), 375-383.